Aromaticity and Ring Currents

J. A. N. F. Gomes

CEQUP/Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 697, 4150–049 Porto, Portugal

R. B. Mallion*

The King's School, Canterbury, Kent, CT1 2ES, England, U.K.

Contents

I. Introduction

Accepting a commission to review progress in the subject embodied in our title is, perhaps, to take up something of a 'poisoned chalice'. One of us, contributing on this same topic more than 20 years ago at the 1979 International Symposium on Aromaticity in Dubrovnik, wrote[1] "A cynic would say that there are actually only two difficulties in discussing the subject of 'aromaticity' and 'ring currents'—deciding what is meant by 'ring current', and assigning a meaning to the term 'aromaticity'!" That comment, though ostensibly facetious, had serious intent: it did encapsulate, with only a modicum of exaggeration, the problems that inherently beset any assessment such as the one attempted at Dubrovnik[1] and in the present review. At the heart of the matter lies the undeniable fact that *neither ring currents nor aromaticity are physical observables*.

Nevertheless, the intervening period has seen the ring-current idea, at least, become generally less controversial and more accepted than it once was. At the time of our opening quotation, one of us and Haigh had just published an exhaustive review[2] of the ring-current concept covering the period up to about 1980—the end of what might now be regarded as the era of semiempirical calculations in this field.[2] This review[2] (1979/1980) concluded that "the 'ring current' picture has proved itself ... to have great power in rationalising, at least qualitatively, the magnetic properties of π-electron systems. It is so pictorial that one can almost *feel* what is happening when a [conjugated] molecule is subjected to a magnetic field. Whatever advances the future may bring, it may be that the favourite habitat of the 'ring current' will be that in which it was born and brought up, namely, that of semi-empirical π-electron theory". In other words, these authors were sanguine that, at the time (ca. 1980), the ring-current idea was gently coming to the end of its natural, useful life. However, as recently as 1997, when reviewing progress concerning the status of the ring-current model during the decade and a half or so *after* 1980—a period in this field that we have dubbed[3] 'the ab initio era'—the present authors[3] were initially somewhat surprised to find themselves concluding that "the 'ring-current' idea has well survived the first 15 years of the *ab initio* era." Lazzeretti's subsequent *magnum opus*[4] on ring currents has more than confirmed this. By contrast, the sheer fact that in 2001—the very first year of the 21st century—the American Chemical Society has seen fit to run this particular issue of *Chemical Reviews* shows that the concept of Aromaticity is as elusive as it ever was (see section II).

There are three reasons for our not feeling obliged or inclined to present, in this review, an exhaustive, systematic, or historical critique of the ring-current concept itself. First, as we have just claimed, the idea of a ring current seems more secure now than it was 20 years ago, and it would appear that less apology or justification is needed for invoking it. Second, we ourselves have, in any case, only recently updated
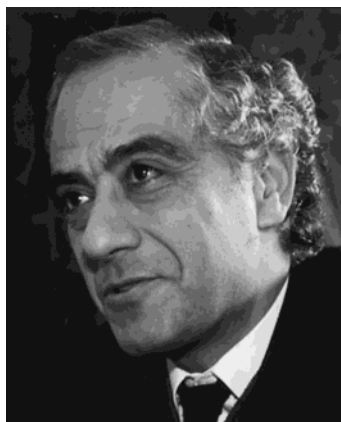
José Alberto Nunes Ferreira Gomes was born in Penafiel (Portugal) on July 14, 1947, and received his first degree, in Chemical Engineering, from the University of Porto in 1971. From 1972 to 1976 he was at Linacre College, University of Oxford (England, U.K.), where he obtained his M.Sc. degree in Mathematics under the supervision of Professor C. A. Coulson and his D.Phil. degree in the Faculty of Physical Sciences (Theoretical Chemistry) under Professor P. W. Atkins. Since 1976, he has been a Professor at the Department of Chemistry of the University of Porto. His major contributions have been in the topology of the magnetic current-density field and in several aspects of the simulation of liquid/metal and liquid/liquid interfaces. He has served at different levels of responsibility in the University of Porto and as an evaluator for the national research financing agency, *Fundação para a Ciência e Tecnologia*. He is currently the Vice President of the Portuguese Chemical Society and the Vice Rector of the University of Porto.

Roger Blakeney Mallion was born in Manchester (England, U.K.) on December 17, 1944, and received his B.Sc. degree in Chemistry from the University of Wales (University College, Swansea) in 1966. He remained at Swansea to work for his Ph.D. degree, under Mr. C. W. Haigh, on the ^{1}H NMR spectra of the condensed, benzenoid hydrocarbons. This degree was awarded by the University of Wales in 1969, and he then moved as a Science Research Council Postdoctoral Fellow to the Wave Mechanics and Quantum Theory Group of the late Professor C. A. Coulson, F.R.S. (then the Rouse Ball Professor of Mathematics) at the Mathematical Institute, University of Oxford. In 1971, he was elected to a *Research Lectureship of the House* at Christ Church, Oxford, a post that he occupied until 1976. During this period, he moved with Professor Coulson to the newly created Department of Theoretical Chemistry, where Coulson was the founding professor of that discipline at Oxford, holding a personal chair from 1972 until his death in 1974. In 1976, Roger Mallion left Oxford to take up his present position as Assistant Master in Mathematics at The King's School, Canterbury. He recevied his D.Phil. degree from Oxford in 1979, submitting a thesis that made an empirical appraisal and examined some graph-theoretical aspects of simple theories of the ring-current effect in conjugated systems. His research activities over the last 35 years have been in three different areas: (a) experimental ^{1}H NMR of the condensed, benzenoid hydrocarbons and theoretical calculations of ring-current contributions to the magnetic properties of these and other conjugated species; (b) chemical applications of graph theory; (c) aspects of purely mathematical graph theory—especially those that concern enumeration of spanning trees in planar and nonplanar graphs, and properties of the eigenvalues and eigenvectors of general, abstract graphs.

the Haigh−Mallion review[2] of 1979/1980—which has held sway in the field for some 20 years—and have, thereby, extended an evaluation of the ring-current model into the present ab initio era, by means of the 1997 book chapter[3] from which we quoted above. Third, as we have alluded, Professor Paolo Lazzeretti of the University of Modena has just given the benefit of his own 30 years' experience of the subject via a scholarly, authoritative, and highly readable account, simply entitled *Ring Currents*, published in a recent issue of *Progress in Nuclear Magnetic Resonance Spectroscopy*[4]—which is enthusiastically commended to readers of this present issue of *Chemical Reviews* for the very latest information on the status of the ring-current hypothesis. This policy of merely referring to refs 2−4 instead of formally reviewing the detailed history of ring currents has the added advantage that we, and our readers, are spared the ritual—felt to be obligatory, it seems, by the majority of writers on ring currents over the last 35 years—of rehearsing and retailing the arguments against the ring-current concept put forward in the mid-1960s by the late Jeremy Musher[5−7] and the refutation of them by several authors[8−13] (one of the present included[11,12a,13]). Instead, we shall here simply confine ourselves to a consideration of how workers in this field have tried to correlate the notion of ring currents with the idea of aromaticity. We shall take as our brief any suggested connections between aromaticity and the several ways in which a ring current is conventionally believed[2−4] to manifest itself experimentally—i.e., via an anisotropy of magnetic susceptibility and an exaltation of magnetic susceptibility in bulk magnetism (section III) or by means of nuclear shielding ('chemical shift') in a nuclear magnetic resonance experiment (section IV). We shall

also be considering the relevance of theoretically calculated estimates of individual ring-current intensities themselves, as computed by methods of varying degrees of sophistication (section V). In other words, we shall generally evaluate *magnetic criteria for aromaticity* (see also sections VI−IX). For an assessment of magnetic criteria based on the Faraday effect,[12b] however, we merely refer the reader to the lucid, vivid, and even passionate accounts of Labarre and Crasnier.[14,15] Before doing so, though, we turn first (in section II) to just a few of the many problems that surround the notion of aromaticity.

II. Aromaticity: The Difficulties

The literature on aromaticity is so vast that we must be content here with making comprehensive reference only to a selection of the major books and reviews that have established themselves in the field in the 50 years[15−51] after Hückel,[16] as well as to a few more-recent assessments of the aromaticity concept from approximately the past decade.[52−61] (It is perhaps significant to note in passing that two of the most recent references cited in that list—refs 58 and 59, both from 1996—are entitled *What Is Aro-*

maticity?) Neither do we review all the history, the definitions, and the difficulties regarding the concept of aromaticity; that has been done exhaustively (and, some might say, exhaust*ing*ly) in refs 15−61, and this same exercise will, no doubt, be continued in other articles in this very issue of *Chemical Reviews*.

Following Labarre and Crasnier,[15] one of us summarized the crucial problem in ref 1: it is whether *every* molecule that is deemed to be aromatic by (say) the magnetic criteria being considered in this review "would also be declared to be 'aromatic' when judged by the several other physical and chemical criteria— a particularly pleasant smell, a predisposition to nitration and sulphonation, a high resonance-stabilisation energy, an approximate equality of bond length, characteristic ultra-violet absorptions and (in the case of ions and radicals) a strong delocalisation of spin—which a given molecule is often considered to be required to satisfy in order to merit the description 'aromatic'; and, conversely, we should require a unanimous verdict[15,1] from all criteria on which molecules it is appropriate to call 'non-aromatic' and which should be termed 'anti-aromatic'." The position is exquisitely (and humorously) summarized by the splendid parable of 'Balaban's Dog', on p 1415 of ref 47, which is highly commended to the reader as some light (but philosophically quite deep) relief in this otherwise somewhat overwhelming subject. (In our view, Balaban's Dog—at least in the context of aromaticity—should possibly rank in scientific status with Schrödinger's Cat.)

The situation regarding aromaticity has reduced some authors to the point of despair. In a telling *crie de cœur* entitled *Aromaticity — an Exercise in Chemical Futility*?, Binsch[39] wrote "It is indeed suspicious how often magic rules had and have to serve as an alibi for creating an aura of intellectual respectability for chemical research which is on the verge of turning stale". He allowed himself to speculate[39] whether much activity in this field is "not simply contributing another tombstone to an already enormous data cemetery". In an attempt to give an anlalogy about how, he felt, chemists are wasting time and energy in grappling with the concept of aromaticity while other, more rewarding, chemical activities beckon, Binsch was even moved to quote Goethe (from *Faust*) in support of his cause: "*Ich sag' es dir: ein Kerl, der spekuliert, Ist wie ein Tier, auf dürrer Heide, Von einem bösen Geist im Kreis herum geführt, Und rings umher schöne grüne Weide*". An approximate English translation (which is the responsibility of J.A.N.F.G and R.B.M.) is "I tell you: a fellow who speculates is like an animal on the barren heath, driven round in circles by an evil spirit, whilst all around are verdant meadows".

There was a considerable outpouring of criticism about the concept of aromaticity (all fully and entertainingly documented in refs 30 and 47) at the 1971 Jerusalem Symposium, with especially strident comments emanating from a number of established and distinguished authors in this field. Heilbronner[62] was of the opinion that "the amount of confusion caused by the term 'aromaticity' in the student's mind is not compensated by gain in the understanding of the chemistry and physics of the molecules so classified". He also made the self-evident, though little quoted, remark[62] that "nobody can claim that the vague concept of 'aromaticity' must be introduced at any stage to make quantum-mechanical theories work". Despite the fact that Lloyd is the author of several definitive books[20,49,53] and reviews[58,63] on the subject, he and Marshall stated[63] (in Jerusalem) "The term aromatic was interpreted at different times in terms of molecular structure, of reactivity and of electronic structure, and, in consequence, there has been much confusion over its precise meaning and definition. We suggest that because of this confusion, it would be better if the use of the term 'aromatic' were discontinued, save perhaps with its general and original connotation of 'perfumed', and that it should perhaps pass with other technical terms which have outlived their precision and usefulness to the realm of the historian of chemistry". Labarre, in his own Jerusalem contribution,[64] made the point that "the considerable number of prefixes joined to the term 'aromaticity' (non-, anti-, quasi-, pseudo-, homo-, etc.) indicates sufficiently that the term is outdated. The solution to this problem is not as Coulson has remarked ... to look for a new word to replace aromaticity. It is preferable to propose several ... new words, so that each one of them refers to one of the multiple chemical or physical properties that were intended to be expressed by the term 'aromaticity'. We have considered introducing the concept of potential strobilism to describe the phenomenon measured by the Faraday effect and by NMR in the case of cyclic molecules that are the seat of a π-electron delocalization, that is, of a ring current".[15,64]

As for the present authors, in our own extensive works in this field over a 30-year period (see refs 1−4 for citations), we have consistently been cautious and circumspect and have always fastidiously and deliberately avoided describing the molecules we have studied as aromatic, invariably preferring instead to refer to them as 'conjugated systems' or, where appropriate, 'benzenoid hydrocarbons'. Indeed, in ref 2, Haigh and Mallion explicitly wrote "we have been careful to use terms such as 'conjugated molecule' rather than 'aromatic molecule', for it is not the intention of this review [ref 2] to enter into the wide-ranging (and one might even say 'semantic') controversy which has arisen concerning an alleged connection between 'ring currents' and 'aromaticity'. As early as 1961, it was the striking 'ring current' effects on proton chemical shifts which led to the suggestion[65,66] that these become a new criterion of 'aromaticity', rather than those then extant. Furthermore, those species which, as a result of their ^{1}H NMR spectra, have been called paratropic,[36,50] have been described[67] as 'anti-aromatic' in a wider sense. Since then, there has been a further proliferation of 'hyphenated' aromaticities[30]... The late S. Winstein[23c] has interpreted the diamagnetic exaltation[68] and ^{1}H NMR spectra of the 'homo-aromatic'[69] homotropylium ion in terms of a 6π-electron 'ring current'. The same school,[70] and others,[71−74] have even written of a 'ring current' in cyclopropanes, which can only be

called 'aromatic' (with or without hyphenation!) by yet a further stretching of the meaning of this term."[75] One of the present authors was also fairly withering about suggested connections between aromaticity and ring currents in a Chemical Society *Specialist Periodical Report* many years ago[76] and, with Coulson, issued a similar disclaimer on the matter at the very end of ref 77.

All these comments were, however, made a long time ago, and we must not, perhaps, give the impression that everything concerning the concept of aromaticity is negative; some recent work has indicated the opposite. In an impressive, careful, and systematic series of papers under the generic title *Aromaticity as a Quantitative Concept* (of which refs 52 and 78−80 are representative), Katritzky et al.[52,78−80] claimed to have demonstrated, by 'principal component analysis', that 12 common quantitative criteria of aromaticity define two independent scales of aromaticity, which they labeled 'classical' and 'magnetic' (geometric and energetic criteria specifically being categorized as classical). They concluded[52] that "the classical ... and magnetic concepts of aromaticity are almost completely orthogonal" [i.e., are separate and unconnected] and that "there are at least two types of aromaticity", the geometric and energetic criteria correlating well.[52] von Ragué Schleyer and Jiao[59] have, however, somewhat poured cold water on this suggestion, being of the opinion that "although Katritzky's analysis was based on a large number of common aromatic systems, the range of the magnetic properties was too limited, in view of the likely experimental uncertainties, for a definitive assessment." Further, the same authors pointed out that Jug and Köster[81] also subsequently found that "aromaticity is at least a two-dimensional phenomenon", but that the latter concluded that it is the *geometric* and *energetic* criteria that are the ones 'orthogonal' to each other (and *not* these two—allied—versus magnetic, as Katritzky et al.[52,78−80] had concluded), while the magnetic and energetic criteria correlate. von Ragué Schleyer and Jiao[59] emphasized that this is in contradiction to Katritzky's results[52,78−80] but then (referring to the work of Jug and Köster[81]) added their own view[59] that "again, the quality and extent of the data employed (in ref 81) were insufficient." In a later paper,[82] von Ragué Schleyer et al. stated that contrary to the views of Katritzky et al.,[52,78−80] "classical and magnetic concepts may not be orthogonal" and claimed that, after all, linear relationships do exist among the energetic, geometric, and magnetic criteria of aromaticity and that[82] "these relationships even extend to antiaromatic systems". During the 1990s, Professor von Ragué Schleyer (our commissioning editor!) and his school stalwartly published an overwhelming number of papers on magnetic criteria for aromaticity, of which refs 59 and 82−100 are merely a representative selection. During the middle of the decade, they strongly favored magnetic exaltation[59,82−87] (section III.A.4) which was (repeatedly[59,86]) stated to be "the only uniquely applicable criterion" for characterizing aromaticity (though the cited justification for this rather substantial and crucial claim appeared to hinge[59] mainly

on the thesis of one of the authors, which we ourselves have not examined). However, since 1996, von Ragué Schleyer et al.[88−100] have been equally vigorous and enthusiastic proponents of their newly defined nucleus-independent chemical shift (given the acronym NICS) as the major criterion for aromaticity (see section VI). However, that is for later, and it is to a consideration of their former criterion, and of bulk magnetic susceptibility in general, that we now turn.

III. Criteria Based on Bulk Magnetism

A. Definitions

1. Bulk Magnetic Susceptibility

The (volume) magnetic-susceptibility tensor, χ^v, is defined by[2]

$$\mathbf{M} = \chi^v \mathbf{B} \tag{1}$$

where $\mathbf{M}$ is the magnetization vector and $\mathbf{B}$ is the magnetic-flux density. They both have dimensions $[MT^{-1} Q^{-1}]$, and so χ^v itself is actually dimensionless. Related to this is the more commonly used molar magnetic-susceptibility tensor, defined

$$\chi^m = (m/d)\chi^v \tag{2}$$

where m is the relative molecular mass and d is the density. χ^m thus has the dimensions of a volume per mole. Haigh and Mallion[2] reported in 1979/1980 that, up to that time, "essentially the whole of the voluminous literature ... [used] ... the unrationalized cgs system, in which the units become cm^3 mol^{-1}; the commonly used abbreviations are cgs emu, or just cgs units. All values turn out to be somewhat more than 10^{-6} of these units". Twenty years later—and some 25−30 years after the general launch of the *Système International d'Unités*[101]—this situation has hardly changed and almost all modern authors in the field persist in using ppm cgs emu. Those guilty in this regard are not just workers who are based in the United States, where SI units have been notoriously slow to take root: numerous European authors, too, continue to use ppm cgs emu. Since, however, this *is* the year of Grace 2001 (and we, the authors, regard ourselves as 'good Europeans') we do feel obliged to give the conversion factor to proper SI units. It is

$$\chi^{m,SI}/(m^3\ mol^{-1}) \equiv (4\pi \times 10^{-6})\chi^{m,cgs}/(cm^3\ mol^{-1}) \tag{3}$$

However, it may be noted in passing that Chestnut[102] has given a powerful argument for the retention of the unrationalized cgs-Gaussian system of units—where, specifically, *electromagnetic* quantities are involved.

2. Molar Magnetic Anisotropy

These magnetic-susceptibility tensors may be diagonalized by an orthogonal transformation to principal axes, with components χ^m_{xx}, χ^m_{yy}, and χ^m_{zz} along

those axes. In planar molecules, we shall frequently take the molecular z-axis as being perpendicular to the molecular plane and shall thus define the anisotropy of magnetic susceptibility, $\Delta\chi^m$, as

$$\Delta\chi^m = \chi_{zz}^m - \frac{1}{2}\{\chi_{xx}^m + \chi_{yy}^m\} \qquad (4)$$

$\Delta\chi^m$ has been proposed by Flygare (e.g., ref 103) as a criterion of aromaticity (see section III.B).

3. Mean Molar Susceptibility

In isotropic media such as liquids, solutions, and gases, what is measured is the *mean* molar magnetic-susceptibility, $\bar{\chi}^m$, defined as

$$\bar{\chi}^m = \frac{1}{3}\{\chi_{xx}^m + \chi_{yy}^m + \chi_{zz}^m\} = \frac{1}{3}\mathrm{tr}\,\chi^m \qquad (5)$$

Many more mean values have been reported than full tensors or anisotropies (see, for example, refs 104–109). Very early in the development of this field it was found that these mean values were additive, being sums of atomic terms plus some so-called 'constitutive corrections' (see, for example, refs 110 and 111 and Chapter 6 of ref 106). Any deviation from these (Pascal's[110]) rules was said to be a measure of 'magnetic exaltation' (see section III.A.4, which follows).

4. Incrément de Delocalisation/Magnetic Exaltation

Pacault and Hoarau et al.[105,112–114] introduced the notion of *incrément de delocalisation*, later modified slightly and these days more generally known as 'magnetic exaltation'. Originally[112] this was defined[4] as

$$\Lambda^m = \bar{\chi}^m - (\Sigma\chi_A^m + n\lambda_{C=C}) \qquad (6)$$

in which $\bar{\chi}^m$ is the previously defined mean molar susceptibility, $\Sigma\chi_A^m$ is the sum of Pascal's atomic susceptibilities, n is the number of C=C bonds, and $\lambda_{C=C}$ is the increment arising from the presence of each double bond within the additive scheme. This form of definition came eventually to be rendered more generally as

$$\Lambda^m = \bar{\chi}^m - \chi_{calc}^m \qquad (7)$$

where χ_{calc}^m is the molar susceptibility calculated by means of a hypothetical, additive, incremental scheme in which the double bonds are assumed to be nonconjugated. Following Pacault,[115] Lazzeretti[4] observed that the subtractive term in brackets in eq 6 may frequently be approximated as χ_{xx}^m; if, in addition, we can set $\chi_{xx}^m = \chi_{yy}^m$, then, by invoking eq 5, eq 6 may be rewritten as

$$\Lambda^m = \frac{1}{3}\{\chi_{xx}^m + \chi_{yy}^m + \chi_{zz}^m\} - \chi_{xx}^m \qquad (8)$$

$$= \frac{1}{3}\{2\chi_{xx}^m + \chi_{zz}^m\} - \chi_{xx}^m \qquad (9)$$

from which

$$3\Lambda^m = \chi_{zz}^m - \chi_{xx}^m = \Delta\chi^m \text{ (from eq 4, if } \chi_{xx}^m = \chi_{yy}^m) \quad (10)$$

and so

$$\Lambda^m = \frac{1}{3}\Delta\chi^m \qquad (11)$$

If the further assumption be made that $\Delta\chi^m \approx \Delta\chi_{London}^m$—i.e., that the only contributions, $\Delta\chi_{London}^m$, to χ_{zz}^m come from London π-electron ring currents[2–4,116–118]—then

$$\Lambda^m = \frac{1}{3}\Delta\chi_{London}^m \qquad (12)$$

$\Delta\chi_{London}^m$ is, accordingly, a theoretical estimate, based on the London ring-current model,[2–4,116–118] (see also Section V) of the 'Λ^m' that would in practice be deduced by a combination of experiment and one of the additive 'recipes' mentioned earlier. This was why Pacault and Hoarau et al.[105,114] regarded Λ^m as what Lazzeretti[4] describes as "a signature of aromaticity". Diamagnetic-susceptibility exaltation has been strongly favored by Dauben et al.[68,119] as a prime criterion for aromaticity (see the next section, section III.B).

B. Criteria for Aromaticity Involving Anisotropy of Magnetic Susceptibility and Magnetic Exaltation

The major impetus for using anisotropy of magnetic susceptibility, $\Delta\chi^m$ (section III.A.2, eq 4), as a means of diagnosing aromaticity came from the group of Flygare et al. in a substantial series of papers in the period 1969–1974 (see, for example, ref 103). Likewise, during almost the same period (1968–1971), the late H. J. Dauben et al.[68,119] were the main proponents of diamagnetic exaltation, Λ^m (section III.A.4, eq 7), as the preferred magnetic criterion for aromaticity (see, for example, ref 119). The relative merits of the Flygare and Dauben contributions to this field have been so thoroughly and meticulously assessed by Lazzeretti in his recent review (pp 14–19 of ref 4) that we eschew a detailed consideration and merely note the main conclusions here. The Flygare group[120] claimed that "there is substantial evidence to indicate that ring molecules with more negative values of $\Delta\chi^m$" than those predicted by summation of 'local' terms "possess ring delocalization and a degree of aromaticity".[120] They even extended their deductions to '$4n$'-systems, concluding that "all four-membered rings have a more paramagnetic ring susceptibility than predicted on the basis of additivity rules".[121]

As for magnetic exaltation, Λ^m (section III.A.4, eq 7), as an index for aromaticity, Dauben et al.[68,119,122] classified those molecules with $\Lambda^m > 0$ as aromatic, those exhibiting $\Lambda^m = 0$ as nonaromatic, and found that all the condensed, benzenoid molecules have large positive values of Λ^m. Dauben et al.[68,119,122] drew attention to Salem's observation[22] that 'local effects' and 'Van Vleck paramagnetism' [123] are also important, and they claimed that "one cannot expect agreement between the calculated 'London' or ring-current diamagnetism and the magnetic anisotropy $\Delta\chi^m$ because the important contribution of Van Vleck

paramagnetism to anisotropy is not included". Dauben et al.,[68] drawing essentially on the arguments of our section III.A.4, above, suggested that "London diamagnetism is related to exaltation and should correlate with it". As Lazzeretti[4] has summarized, Dauben et al.[68] concluded that "Λ^m should be preferable to $\Delta\chi^m$, as an indicator of electron delocalization".

However, not all of this was, by any means, accepted by Flygare's school. In ref 124, they claimed that "the exaltation values, which depend on nonlocal effects, are probably more qualitative than quantitative, especially for small molecules. This is because they depend on estimates, not direct measurements, of the bulk susceptibility values in noncyclically delocalized systems." In another context,[125] the same group stated that "it is only the out-of-plane component of the magnetic susceptibility which shows nonlocal effects in aromatic systems. By this criterion, a compound is judged to have delocalized electrons not because it has a large out-of-plane magnetic susceptibility but because it has a more negative susceptibility than that which would be predicted from a localized model." [120,125,126] Their conclusion[127] was that "if the nonlocal contributions to molecular magnetic susceptibilities are considered to correlate with cyclic electron delocalization, then perforce these values provide one measure of aromatic character." [127] After discussion of how the paramagnetic-susceptibility term may be calculated theoretically, with a view to giving quantitative estimates of π-electron delocalization and aromaticity, Flygare et al.[127] were of the opinion that "the total out-of-plane susceptibility would have its most negative value for a completely delocalized system and would become progressively less negative as the electrons become more localized."

There was, however, considerable agreement—even in this 'semiempirical era' [3,4]—that, in the words of Benson and Flygare,[124] "the anisotropies in the ring molecules must be described in terms of *both* local and nonlocal contributions." Pople[128] estimated that about 30% of the total susceptibility-anisotropy of benzene should properly be attributed to local contributions; writing with Ferguson,[129] he stated that "the local paramagnetic terms make a fairly large contribution to the over-all anisotropy, and, as a result, the ring current contributions are decidedly less than suggested by the total susceptibilities." Dailey[130] likewise felt that the estimate (-49 ppm cgs emu) of the ring-current contribution to the anisotropy in the diamagnetic susceptibility of benzene that was based on the Pauling/Lonsdale classical model[2-4,131,132] ought to be reduced by some 40%.

Moving ahead now some 30 years, to the mid-1990s and the ab initio era,[3,4] we again recall that von Ragué Schleyer and his school[59,82-87] resurrected the idea of using magnetic exaltation as a diagnosis for aromaticity. In a review entitled *What Is Aromaticity?*,[59] von Ragué Schleyer and Jiao categorically asserted that "magnetic susceptibility exaltation is the only uniquely applicable criterion" and proposed the following definition: "*Compounds which exhibit significantly exalted diamagnetic susceptibility are aromatic.*" As a corollary, they added the proposition that "*those compounds with exalted paramagnetic susceptibility may be antiaromatic*" [original authors' italics]. Their work on magnetic exaltation[59,82-87] was based on good-quality ab initio calculations that made use of the IGLO method (individual gauge for localized orbitals) of Schindler and Kutzelnigg[133-135] or, alternatively, of the standard approach of GIAO[136-140] (gauge-invariant [-independent, -included] atomic orbitals), as programmed in GAUSSIAN (e.g., ref 141; see refs 3 and 4 and section IX for explanations of the ab initio jargon involved). The group of von Ragué Schleyer pointed out in ref 83 that following Dauben et al.,[68,119,122] Cremer et al.[142-144] used the criterion of magnetic exaltation to characterize the homo- and bishomoaromaticity in the homo- and bishomotropenylium cations as well as in the barbaralyl cation, and they went on to reason that the larger magnetic-susceptibility exaltation and anisotropy than in benzene clearly reveals what they term the 'doubly aromatic nature' of the 3,5-dehydrophenyl cation. In ref 82, Jiao and von Ragué Schleyer claimed to "dispel Katritzky's pessimistic conclusion[52,78-80] by demonstrating that *linear relationships exist among the energetic, geometric and magnetic criteria of aromaticity, and that these relationships even extend to anti-aromatic systems*" [original authors' italics]. They asserted that "the exaltations ... are negative (diamagnetic) for the aromatic compounds, but positive (paramagnetic) for the anti-aromatic cases" and that the aromaticity order pyrrole > thiophene > furan "is established firmly, and the cyclopentadienyl anion is the 'most aromatic' five-membered ring system." In ref 87, von Ragué Schleyer et al. applied these criteria to the 1,6-didehyrdo[10]annulene, then recently synthesized by Myers et al.[145] and long ago viewed by Sondheimer[146] as what von Ragué Schleyer et al.[87] call "an attractive conjugated 10-membered ring candidate." Those who synthesized it reported[145] that "the ^{1}H NMR chemical shifts show clear evidence of a diamagnetic ring current, supporting the notion that [this molecule] is an 'aromatic' compound." We have more to say on these matters in sections V, VIII, and IX.

IV. Nuclear Magnetic Resonance Chemical Shifts

A. Definitions

The resonance condition for a nucleus in an isotropic medium in an NMR experiment stipulates[2,147-150] that the required resonance frequency, ω_0, is given by

$$h\omega_0 = g_n\mu_nB^{\text{local}} = g_n\mu_nB_0(1-\sigma) \qquad (13)$$

In the case of a proton, $g_n = g_{\text{proton}}$, which has the approximate numerical value[2] 5.585, $\mu_n = e\hbar(2M_{\text{proton}})$, where M_{proton} is the mass of the proton, B_0 is the magnitude of the uniform, external magnetic field, and σ is a dimensionless constant, called the shielding constant, for that proton. In an isotropic medium, the scalar σ observed is in fact one-third of the trace of a tensor; in theoretical treatments, therefore, the three diagonal elements of this tensor have to be calculated.[2] For a peripheral proton in a conjugated

molecule subjected to an external magnetic field $\mathbf{B}_0$, at right angles to its molecular plane,[2,147−150]

$$\mathbf{B}^{local} = \mathbf{B}_0 + \mathbf{B}^{core} + \mathbf{B}' \qquad (14)$$

Here, $\mathbf{B}^{core}$ derives from the inner-shell and σ-electrons and can be thought to include a 'local' contribution from the π-electrons (though—as one of us and Haigh have pointed out previously[2]—this cannot be rigorously defined, even classically) and $\mathbf{B}'$ is the contribution[2,147−150] from the induced π-electron ring currents. The latter is according to the familiar models put forward by Pople,[151−153] very much in the spirit of the Pauling[131]/Lonsdale[132] approaches and much extended by others, both classically[139,147−150,154−160] and—though still semiempirically— quantum mechanically.[161−176] When $\mathbf{B}'$ is positive, as for a benzene proton, then at constant frequency (and, hence, constant $\mathbf{B}^{local}$), a lower value of $\mathbf{B}_0$ would be required for resonance. This term thus makes the benzene proton resonate at comparatively *low* field; the opposite is true for the cyclophane protons above a benzenoid ring, which therefore absorb at *high* field.[2,177] In, at least, semiempirical work, it is customary to subtract the resonance position of a given proton in a conjugated molecule from that of a hypothetical olefinic proton (similar, perhaps, to the olefinic proton in cyclohexa-1,3-diene[154]) in the optimistic hope that both $\mathbf{B}_0$ and $\mathbf{B}^{core}$ in eq 14 may be eliminated, as localized effects would be expected to be very similar in the two cases. Hence, a direct estimate of $\mathbf{B}'$ could be obtained if this assumption turned out to be justified.[2] The dimensionless quantity B'_r/B_0 can then be defined, where B'_r is the magnitude of the secondary magnetic field, due to ring currents in the molecule as a whole, at the rth proton; this ratio is usually expressed as parts per million of the applied field. For a benzene proton, B'_r/B_0 $(= B'_{benzene}/B_0)$ is negative, and this implies deshielding. For comparisons with experiment, it became the practice, during the semiempirical era,[3] frequently to confront the calculated *ratios* $B'_r/B'_{benzene}$—for every proton r—with the corresponding experimentally observed ^{1}H NMR chemical shifts in many of the systematic studies that involved the condensed, benzenoid hydrocarbons (e.g. refs 139, 178−187; see also the next section, section IV.B).

B. Experimental and Semiempirical Considerations of ^{1}H NMR Chemical Shifts in the Condensed, Benzenoid Hydrocarbons

In the 20−25 years after the proposal of Pople's models[151−153] for estimating the effect of π-electron ring currents on ^{1}H NMR chemical shifts in conjugated molecules, many investigations[139,178−187] confirmed that the simple ring-current models, based on semiempirical[139,178−187] or even just classical[183,187] theories, could yield ($B'_r/B'_{benzene}$) ratios that would satisfactorily rationalize experimental trends when they were confronted with ^{1}H NMR chemical shifts that had been obtained *under consistent experimental conditions* for a large number of protons in a wide range of planar, condensed, benzenoid hydrocarbons; this is perhaps the one class of molecules over which

there would be absolutely no dispute from any quarter about the appellation aromatic! It was for this purpose that Haigh and one of the present authors devoted considerable effort in the late 1960s/ early 1970s to obtaining high-quality ^{1}H NMR chemical shifts[181,188,189] for 66 nonhindered protons in 16 different condensed, benzenoid hydrocarbons, from benzene to coronene[189] (via—among other well-known carcinogens—the classic 3,4-benzopyrene[188]). All data were obtained at infinite dilution, or at very low concentration, in a single, isotropic solvent (CCl_4), chosen to be as inert as possible while still, of course, allowing at least some process of solution to be effected. In the case of those ^{1}H NMR chemical shifts reported at infinite dilution,[188,189] spectra at each concentration employed were separately analyzed by computer iteration and the chemical shifts of each of the protons so obtained at the several concentrations were then individually extrapolated to infinite dilution. Haigh and Mallion believed[188,189] that it was vitally important to eliminate solvent effects (e.g., refs 190 and 191) and dilution effects (e.g., refs 188, 190, and 192) on the experimental ^{1}H NMR chemical-shift data before subjecting them to regression correlation with calculated ($B'_r/B'_{benzene}$) ratios computed via an application of classical or semiempirical ring-current theories. Furthermore, only ^{1}H NMR chemical shifts of protons that were not considered to be 'sterically hindered' were to be included in the comparison with theoretically calculated ($B'_r/B'_{benzene}$) ratios, for it was estimated[178−182] that overcrowded protons, such as the ones that Martin[193] called the 'Hα3' protons in phenanthrene (**1**), suffered an additional downfield shift of some 0.6 ppm by virtue of van der Waals steric effects.[194,195] The 'Hγ3,3' proton (on Martin's terminology[193]) in 1,2;7,8-dibenzanthracene (**2**) was, as expected, observed[182] to exhibit a 'double' steric effect, to the extent of about 1.2 ppm.


(1)   **(2)**
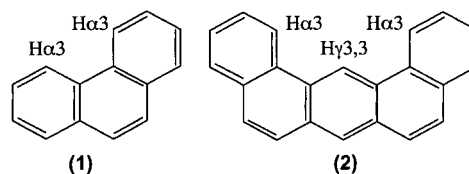
These experimental data have been used to evaluate the Hückel−London−McWeeny ring-current theory[2−4,149,161,196] (in ref 182), the Waugh−Fessenden/ Johnson−Bovey classical ring-current approach,[147,148,150,154,155] (in ref 183), both the uncoupled[164−166] and coupled[162] Hartree−Fock SCF ring-current formalisms (in refs 184 and 185, respectively), and ring-current models based on the idea of line currents[22,139,158−160] and their magnetic effects via the Biot−Savart Law[197] (in ref 139). The Haigh−Mallion experimental data[188,189] were also used (though not without some reservations about and criticisms of their quality—especially where chrysene was concerned) in an extensive attempt by Blustin[198−200] to account, *à la* Musher,[5−7] for ^{1}H NMR chemical shifts in the condensed, benzenoid hydrocarbons by means of his 'localized π-bond' model.[198−200] Blustin claimed[200] that his "simple calculations give results which compare well with experiment and with cal-

culations based on the ring current model." Like Musher[5−7]—indeed, Blustin's third paper[200] was enticingly entitled *Aromatic Proton Chemical Shifts Without Ring Currents*—Blustin felt that[200] "the overall results suggest that there is no need to associate a special ring current attribute to π-conjugation in aromatic molecules." Blustin also proposed[200] a scale of aromaticity based on his localized π-bond model; he was of the opinion that a comparison of the π-electron contributions to anisoptropy should provide "a straightforward method for ordering [the aromaticity of] a group of molecules" but he pointed out that "this approach fails when an increase in anisotropy is due to factors unconnected with π-conjugation." [200] There have also been suggestions[201−203] that correlations can be obtained between ^{1}H NMR chemical shifts in the planar, condensed, benzenoid hydrocarbons and reactivity indices (such as free valence[204]) in these molecules. The proposition[201−203] that 'causative' relations could be expected between these quantities has, however, been vigorously contested.[205−207] The Haigh−Mallion experimental data[188,189] on ^{1}H NMR chemical shifts in the planar, condensed, benzenoid hydrocarbons have even been correlated with graph-theoretical, 'topological' indices that Mekenyan et al.[208] call 'hierarchically extended connectivities'. Furthermore, Westermayer et al.[209] have had some success by comparing the Haigh−Mallion data[188,189] with predictions from what they describe as an 'empirical atomic point-dipole model'.

Finally, in a comprehensive overall assessment made in 1981, right at the end of the semiempirical era,[2−4] one of us[187] confronted the Haigh−Mallion experimental data[188,189] on the planar, condensed, benzenoid hydrocarbons with the predictions of no fewer than *10* different variants of the several classical and semiempirical ring-current theories. The overall conclusion was that "*within this context of taking ratios to benzene* [present authors' emphasis] the crude Pople point-dipole method[151,152] based on McWeeny[161] ring-currents does, after all, occasion a fit with experimental ^{1}H-NMR chemical-shifts in a wide range of condensed, benzenoid hydrocarbons, which is as good (correlation coefficient −0.97) as that obtained with the Waugh-Fessenden[154,155] (−0.96), McWeeny[161] (−0.96), Hall-Hardisson[162] (−0.96), and 'Biot-Savart' [139] (−0.98) methods." Mallion[187] also observed that "provided that it is based on relative ring-current intensities calculated *via* McWeeny's[161] (or Pople's[153]) quantum-mechanical formalism, the Pople point-dipole model[151] even gives rise to a better correlation coefficient, 0.97—for what that is worth—when its predictions are regressed against experimental proton chemical shifts than that obtained when calculations based on Blustin's ... π-bond model[198−200] are confronted with the same experimental data."

Blustin had pointed out that, on his model,[200] the interplay between the distance of a given proton from a particular bond and the position and orientation of the proton in question with respect to that bond determine that the protons in linear acenes (such as **3**−**10**) similar to Hα in naphthalene (**4**) (Martin's

terminology[193]) and Hα and Hγ in anthracene (**5**)[193] will always be shifted successively downfield, whereas the downfield shift associated with Hβ protons[193] will increase steadily, but only slightly, as the polyacene chain lengthens; the change in the shielding of the Hβ protons will thus be smaller than that for Hα and Hγ protons. Blustin also stated that, on his π-bond model,[200] the chemical shift of the Hβ protons will come to a limiting value more rapidly than will the shift of the central one or two protons of large polyacenes. In reply to this, Haigh and one of the present authors[210] likewise considered the homologous series benzene (**3**), naphthalene (**4**), ..., octacene (**10**) and, by an application of the London−McWeeny[161] approach, showed that, qualitatively, the traditional ring-current picture predicts essentially similar limiting trends. They calculated the ratios (B'_r/B'_{benzene})
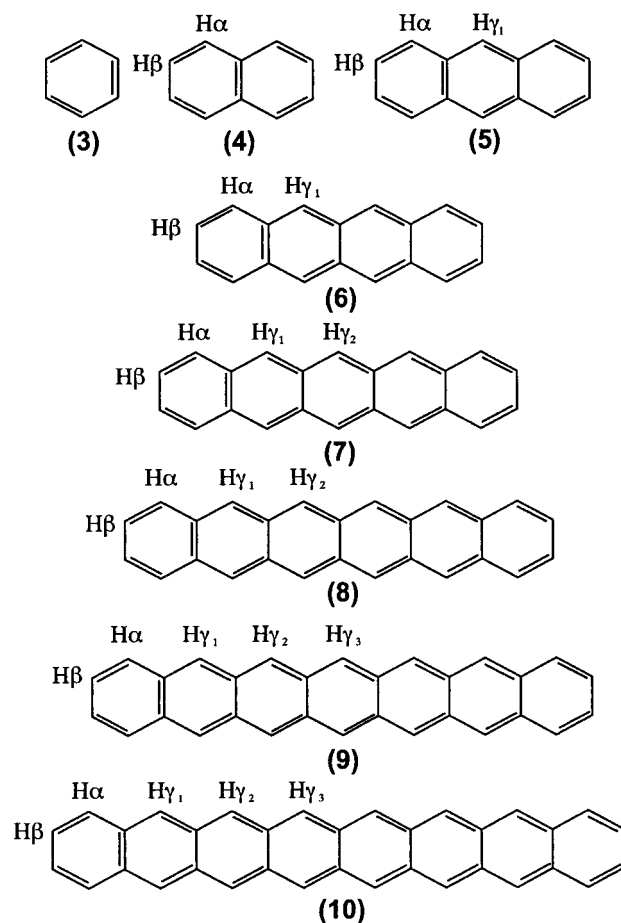
for the rth proton by means of the equation

$$B'_r/B'_{\text{benzene}} = \sum_{\text{rings, } i}^{n} (J_i/J_{\text{benzene}})(K_i^r/K_{\text{benzene}}) \quad (15)$$

where J_i/J_{benzene} is the ring-current intensity, J_i, expressed as a ratio to J_{benzene}—the ring-current intensity calculated, by the same method,[153,161] for benzene—in the ith ring of an n-cyclic molecule (see eq 16 (section V) for the minute details of its definition). J_i/J_{benzene} is a function of molecular geometry and topology.[211] The quantity K_i^r/K_{benzene} is a purely *geometric* factor that depends merely on the physical position in space of the rth proton with respect to the
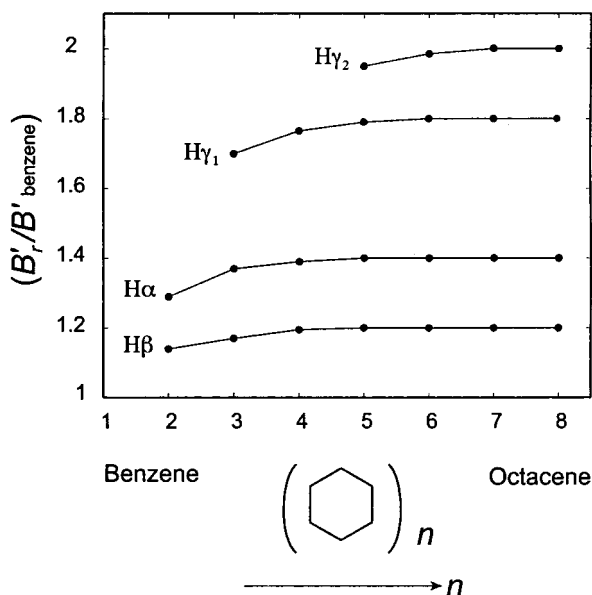
Figure 1. Variation in the ratio (B'_r/B'_{benzene}) calculated[210] by McWeeny's method[161] for the different types of protons[193] (Hα, Hβ, Hγ_1, Hγ_2, etc.) in the linear acenes **3**–**10**. (Adapted and reprinted with permission from ref 210. Copyright 1982 American Institute of Physics).

ith ring; its magnitude is determined solely by molecular geometry, and it is a measure of the effect that the ring current in ring i of the n-cyclic molecule has on the secondary magnetic field at the rth proton. Figure 1 shows the variation in calculated[181,210] B'_r/B'_{benzene} ratios for the corresponding Hα, Hβ, and Hγ protons (on Martin's terminology[193]) in the linear acenes benzene (**3**) to octacene (**10**). It would thus appear that in an n-acene (where n is large) the Hα, Hβ, and Hγ_1 protons would have calculated B'_r/B'_{benzene} ratios very close to 1.40, 1.18, and 1.85, respectively; these could then be converted, by means of the empirical eq 2 of ref 182—and by recalling that $\delta = 10 - \tau$—to predicted δ values (at infinite dilution in CCl$_4$, as *per* refs 188 and 189) of ca. 7.84, 7.50, and 8.55, respectively. Haigh and Mallion thus claimed[210] that "predictions of ^{1}H-NMR chemical shifts arising from Blustin's ... π-bond model [our refs 198–200] are at least in qualitative agreement with those of the more traditional ring current concept." They also added that "given the empirical nature of both approaches, such qualitative agreement is all that can properly be hoped for."

The discussion so far in this section has centered on the *planar*, condensed, benzenoid hydrocarbons, these being the archetypal aromatic molecules; if, however, benzene rings are successively condensed onto phenanthrene, but always in angular rather than linear fashion, the steric interactions that arise when these further rings are added cause distortion to a nonplanar geometry and subsequent members of the series are severely nonplanar. The first three benzenoid hydrocarbons in this remarkable family, appropriately termed 'helicenes', are shown below: 3,4 benzophenanthrene (**11**), pentahelicene (**12**), and hexahelicene (**13**). These beautiful molecules have been elegantly synthesized by Newman and Lednicer[212] and by Martin and his school.[213,214] Haigh and Mallion studied[215] the ^{1}H NMR spectra of **11**–**13**

(11) **(12)** **(13)**
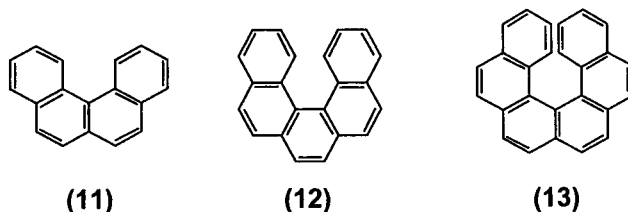
under the same careful and consistent experimental conditions as had been employed for their earlier study of the planar, condensed, benzenoid hydrocarbons;[188,189] they then tried[172] to extend McWeeny's analysis[161] (which applies strictly only to *planar* molecules[161,172,181,182]) to develop an approximate formalism[172] that would enable a similar treatment of the helicenes to be effected—with, however, only limited success.[172] Despite this, a beneficial byproduct of this exercise was the subsequent availability of a semiempirical, quantum-mechanical equivalent[173] of the classical Johnson–Bovey tables[148,150,154,155] for estimating the three-dimensional shielding, due to a ring current of unit intensity, in the vicinity of a standard, benzenoid ring.[173] Both the Johnson–Bovey tables[148,150] and these quantum-mechanical tables[173] have been widely used over the course of the last 30 years by practising organic chemists and biochemists (refs 216 and 217 are just two representative examples) in order to aid structural determinations in large molecules containing benzenoid moieties—though very little heed has generally been paid by the majority of users to the warnings of *caveat emptor* concerning these two sets of tables that one of us gave at the Eleventh Jerusalem Symposium[218] in 1978. It had always been something of a minor mystery to the present authors why no-one, apparently, had updated the classical Johnson–Bovey[148,150,154,155] tables and the semiempirical Haigh–Mallion tables[173] during the (post-1980) ab initio era; this want has at last been satisfied by Martin et al.'s very recent[219] provision of a shielding map in the vicinity of a benzene ring, calculated by means of GIAO[136–140] and an ab initio subroutine of GUASSIAN 94.[141]

We conclude this section by returning to a consideration of the *planar*, condensed, benzenoid hydrocarbons—a family of molecules that must be regarded, by anybody's criteria, as the classic, aromatic species; if *these* are not to be classified as aromatic, then surely the term really does have no meaning at all in the wider context. The large number of systematic classical and semiempirical quantum-mechanical investigations cited here have shown that ring-current theory *can* successfully account semiquantitatively for the relative trends in the experimental ^{1}H NMR chemical shifts of the condensed, benzenoid hydrocarbons *provided that*, before being confronted with these experimental shifts, *shieldings at the various protons in these molecules—calculated via any of the several ring-current models—are expressed as a* ratio *to the shielding calculated, by the same method, to prevail at a standard benzene proton, because of the ring current in benzene.* The fact that this procedure appears efficiently to mask the effects of the large number of far-fetched and drastic approximations inherent in semiempirical ring-current calculations[2–4] has been emphasized on many occa-

sions, by the present authors[77,139,172,187,210,218,220] and by numerous others.[169,174,198−200,214,221,222] It may also be mentioned in passing that this practice of taking ratios to benzene was one that much exercised even the pioneers in this field, when they were dealing with properties of bulk magnetism (section III). Referring specifically to predominantly diamagnetic, alternant hydrocarbons, O'Sullivan and Hameka[223] wrote that "London's calculation [our refs 116−118] is perhaps less accurate than Hall and Hardisson's [our ref 162]" but that when only the *ratios* of London's results are used, it seems likely that "these ratios are quite accurate." Furthermore, Davies[224] has stated the opinion that "the comparative success of London's method [our refs 116−118] for aromatic hydrocarbons may be attributed to the dependence of the theoretical anisotropy on the square of the areas of the rings in a molecule" and that "any method that takes this into account is likely to give reasonable results for the ratio" of a given calculated anisotropy to that calculated, by the same method, for benzene (see also ref 225). Several recent papers by the group of von Ragué Schleyer (e.g., refs 59, 87, 88, 97, and 226) have made specific mention of this 'ring-area' effect, and the matter was also much discussed in refs 139, 181, 182, 211, and 227−229 and elsewhere. However, it transpires that these observations and deliberations were, in fact, all anticipated much earlier, by Brooks, in a little-cited and much-neglected seminal paper[230] published more than 60 years ago in 1940; Brooks stated[230] "The fact that both theories [London's[116−118] and Pauling's[131]— and, we might add, Lonsdale's[132]] are in such good agreement with experiment, in spite of the many approximations involved, is evidence that the ratios of the anisotropies reduce to purely geometric quantities, which have a significance beyond that of the particular model adopted for specific calculations." Brooks[230] evidently had correspondence with London himself on the matter, for he flagged the above statement in ref 230 with the following footnote: "I am indebted to Professor F. London for this observation." Thus, this is convincing evidence that even London himself, as well as his contemporaries way back at the beginning of the semiempirical era of ring-current calculations,[2−4] (rightly) worried about this procedure of taking ratios to benzene. Much more recently, and in this same vein, Blustin[200] noted that "it is of course possible to perform a regression analysis of the ring-current shifts to experimental values. This can produce relative values in very good agreement with experiment. Haigh, Mallion and Armour [our ref 182] have obtained remarkable success by fitting to experiment the extremely inaccurate proton chemical shifts obtained from Hückel orbitals." He added[200] that "although this is a practicable procedure for the prediction of proton chemical shifts, it should be used with caution because it is difficult to understand the significance of such a method." Indeed, one of the present authors had earlier concluded ref 139 by stating the view that "the very good account which the simple MO theory of π-electron 'ring currents' ... has given of the observed chemical shifts in conjugated molecules may well be due to fortuitous cancellations, and compensations of errors and approximations, arising from the common practice of (1) taking a ratio of all calculated screening constants to the screening constant evaluated for a standard benzene proton, and then (2) of regressing these calculated ratios against experimental proton chemical shifts." [139]

The convention of taking ratios of calculated quantities to the corresponding ones evaluated, by the same method, for benzene will again feature prominently in our next section (section V), which is on the question of using calculated ring-current intensities as a criterion for aromaticity; it will not, however, trouble us eventually when we come to our last five sections (sections VI−X) in which we shall finally be emancipated from the constraints—and from at least *some* of the uncertainties—of the semiempirical approaches, when ab initio calculations are considered.

V. Calculated 'Ring-Current' Intensities as a Criterion for Aromaticity

The idea of breaking down the overall ring-current effect in a polycyclic system into contributions attributable to each of its individual constituent rings was not one that was followed up in the 1930s, at the time of the original work of London who, in his own papers, wrote only of interatomic currents and, even, of superconductivity.[116−118,231] Indeed, the term 'ring current' was not used until the 1950s, when the phenomenon of ^{1}H NMR chemical shifts caused a widespread revival of interest in London's late-1930s work on the 'mobile' π-electron magnetic properties of conjugated systems—a formalism that (largely, it may be presumed, because of the interruption occasioned by World War II) had been only intermittently applied, in the intervening period, to estimate π-electron contributions to the overall magnetic-anisotropies of such species (for a detailed discussion see, for example, section 4.1.11 (pp 325 and 326) of ref 2). However, according to a recent claim by Bilde and Hansen,[232] it was Pople[153] who "allowed 'interatomic currents' to become 'ring currents'." (Despite having studied the field for some 30−35 years, the present authors have never previously felt able to state with any confidence who actually did coin the term 'ring current'; see p 210 of ref 3). It is indeed true that, as Bilde and Hansen claimed,[232] Pople[153] used the term ring current in 1958—he even mentioned it in his title: *Molecular Orbital Theory of Aromatic Ring Currents*—in the course of his classic paper beginning on page 175 of the first volume of *Molecular Physics*; furthermore, McWeeny,[161] presenting his own seminal work in the same volume only 136 pages later, similarly—and equally definitively—entitled it *Ring Currents and Proton Magnetic Resonance in Aromatic Molecules.* However, closer examination of the literature reveals that the appellation 'ring current' was explicitly used at least two years earlier, in 1956, by Bernstein, Schneider and Pople, in the course of their celebrated experimental investigations, reported in the *Proceedings of the Royal Society of London* (ref 152). It may be noted that the words ring and current were *not* actually

adjoined consecutively in Pople's very first, and much cited, note on the subject, in the 1956 *Journal of Chemical Physics*,[151] which dealt specifically and exclusively with the monocycle benzene.[151] As far as we can tell, therefore, it seems to be the 1956 *Proceedings of the Royal Society* paper of Bernstein, Schneider, and Pople[152] that contained the first explicit reference to a ring current.

A large proportion of the studies that attempted to relate ring-current intensities in conjugated molecules to the idea of aromaticity were published in the semiempirical era[2-4] (i.e., before ca. 1980), and it is mainly to this period that we devote attention in this section. By far the most-used ring-current approaches in this context were those of Pople[153] and McWeeny.[161] Ostensibly, the Pople[153] and McWeeny[161] formalisms appear, at first, to be superficially very different, but when each are based on simple Hückel molecular-orbitals[16,204] (which, though naive, are, by their very simplicity, conceptually appealing—see later in this section) and when they are based on a common geometry, both methods give the *same numerical values* for calculated ring-current intensities, *provided that* these are expressed as a ratio to the ring-current intensity calculated, *by the corresponding method*, for benzene. These ratios are the quantities J_i/J_{benzene} that feature in eq 15 of section IV.B, and (as they are dubbed in ref 187) they will subsequently be referred to in this review as 'relative ring-current intensities'. Another formulation that, numerically, is also identically equivalent to those of Pople[153] and McWeeny,[161] if the above conditions are fulfilled, was devised in 1953—but was, at the time, left unpublished[233]—by the late Professor C. A Coulson, F.R.S. and was independently re-worked by Mizoguchi nearly 35 years later.[234] Coulson[233] and Mizoguchi[234] both re-cast the Hückel–London theory of magnetic susceptibility[116-118] in terms of the Coulson 'contour-integral' approach.[235] (Coulson's contour-integral device[235] for calculating total π-electron energies within the format of simple HMO theory was much favored by its originator[2,186,236] but, possibly because of its rather esoteric nature,[2,186,236] was less generally and less enthusiastically taken up by other authors.) The appearance of Mizoguchi's paper[234] in 1987 prompted one of us and O'Leary[236] to make available in full, to a wider public, Coulson's 1953 work which until then had lain unpublished in the Coulson Archives[233] since his death in 1974 and had, during all that time, received only scant mention, as footnotes, in a review (ref 2, p 323) and in a thesis (ref 186, p 55). Coulson's treatment is, like McWeeny's,[161] based on bond–bond polarizabilities,[204] and it therefore provides an interesting parallel to certain aspects of the McWeeny 'polarizability' approach,[161] published five years later. McWeeny's own method[161] was itself elegantly adapted by Veillard[163]—in a much under-rated and little-cited paper (ref 163)—so as to be applicable to heterocyclic conjugated systems. One of the present authors has applied Veillard's refinement[163] to calculate relative ring-current intensities in heterocyclic conjugated systems containing sulfur[227] and nitrogen.[237] With some modifications, Veillard's formalism[163] has been
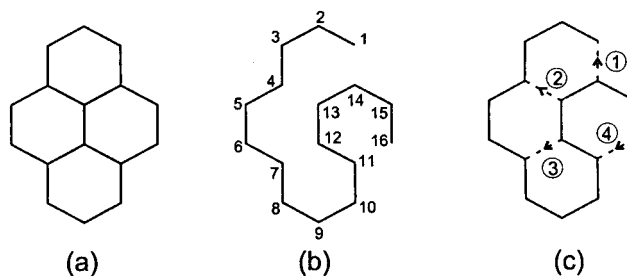

Figure 2. Open chains (spanning trees[211]) that could be used for an application of McWeeny's method[161] via eq 16 (section V) in order to perform a ring-current calculation on the conjugated hydrocarbon pyrene (**14**): (a) the carbon–carbon σ-bond connectivity of pyrene; (b) a continuous open chain (from this semi-Hamiltonian molecular-graph[211]) for pyrene; (c) circuit-completing bonds associated with the open chain in part b. (Adapted and reprinted with permission from ref 3. Copyright 1997 Research Studies Press Ltd.)

applied to heterocycles and macrocycles by Ege and Vogler[238-240] and to heterocyclic systems by Vincent et al.[241] Figeys et al.[242-244] and Gayoso and Bou-cekkine[245-247] further introduced the refinement of variation of resonance- and Coulomb integrals into the original McWeeny–Veillard method.[161,163] The London–McWeeny–Veillard[116-118,161,163] formalism based on various iteratively self-consistent HMO wave functions has been used to calculate magnetic anisotropies,[245-252] ^{1}H NMR chemical shifts,[246] and individual ring-current intensities.[1,77,220,242-244,253,254-56]

Of the two main (and, as we have emphasized, *equivalent*) basic approaches—namely, those of Pople[153] and McWeeny[161]—far more use has been made of McWeeny's method for practical numerical applications than of Pople's. Indeed, the present authors are aware of only three papers[257-259]—in addition to Pople's own application of his method to azulene as an illustrative example in his initial paper[153]—in which Pople's formulation has been invoked, 'in anger', as-it-were, for actual numerical computation of relative ring-current intensities. Applications of McWeeny's method, in its original, unmodified form,[161] to calculate relative ring-current intensities are, by contrast, legion.[1,77,181,186,210,211,229,253,259-267] It is almost certain that the list just cited is not exhaustive. This discrepancy in public take-up of the two formulations on the part of theoretical and organic chemists is curious in that it arises despite the fact that Pople gave an *explicit* expression for relative ring-current intensity (eqs 2.23 and 2.24 on p 179 of ref 153) whereas McWeeny[161] did not: in the latter's original paper,[161] the quantity J_i/J_{benzene} was left only *implicit*. An *explicit* expression—also incorporating Veillard's generalizations[163]—was, however, later supplied by one of the present authors;[139] it is

$$(J_i/J_{\text{benzene}}) = 9\{\sum_{(\mu)} [P_{(\mu)}\eta_{(\mu)} + \beta\bar{\pi}_{(\mu)(\mu)}(\eta_{(\mu)})^2]S_{(\mu)}C^i_{(\mu)} +$$

$$\sum_{(\mu < \nu)}\sum \beta\bar{\pi}_{(\mu)(\nu)}\eta_{(\mu)}\eta_{(\nu)}[S_{(\mu)}C^i_{(\nu)} + C^i_{(\mu)}S_{(\nu)}]\} \quad (16)$$

The symbols in eq 16 are explained with reference to Figure 2. Figure 2a shows the carbon–carbon σ-bond connectivity of the pyrene molecule (**14**). In
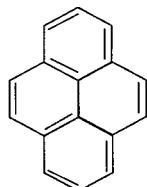
(14)

Figure 2b, a so-called 'spanning tree' [211] is depicted in which certain carbon–carbon bonds of the pyrene σ-bond network have been deleted so as to leave a continuous, open chain (without circuits or rings) that does, however, still connect all the carbon atoms that were in the original conjugation network of pyrene. The carbon atoms in this chain have been numbered consecutively. (We are here referring, in an informal and intuitive fashion, to the graph-theoretical aspects that underlie the ring-current concept; this is a topic that has claimed the present authors' attention over the years[211,268–275] but it is outside the scope of the present review; any interested reader requiring a more rigorous discussion is directed, for example, to refs 211 and 268–276). Figure 2c shows, as dotted lines, those carbon–carbon σ-bonds that have to be added to the open-chain spanning tree of Figure 2b in order to reconstitute the carbon–carbon σ-bond network of the original (pyrene) molecule depicted in Figure 2a. Following in the spirit of McWeeny,[161] we may conveniently think of these as 'circuit-completing links'. Note that, by means of arrows, we have associated a *direction* with them: in Figure 2c, the convention has been followed that the circuit-completing bonds are defined *from* the carbon atom whose label in Figure 2b is *higher to* the carbon atom whose label is *lower*. In eq 16, all the Greek subscripts refer to circuit-completing bonds, as described, as well as to the circuits that they complete; specifically, in that equation

(i) $\beta_{(\omega)}$ (the resonance integral for the

ωth circuit-completing bond) $= \beta\eta_{(\omega)}$

$\eta_{(\omega)}$ is a dimensionless number, somewhere in the vicinity of 1, that is (rather subjectively) considered, on physical grounds,[277] to be appropriate for the particular σ-bond (ω) in question (see, for example, refs 227 and 237 for specific applications).

(ii) $S_{(\omega)}$ is the *signed* (algebraic) area of the

ωth circuit (i.e., the enclosed area formed
when the ωth circuit-completing bond, *only*,
is inserted)

These areas are to be counted *positive* if the arrow on the ωth circuit-completing bond points in the *counterclockwise* sense around the circuit that it completes (the ωth circuit) and are to be counted *negative* if that arrow points in the *clockwise* sense around the circuit that the ωth circuit-completing bond completes. Thus, in Figure 2, $S_{(1)} = 3$ (measured in benzene ring-area units), $S_{(2)} = 2$, $S_{(3)} = 1$, and $S_{(4)} = -1$.

(iii) $C^i_{(\omega)} = 0, \pm 1$, according to the following rules

(1) $C^i_{(\omega)} = 1$ if (a) the ωth circuit-completing bond contains the ring i *and* if (b) the ωth circuit-completing bond is defined in the *positive (counterclockwise)* sense around the circuit that it completes (the ωth circuit); (2) $C^i_{(\omega)} = -1$ if criterion a, above, applies *and* if (b) the ωth circuit-completing bond is defined in the *negative (clockwise)* sense around the circuit that it completes (the ωth circuit); (3) $C^i_{(\omega)} = 0$ if the ωth circuit *does not contain* the ring i. (It should be noted that in the form in which eq 16 is given in ref 211, as eq 15 on p 442 of that reference, it was assumed that all $\eta_{(\omega)} = 1$, as only 'topological' considerations were material there; we shall have more to say about this simplified topological version of eq 16 later in this section. The full form of eq 16, above, is, however, given in refs 3 and 139) Also in eq 16, $P_{(\omega)}$ is the ordinary (Coulson) bond order[204] of the ωth circuit-completing bond, $\bar{\pi}_{(\omega)(\omega)}$ is the imaginary self-polarizability of that bond, and $\bar{\pi}_{(\mu)(\nu)}$ ($\mu \neq \nu$) is the imaginary, mutual bond–bond polarizability of two distinct circuit-completing bonds.[161] Coulson and Longuet-Higgins[278] previously defined the *real*, mutual bond–bond polarizability of two bonds, μ and ν, as

$$\pi_{(\mu)(\nu)} = \frac{1}{\beta}(\partial P_{(\mu)}/\partial \beta_{(\nu)}) \tag{17}$$

Here, $P_{(\mu)}$ is the Coulson bond order[204] of bond μ, $\beta_{(\nu)}$ is the resonance integral for bond ν, and β is the standard Hückel resonance-integral.[204] By analogy with this, the *imaginary*, mutual bond–bond polarizability, $\bar{\pi}_{(\mu)(\nu)}$—required for the *complex* perturbations that arise in the presence of an external magnetic field[161]—is the *imaginary* part of the change in the bond order $P_{(\mu)}$ per unit change in the *imaginary* part of the resonance integral $\beta_{(\nu)}$. Once given a ground-state electronic configuration for the molecule, deduced from the *Aufbau* Principle,[279,280] $P_{(\omega)}$, $\bar{\pi}_{(\omega)(\omega)}$, and $\bar{\pi}_{(\mu)(\nu)}$ are all calculable solely from the standard *field-free* Hückel Hamiltonian matrix. The latter depends purely on molecular topology—i.e., the carbon–carbon (or heteroatom) σ-bond connectivity of the conjugated system in question.[211] As one of us emphasized previously,[77,211,229] however, because its calculation also involves a knowledge of (or, at least, an *assumption* of) molecular *geometry*, the ring-current index itself is *not* a completely topological quantity, even when a purely topological *wave function* (such as the simple Hückel one,[16,204] with all $\eta_{(\omega)}$ in eq 16 set equal to 1) has been used to calculate it.[77,211,229] We have also previously[3] drawn attention to the fact that the actual formulas for calculating the quantities featuring in eq 16 are quite complicated and that, furthermore, the expression for $\bar{\pi}_{(\mu)(\nu)}$ given originally by McWeeny[161] as being applicable to the alternant hydrocarbons[204] contains a misprint. Accordingly, to clarify matters, one of us gathered together all the relevant equations for defining $\bar{\pi}_{(\mu)(\nu)}$, applicable under all circumstances, into the Appendix of ref 211.

To obtain the summation over *rings*—and hence to bring out the fundamentals of the ring-current idea—
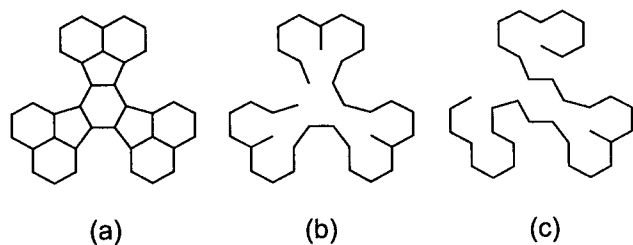
Figure 3. (a) Graph representing the carbon–carbon σ-bond connectivity of decacyclene (**15**); (b and c) two different branched spanning trees of this (non-semi-Hamiltonian[211]) molecular graph. (Adapted and reprinted with permission from ref 211. Copyright 1975 The Royal Society of London.)

McWeeny[161] performed an ingenious unitary transformation on the original basis orbitals in such a way that all the perturbation brought about by the external magnetic field was concentrated into *just one bond in each ring* of the conjugated system under study—the very bonds that we have called the circuit-completing bonds. This latter observation alone serves to emphasize the fact that on the London–Pople–McWeeny model,[116–118,153,161] the applied, external magnetic field manifests itself through *ring fluxes*[2,3,153,161] and that without the rings and other closed circuits (see, for example, Figure 2c)—which, by virtue of their areas, give rise to these magnetic fluxes when the external magnetic field is perpendicular to the molecular plane of the conjugated system in question—such a field can have no effect whatsoever in exciting ring currents.

To be able to apply the unitary transformation that McWeeny described in his original paper,[161] it *is* necessary to base the ring-current calculation on a spanning tree that is a continuous, open chain, without branches, as is the pyrene spanning tree shown in Figure 2c. It *is* always possible to find such a spanning tree if the graph representing the conjugation network is what graph theorists call 'semi-Hamiltonian'.[211] The conjugation networks of some molecules, however, are represented by graphs that are *not* semi-Hamiltonian and, for such, an unbranched spanning tree (required for an application of the original McWeeny unitary transformation[161]) cannot, by definition, be found. The molecule decacyclene (**15**) is a case in point.[211,281] Figure 3 parts b
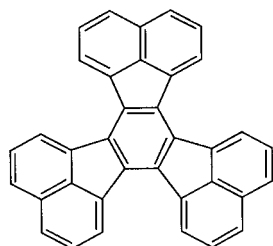

(15)

and c show two branched spanning trees for the molecular graph[211] of decacyclene shown in Figure 3a. To cope with these situations, Gayoso and Boucekkine[245] generalized McWeeny's unitary transformation[161] in such a way that despite the restriction implied by the recipe that McWeeny initially de-

Figure 4. The 35 graph-theoretically distinct spanning-trees of the graph representing the carbon–carbon σ-bond connectivity of naphthalene (**3**). (Adapted and reprinted with permission from ref 211. Copyright 1975 The Royal Society of London.)

vised[161] for the required unitary transformation, it would suffice to base a ring-current calculation by McWeeny's method[161] on *any* spanning tree, branched or not, to be found within the molecular graph representing any arbitrary conjugated system. With the Gayoso–Boucekkine extension,[245] therefore, eq 16 is applicable for the calculation of relative ring-current intensities in *any* such species. The actual number of spanning trees in a molecular graph is an intriguing graph-theoretical problem (e.g., refs 211, 268, 270–276); this number goes up rapidly as the size of the conjugated system increases. In the case of naphthalene (**4**), for example, there are 35 graph-theoretically distinct spanning trees extant in its molecular graph,[211,268] and they are all illustrated in Figure 4; in the molecular graph (Figure 3a) of decacyclene (**15**) there are 22 317 981 such spanning trees and in Buckminsterfullerene[271–273,276] there are ca. 3.75×10^{20} of them! For the purpose of a ring-current calculation by application of eq 16, however—via either the McWeeny[161] or the Gayoso–Boucekkine[245] unitary transformations—*any one* spanning tree will be adequate. (Somewhat surprisingly, in ref 282 there is a puzzling misunderstanding/confusion on this point concerning ref 271.)

It is now precisely 40 years since Elvidge and Jackman[65] proposed that a system should be described as aromatic if it "will sustain an induced [π-electron] ring-current" and that the magnitude of this ring current may be taken as a quantitative measure of aromaticity. Although they did not say so explicitly, the implication was that the ring current
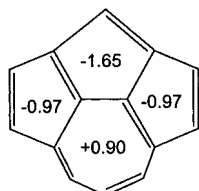
(16)

Figure 5. A molecule (illustrated by Jung in ref 259) apparently bearing both diamagnetic (positive sign) and paramagnetic (negative sign) ring currents. Numerical values in the rings indicated were calculated by Jung,[259] by use of the Pople[153] and McWeeny[161] methods, and represent ring-current intensities expressed as a *ratio* to the ring-current intensity calculated, by the corresponding method, for benzene.

was to be taken to be *dia*magnetic. These authors[65] were careful to point out at the time that their treatment was applicable only to *six*-membered, *mono*cyclic species (see also refs 14, 33, 60, 67, and 283−291), though they did express the hope that ^{1}H NMR chemical shifts might lead to a quantitative assessment of aromaticity in a general, arbitrary, conjugated system. Furthermore, as one of us pointed out previously,[1] around about 1966 half a dozen groups[22,107,238,242,258,292] drew attention (on the face of it, independently) to the observation that *para*magnetic ring currents are to be expected in the [4n]-annulenes—although (as one of us has already emphasized[1]) this conclusion was in fact implicit in the much earlier work of Berthier, Pullman et al.,[293−295] and Wagnière and Gouterman.[296] As one of us commented when last[1] discussing aromaticity and ring currents, "after this, it became almost common folk-lore in the NMR−Literature that, in some kind of heuristic and ill-defined way, Elvidge and Jackman's idea could be extended to declare that *any* conjugated system (whether monocyclic or polycyclic, heterocycle or hydrocarbon) which appears—either from NMR-measurements or from direct calculations—to support an overall π-electron *para*magnetism is necessarily 'anti-aromatic.'"

Several objections have been raised concerning these suggestions. A very cogent one has been expressed by Jung,[259] who doubted the value of extending these ideas to *poly*cyclic hydrocarbons for the very convincing reason that molecules of this type exist—e.g., structure **16**, shown in Figure 5—for which eq 16 predicts some rings to bear diamagnetic currents while other rings, within the *same* molecule, appear to sustain paramagnetic ring currents. Jung came upon this problem in the course of his own calculations (essentially, though not actually and explicitly, using our eq 16) in ref 259, and its reality has subsequently been confirmed by the present authors[1,77,220,253] and by others (e.g., refs 254−256). One way around this difficulty would be simply to take the easy way out and restrict the ring-current criterion for aromaticity to monocycles but, to be able to extend consideration to the case of polycyclic systems, it might be possible to rely on the *overall* 'London' contribution to magnetic susceptibility perpendicular to the molecular plane as a criterion of aromaticity. For example, Haddon[291] has shown that,

to a good approximation, there is an analytical relation between resonance energies and ring-current intensities in the [4n + 2]-annulenes, and Aihara[297] used an elegant graph-theoretical formalism to demonstrate that diamagnetic-susceptibility exaltation (section III.A.4) reflects the sign and, to a lesser extent, the magnitude of the (Dewar[28,297]) resonance-energy of a general, conjugated hydrocarbon. Aihara even felt himself able unambiguously to conclude, in ref 297, "Now we can safely use diamagnetic susceptibility exaltation as a definite criterion of aromaticity." While having some reservations about this claim in ref 1, Mallion did concur that "although breakdown of the overall 'London'-susceptibility into contributions from individual rings [i.e., the individual ring-currents] is often conceptually and aesthetically valuable, for the purposes of establishing a criterion for 'aromaticity' the overall magnetic-susceptibility anisotropy (or exaltation [cf. our eqs 11 and 12) would appear to be more useful." At about the same time, Benassi et al.[288] concluded, from calculations based on coupled-Hartree−Fock Pariser−Parr−Pople semi-empirical wave functions,[167,168,298,299] that the contribution to the magnetic-susceptibility component perpendicular to the molecular plane "serves as a more reliable aromaticity index than that based on magnetic anisotropy or NMR data."

The second difficulty about the Elvidge−Jackman idea[65] (raised by one of us in ref 1) was much more serious in the semiempirical era[2−4] (i.e., before about 1980) than it is now. This concerns the following question, formulated in ref 1: "Even given the premise that Elvidge and Jackman's definition *is* a constructive starting-point for an assessment of 'aromaticity', how reliably can any particular molecule be stated to exhibit diamagnetic or paramagnetic 'ring-currents'?" To illustrate the apparent difficulties arising from this deceptively simple question, one of us[1] calculated the ring-current contribution to the magnetic susceptibility perpendicular to the molecular plane in pyracylene (**17**) and its dianion by six different semiempirical methods of varying—and, as we have listed them below, increasing—degrees of sophistication. These were (i) simple Hückel−
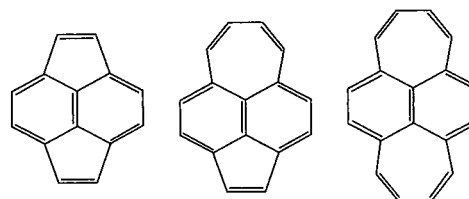

(17)   **(18)**   **(19)**

McWeeny,[161] (ii) noniterative, coupled-Hartree−Fock (Hall−Hardisson[162]), (iii) noniterative, coupled Hartree−Fock (Coulson et al.[253]), (iv) London−McWeeny,[161] based on an iterative ($\beta\omega'\omega''$ [77,245−247]) Hückel molecular orbital, (v) coupled-Hartree−Fock (Hall−Hardisson[162]) with variable resonance integrals, and (vi) coupled-Hartree−Fock (Coulson et al.[253]) with variable resonance integrals. When, in the preceding, we refer to variable resonance integrals, we mean that a wave function has been used that is

iteratively self-consistent with respect to resonance integrals and calculated bond orders. The remarkable finding in ref 1 was that in the case of pyracylene (**17**) (considered by some[77,220,300−302] as a candidate for being a 'perturbed [4*n*]-annulene'), the 'London' contribution to the magnetic susceptibility perpendicular to the molecular plane, when expressed as a ratio ($\Delta\chi^m_{London}$(species)/$\Delta\chi^m_{London}$(benzene)) to the benzene value calculated by the same method, varied from −3.84 (a *negative* value for this ratio means that the species in question is *paramagnetic*) when the crudest method (method i) was used, to +0.31 (i.e., marginally diamagnetic overall) when the calculation was effected by the most sophisticated (method vi) of these semiempirical methods. Strikingly, though, the corresponding ratio for the *dianion* of pyracylene (**17**)—a species that could be considered[1,77] to be π-electronically analogous to a [4*n* + 2]-annulene— *hardly changed* when calculated by all six of the methods: it was +2.75 (i.e., diamagnetic, to the extent of about 2³/₄ times the benzene value) by the crudest method (method i) and +2.56 by the best one (method vi), with a total variation of less than 15% over all six approaches adopted—remarkably insensitive to the scheme of calculation employed! Mallion reiterated[1] and enlarged upon an earlier conclusion with Coulson[77] that calculated ring currents are much more sensitive to whether the wave function used to compute them is self-consistent with respect to atomic charges and Coulomb integrals, on one hand, and computed bond orders (or realistic experimental bond lengths[220,254−256]) and resonance integrals, on the other hand, in the case of those π-electron systems (like pyracylene (**17**)) that the crudest method (method i) predicts to have overall *paramagnetic* (or very weakly diamagnetic) 'London' susceptibilities than in the case of those systems (like **17**²⁻) for which a noniterative HMO calculation predicts strongly *diamagnetic* London susceptibilities.[1,77] Coulson and Mallion[1,77] rationalized this by observing that "paramagnetic contributions will be largest when magnetic dipole transitions can take place between the ground-state (occupied) and excited-state (unoccupied) orbitals,[22,23a,107,123,258,292,303] and this activity will be particularly favored when the separation between the highest occupied (HOMO) and lowest unoccupied (LUMO) orbitals is small. The smaller this separation turns out to be, however, the more likely it is to be sensitive to the idiosyncrasies of the particular method used to calculate it. Hence, the predicted magnetic properties of predominantly paramagnetic systems should be much more dependent upon the method used for their calculation than those of diamagnetic systems. In the latter cases, the diamagnetic contribution to the net current is the major one and this is a function only of the electron density in the ground state;[22,23a,107,123,258,292,303] any (relatively minor) paramagnetic contribution which might possibly obtain is [affected] once again by the HOMO−LUMO separation which, in the case of diamagnetic systems, is much larger and estimates of it are therefore much less dependent on the peculiarities of the particular method used to calculate it."[77] Coulson and the present authors[1,77,220] felt

that the question of whether the wave function employed in a semiempirical calculation possesses the self-consistency that has been described "is much more important, for the calculation of magnetic properties, than the question of whether that wave function is of the Hückel or SCF type—at least when the results are expressed as a ratio to the corresponding quantity (ring current intensity or magnetic susceptibility) calculated, by the same method, for benzene."[77] The conclusion just quoted was provisionally reached by Coulson and Mallion[77] in 1976, during their study of pyracylene (**17**), acepleiadylene (**18**), and dipleiadiene (**19**)—potentially regarded by them[77] as 'perturbed' [4*n*]-, [4*n*+2]-, and [4*n*]-annulenes, respectively—and was subsequently confirmed by the present authors[220] in our detailed comparative consideration of the magnetic properties of two isomers (**20** and **21**) of pyracylene (**17**) as well as by

(20)   **(21)**
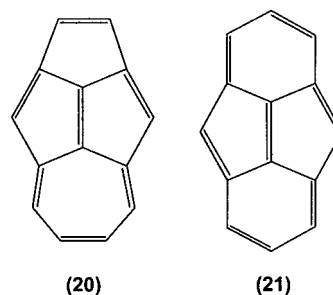
Wilcox and Farley's especially thorough and elegant investigation[255,256] of biphenylene (**22**), cycloocta[*def*]-biphenylene (**23**), and dicyclooct a[*def:jkl*]biphenylene (**24**) and related molecules. In our opinion, the papers


(22)   **(23)**   **(24)**
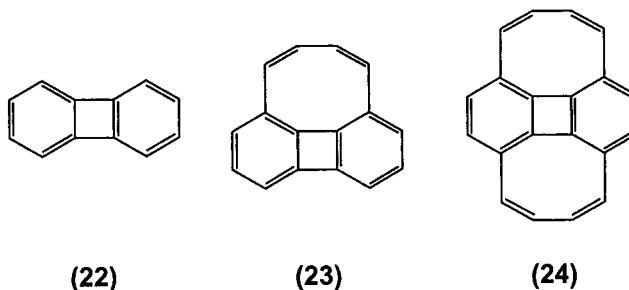
of Wilcox and Farley[255,256,304] that appeared in the mid 1980s—in addition to displaying synthetic ingenuity of some considerable beauty—are among the most valuable contributions to the semiempirical work in this field and are enthusiastically recommended as being particularly worthy of detailed study by any reader who is especially interested in paramagnetic ring currents. Furthermore, the *joie de vivre* that pervades the synthetic work of Vogel et al.[305] in the course of their 1985 'serendipitous' synthesis of dipleiadiene (**19**)—only hypothetical at the time of Coulson and Mallion's[77] semiempirical investigations in the mid-1970s—also makes their account well worth reading.

This sensitivity of calculated π-electron magnetic properties to the sophistication of the methods used to compute them whenever semiempirical approaches are involved—see also, for example, ref 303—did, however, induce in one of the authors an explicit

pessimism the last time[1] that he reviewed the subject of aromaticity and ring currents; on that occasion, he lamented[1] that it was "an unfortunate fact that the very systems which are of particular interest to chemists—namely those that we intuitively feel should be the 'anti-aromatic' ones—are just those whose 'London' magnetic-susceptibilities are the most extremely sensitive to the sophistication of the method (and, particularly, of the *wave function*) used to calculate them!" At the end of the semiempirical era,[2–4] in 1980, Mallion was therefore of the opinion that "this latter point constitutes a major drawback to the potential utility of adopting *calculated* 'London'-susceptibility (or exaltation) as a criterion for defining what we should in future agree to understand by the term 'aromaticity'." [1] This point will *not* be so relevant in sections VI–IX when we move fully to the (post-1980) ab initio era.[2–4]

Before we move to that era, however, we do pay a final semiempirical visit to what the reader will by now have gathered is our favorite series—namely, the condensed, benzenoid hydrocarbons, the archetypal aromatic molecules—and examine especially the treatment that Haigh and one of the present authors presented in ref 229. In the discussion that immediately follows, we shall be considering relative ring-current intensities calculated from eq 16, based on a simple Hückel molecular orbital with all $\eta_{(\omega)}$ set equal to 1, all benzenoid hexagons in the polycyclic benzenoid molecules under study taken to have the same area as the unique ring in benzene, and all ring-current intensities expressed in the form $J_i/J_{benzene}$. This combination of assumptions does, as we shall see, remove all subjectivity (in the form of any further adjustable parameters) from ring-current calculations on this class of molecules, and thus, despite technically being semiempirical, such calculations may be regarded as possibly having an unexpected degree of respectability! Relative ring-current intensities calculated in this way thus depend solely on molecular topology and thus have been dubbed by us[77,211] as 'topological' ring currents. Under these circumstances, the smallest relative ring-current intensity so far reported[264] in a condensed, benzenoid hydrocarbon is 0.236 (in benzo[*b*]perylene (**25**), ring *S*), while in the 19-ring benzenoid hydrocarbon dodecabenzocoronene (**26**) Maddox and McWeeny[260] found a diamagnetic relative ring-current intensity (that in ring *L*) as large as 2.44. Within the domain
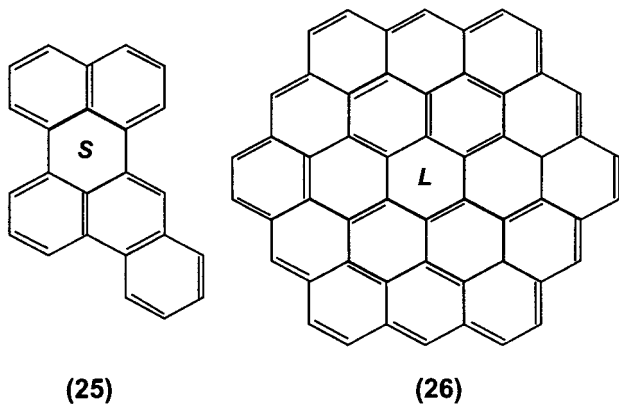
of the condensed, benzenoid hydrocarbons it had been observed empirically[261,262,266] that the more condensed a given ring is, the smaller the ring current it appears to bear. As one of the present authors pointed out three decades ago, however,[266] a dramatic exception to this rule is the central ring (*C*) in peropyrene (**27**) which has an associated relative ring-current intensity of[266] 1.446—over *six times* that[181,182,261] (0.239) in the *formally analogous* central ring (*C*) in perylene (**28**) which, locally, is similarly condensed with four surrounding rings. The exceptionally low-field shift

(**27**)   (**28**)
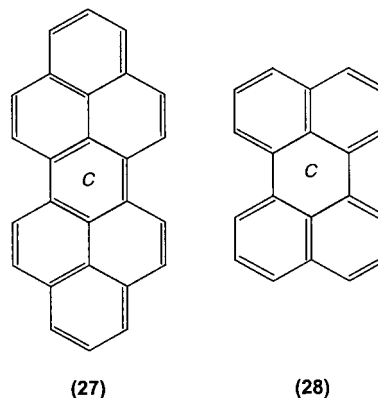
(δ 9.15) of the proton closest to ring *C* observed in the experimental ^{1}H NMR spectrum[306a] of **27**—more than 1 ppm to lower field than the analogous proton in perylene (**28**)[181,189,257]—is certainly consistent with the suggestion of there being a high relative ring-current intensity in ring *C* of **27**. Perturbations brought about by condensation of additional rings in one region of a large, condensed, benzenoid hydrocarbon may often have only a second-order effect on the relative ring-current intensities in rings *distant* from the site of the perturbation—though, evidently, this is by no means always the case as the above comparison between **27** and **28** indicates. In ref 229, Haigh and Mallion established a simple theoretical rationale for connecting the incidence of 'high' and (by comparison) 'low' relative ring-current intensities, such as those just described, with intuitive valence bond resonance theory ideas about bond fixation; these had been pioneered many years before by Clar—notably in his monumental *Polycyclic Hydrocarbons*[19] and in his final book,[34] *The Aromatic Sextet*. Haigh and Mallion[229] showed that there was a connection between the low relative ring-current intensity calculated for the central ring (*C*) in perylene (**28**) and the fact that the unshared carbon–carbon bonds in that ring never appear other than as *single* bonds in any Kekulé structure that can be devised for the molecule as a whole; conversely, the high relative ring-current intensity in the central ring (*C*) of peropyrene (**27**) is related to the fact that when Kekulé structures are written for **27**, the unshared bonds in the central ring are single bonds in some Kekulé structures and double bonds in others. In other words, using the circle notation for the Robinson–Clar[19,34] aromatic-sextet idea, we see (Figure 6) that the central rings in peropyrene (**27**) participate fully in the conjugation between the upper and lower 'naphthalenic' fragments that the central ring con-
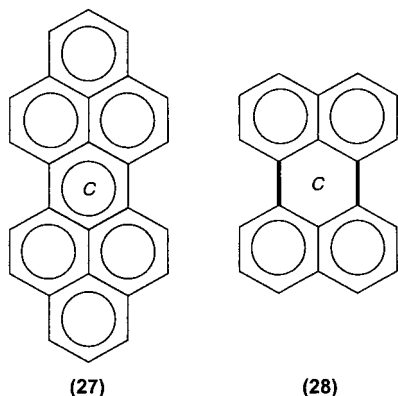

(**25**)   (**26**)

Figure 6. (Left) Peropyrene (**27**) illustrating 'aromatic sextets' [19,34] in all rings, including the central ring, C. (Right) Perylene (**28**) illustrating 'bond fixation' [19,34] in the central ring, C, and 'aromatic sextets' [19,34] in the naphthalenic fragments that ring C connects.
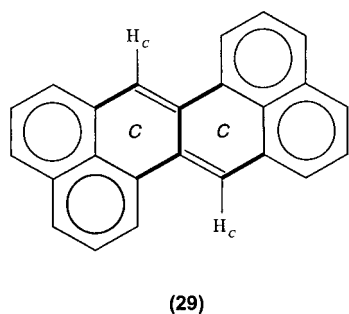

Figure 7. Zethrene (**29**) showing bond fixation[19,34] in the central rings, C, and aromatic sextets[19,34] in the outer rings. H_C are protons directly attached to the rings (C) that are exhibiting the bond fixation. (Adapted and reprinted with permission from ref 229. Copyright 1989 The Croatian Chemical Society.)

nects but that, in perylene (**28**), the unshared bonds in the central ring C—shown in *bold* in Figure 6—are, as it were, frozen as 'single bonds', and thus occurs the phenomenon that the valence bond resonance theory would call 'bond fixation' (see Figure 6). In ref 229, Haigh and Mallion did not achieve their rationalization by devising a ring-current formalism that was itself actually based on a valence bond resonance theory wave function: instead, the philosophy they adopted was (a) to identify and classify those occasions on which simple molecular-orbital theory (in the form of our 'master' equation—eq 16, in its simplest[211] incarnation) predicts specific rings in conjugated hydrocarbons to have exceptionally high and low relative ring currents and then (b) to use topological arguments that rely simply on the carbon—carbon σ-bond connectivity of the conjugated system in question to show that the situations identified in point a, above, are just those in which the absence or presence (respectively) of valence bond resonance theory bond fixation is to be expected.

These ideas were also extended[229] to other systems that manifested bond fixation, such as zethrene (**29**) (see Figure 7; the bonds shown there as double bonds and the single bonds shown as thick lines in the central rings, C, are fixed as double and single bonds, respectively, in all Kekulé structures that can be devised for the molecule as a whole). The interest in the zethrene family is that (unlike in **27** and **28**) they
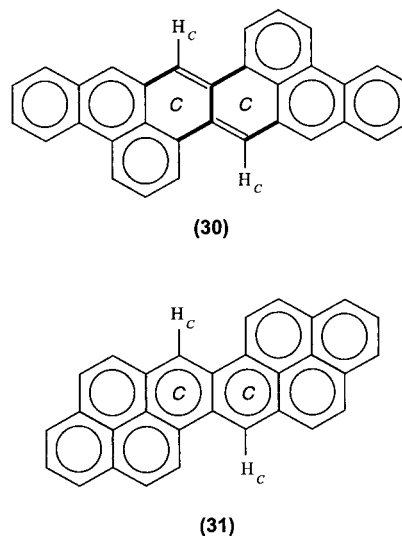

(30)

(31)

Figure 8. Two hydrocarbons (**30** and **31**) which may be considered formally to be derived from zethrene (**29**) by the condensation of two further benzenoid rings. **30** displays 'bond fixation' [19,34] in the central rings, C, while **31** has 'aromatic sextets' [19,34] in the corresponding rings, C. H_C are protons directly attached to the central rings, C, in both cases. (Adapted and reprinted with permission from ref 229. Copyright 1989 The Croatian Chemical Society.)

have protons (shown as H_C in Figure 7) directly bonded to the ring (C) in which there is bond fixation, and thus, these systems are directly amenable to test by means of ^{1}H NMR chemical shifts. Exceptionally dramatic differential ring-current ^{1}H NMR effects were predicted for the protons indicated as H_C in two hydrocarbons formally related to zethrene—one (**30**) exhibiting bond fixation and the other (**31**) being fully conjugated (see Figure 8). The predicted effects on ^{1}H NMR chemical shifts in the case of **30**—molecule **31** had not at the time[229] been synthesized—were experimentally confirmed by the late Professor Clar[306b] (it is perhaps of some historical interest to repeat[229] here that in ref 306b, referring to some then unpublished ring-current calculations on **30** and **31** by one of the present authors, Professor Clar wrote "I was interested to learn that your calculation leads to the same result as the aromatic sextet").

These topological ideas were also extended by Haigh and Mallion[229] to encompass conjugated hydrocarbons outside the condensed, benzenoid family, and they were able to rationalize, for example, why the five-membered ring in fluoranthene (**32**)[265] bears a negligibly small (diamagnetic) relative ring current (while the naphthalenic and benzenoid fragments that the five-membered ring connects in **32** bear relative ring-current intensities very similar to their isolated molecule counterparts)[265] and why the four-membered ring in biphenylene (**22**) is paramagnetic (see also ref 255).

As a postscript to this section, we point out that semiempirical calculations *are* still appearing in the literature, although they are becoming increasingly rare. A recent example is the 1998 paper by Anusooya et al.[307] in which a so-called 'exact' ring-current approach[308] (that makes appeal to the angular-momentum operator[307,308]) has been employed. This "uses correction vectors which implicitly include all

(32)

(34)
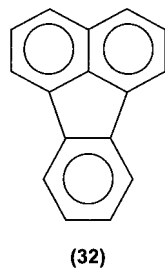
the eigenstates of the Hamiltonian in the space of the chosen configurations." They adopted[307] the Pariser–Parr–Pople approach, carrying out full configuration-interaction calculations for small molecules and approximate ones for large systems. In the polyacenes (e.g., those shown as **3**–**10** in our earlier scheme), Anusooya et al.[307] found that "the aromaticity of the extreme phenyl rings reduces with increasing number of ... rings ... and ... saturates at approximately two-thirds of the benzene value." Although Anusooya et al.[307] referred to ring currents, it is not entirely clear to us what quantities they have in fact actually calculated. It seems to be some kind of *circuit* current rather than a conventional ring current, though apparently without the strict 'Kirchhoff'-type of current conservation at junctions rigorously displayed by the usual ring current[3] (as calculated by the method of McWeeny[161] via our eq 16 or by that of Pople[153]). They claimed, however, to agree qualitatively with the 1982 investigation of Haigh and Mallion[210] concerning the limiting magnetic properties of the linear acenes (exemplified by our Figure 1) and to be in line with earlier ring-current calculations effected by Memory,[261] using McWeeny's[161] formalism. Anusooya et al.[307] examined some fragments to be found on the Buckminsterfullerene (**33**) sphere, such as pyracylene (**17**) and corannulene (**34**);

(33)
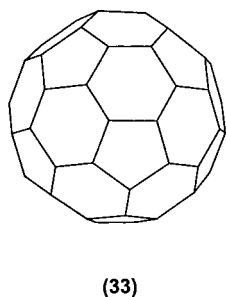
they found a ($4n + 2$) rule, and in corannulene (**34**), the largest C_{60} fragment they studied, the five-membered ring was found to be weakly diamagnetic while the six-membered ring was declared to be more diamagnetic, although much less than in isolated benzene; we note here, in passing, that these conclusions concerning corannulene (**34**) agree with those found in ref 267, though the latter were in fact not actually referred to by Anusooya et al. in ref 307. However, it should be mentioned that the idea of C_{60} surface fragments has been criticized and will be further discussed in section VIII. Anusooya et al.[307] offered an order of aromaticity—the following order— for benzene, pyridene, pyrazene, pyrimidene, and pyridazene. Finally, they claimed that "the ring-current results establish that pyracylene can be
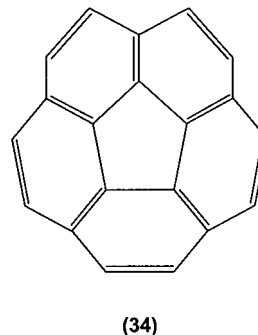
viewed as a $4n$ annulene system with internal vinyl cross-links." However, the present authors believe that the situation is by no means that simple, and although Anusooya et al.[307] made reference to our work of 20 or more years ago,[77,220] there is no mention on their part of our detailed—and by no means straightforward—findings in ref 220 that not all three of pyracylene (**17**) and its two isomers (**20** and **21**) may be regarded as good models for a 'perturbed [4n]- annulene' ($n = 3$): dibenzo[cd,gh]pentalene (**21**) was predicted in ref 220 to be "very paramagnetic", while pyracylene (**17**) and azulenopentalene (**20**) "are marginally diamagnetic and marginally paramagnetic, respectively". Accordingly, of pyracylene (**17**) and its two isomers (**20** and **21**), dibenzo[cd,gh]pentalene (**21**) is the one that[220] "would apparently serve best as a perturbed [12]-annulene" in terms of the model proposed by Trost et al.[300,309]

VI. Nucleus-Independent Chemical Shifts as a Criterion for Aromaticity

An attractive (though, at the same time, potentially troublesome) feature of the semiempirical idea of relative ring-current intensity—which we have discussed at length in the previous section—is that it enables an assessment to be made of the contribution to the aromaticity of a polycyclic molecule *by each of the molecule's constituent rings* rather than merely having to evaluate the overall aromaticity of the molecule as a whole, which is all that criteria such as magnetic exaltation, anisotropy of magnetic susceptibility, and ¹H NMR chemical shifts are capable of. A recent innovation of the ab initio era[2–4] that does, however, retrieve this same advantage that relative ring-current intensities have is the idea of nucleus-independent chemical shift (given the acronym NICS), proposed by von Ragué Schleyer and his school, within the last five years.[88–100] As they also emphasize,[91] "although aromaticity is a global property, the different contributions of individual rings in polycyclic molecules, long of interest, have been evaluated ... in different ways." In their initial paper on the matter,[88] while still reiterating the mantra, as they had consistently done in refs 59 and 82–87, that "diamagnetic susceptibility exaltation is uniquely associated with aromaticity", von Ragué Schleyer et al.[88] did point out—incidentally invoking recollection of the long-standing observations of Brooks[230] and Davies[224,225] to which we drew attention near the end of section IV.B—that this quantity is "highly dependent on ring ... area" (see also refs 59, 87, 88, 97, 139,

181, 182, 211, and 226–229). von Ragué Schleyer et al.[88] also observed that ring-current effects on peripheral attached protons are somewhat modest compared, for example, with those on protons directly above (e.g., ref 177) or inside (e.g., ref 36) a conjugated ring. Furthermore, while the rings of most aromatic systems are too small to accommodate atoms internally, von Ragué Schleyer et al.[88] made the point that ^{1}H NMR chemical shifts have long been used as aromaticity and antiaromaticity probes (e.g., refs 177, 310, and 311) while δ Li^{+} can be employed similarly, with the additional advantage that it is possible[226,312] to effect computations involving Li^{+} complexes with individual rings in polycyclic systems. von Ragué Schleyer et al. therefore proposed[88] the use of absolute magnetic shieldings computed at *ring centers* as a new criterion for aromaticity and antiaromaticity. The ring center was defined as being the "nonweighted mean of the heavy-atom coordinates", available from quantum-mechanics programs such as GAUSSIAN.[141] Accordingly,[91] "NICS is defined as the negative of the absolute magnetic shielding computed ... at the unweighted geometric center of aromatic or antiaromatic rings (NICS(0)) or 1 Å above the ring (NICS(1))." von Ragué Schleyer et al.[91] went on to interpret this by claiming that[91] "significantly negative values indicate the presence of diatropic ring current and therefore aromaticity. Significantly positive values indicate antiaromatic behavior." Lazzeretti noted[4] that such a quantity is very appropriately called nucleus-independent chemical shift "as no nuclear probe actually experiences the effective magnetic field in the centre of most conjugated rings." Lazzeretti[4] also drew attention to the fact that actual, extant physical nuclei entrapped within molecular cages physically big enough to surround them—as well as a hypothetical central test dipole—had already been suggested as aromaticity scales in the fullerenes[313–317] (species about which we shall have more to say in section VIII).

The school of von Ragué Schleyer applied this NICS approach to a large number of conjugated systems over the course of the last five years[88–100] and so have certain others, of which refs 318–321 are a few representative examples. Of particular note is its application by von Ragué Schleyer et al. to the so-called 'superaromatic' kekulene,[86] previously the subject of an elegant topological study by Aihara,[322,323] and by Bühl[320] to the fullerenes (see section VIII). As always, with ab initio calculations—despite the sometimes false reassurance of the appellation 'ab initio'—one should examine the wave functions and the assumptions generally on which they are based; accordingly, we note here that refs 88–100, like those of the same school's work on magnetic exaltation[82–87] discussed in section II.B, were based on good-quality calculations using the IGLO method of Schindler and Kutzelnigg[133–135] or, alternatively, the standard GIAO[136–140] approach, as programmed in GAUSSIAN;[141] in ref 93 they used what they call the 'de Mon NMR program'.[324,325] In ref 99 they used a modified version of this program—the details are all explained there[99] for any interested reader.

In his recent comprehensive review[4] Lazzeretti has, however, been somewhat lukewarm about the NICS concept, stating that "the soundness of an elusive and controversial abstract concept like aromaticity, whose intrinsic difficulties and problematic character have been widely discussed over a long time, can hardly be established by introducing a merely 'virtual' quantity like NICS which, by its very definition, is not observable." Somewhat more technically, Lazzeretti[4] also raised the objection that the likely presence of a paramagnetic vortex which, he claimed,[4] circulates about the highest symmetry axis of all planar, cyclic molecules in the presence of a magnetic field perpendicular to the molecular plane "would seem to limit the plausibility of NICS as an indicator of diamagnetic ring currents circulating along the molecular perimeter, as it evidently contains some spurious information on local paramagnetism." This could, Lazzeretti felt,[4] limit the use of NICS scales as measurements of aromaticity. Nevertheless, Lazzeretti did cautiously concede that the successful applications of the NICS idea[88–100,318–321] seemed "to justify its soundness for the construction of such scales in those cases where this theoretical tool parallels other criteria, [such] as exaltation and anisotropy."

We might also argue here that another indicator that, to some extent, does seem to run parallel with the predictions of NICS, at least qualitatively, is relative ring-current intensity—as calculated, naturally, by our ubiquitous eq 16 and much discussed in section V—in the condensed, benzenoid hydrocarbons as well as in a limited number of other conjugated systems on which von Ragué Schleyer et al. gave data in their founding paper on the subject.[88] To make this point, we have gathered together for comparison in Table 1 relative ring-current intensities (essentially as if calculated via eq 16) and the relative NICS values deduced from those that von Ragué Schleyer et al. quote, in ref 88, for five benzenoid[161,257] and three nonbenzenoid[77,256] conjugated hydrocarbons. In the spirit of section V, above, for the benzenoid hydrocarbons the relative ring-current intensities have been calculated from a noniterative HMO;[161,257] in view, however, of the discussion in section V, for the species **17** and **22** for which a simple HMO calculation predicts some of their rings to be paramagnetic, it seemed only fair for a proper assessment of the comparison to quote relative ring currents[77,256] in which self-consistency had been achieved between atomic charges and Coulomb integrals on one hand and resonance integrals and calculated bond orders (or possibly realistic experimental bond lengths[220,256]) on the other. All NICS values taken from ref 88, with the exception of those for triphenylene (**35**), were calculated by a GIAO–SCF method with basis set 6-31+G*; the absolute value for benzene with this method and basis set is[88] −9.7 ppm, and the values quoted in the right-hand column of Table 1 are those from ref **88** which have subsequently been divided by this benzene value of −9.7 ppm and expressed corrected to two decimal places. The NICS values for the two nonequivalent rings of triphenylene (**35**), taken from

Table 1. Relative Ring-Current Intensities from Various Sources and NICS Values from Ref 88, Expressed as a Ratio to the Value Calculated, by the Same Method, for Benzene

compounds	relative ring current[a]	relative NICS[b]
benzene (**3**)	1.00	1.00
naphthalene (**4**)	1.09[c]	1.02
anthracene (**5**)		
central ring	1.28[d]	1.37
outer rings	1.09[d]	0.85
phenanthrene (**1**)		
central ring	0.98[d]	0.67
outer rings	1.13[d]	1.05
triphenylene (**35**)		
central ring	0.75[d]	0.27[e]
outer rings	1.11[d]	0.94[e]
azulene (**36**)		
five-membered ring	1.15[f]	2.03
seven-membered ring	1.07[f]	0.72
pyracylene (**17**)		
six-membered rings	0.31[g]	0.01
five-membered rings	−1.01[g]	−1.32
biphenylene (**22**)		
six-membered rings	0.61[h]	0.53
four-membered ring	−0.80[h]	−1.96

[a] Calculated via the equivalent of eq 16 (section V) and expressed correct to two decimal places. All relative ring currents quoted here are based on a simple, noniterative HMO,[161,257] with the exception of those for pyracylene (**17**) and biphenylene (**22**) in which certain rings appear to be paramagnetic. Ring-current calculations for these species are, therefore, based on an iteratively self-consistent HMO.[77,256] A positive entry in this column denotes diatropicity—a negative entry indicates paratropicity. [b] Quoted from ref 88. All values except those for triphenylene (**35**) were calculated in ref 88 by a GIAO−SCF method with basis set 6-31+G*; the absolute value for benzene with this method and basis set is[88] -9.7 ppm, and the values listed in this column are those from ref 88 after they were divided by a benzene value of −9.7 ppm and expressed corrected to two decimal places. A positive entry in this column denotes diatropicity—a negative entry indicates paratropicity. [c] From refs 161 and 257. [d] From ref 257. [e] The NICS values for triphenylene (**35**), taken from ref 88, were calculated in ref 88 by a GIAO−SCF method with basis set 6-31G*. The absolute value for benzene with this method and basis set is[88] −11.5 ppm, and the values quoted in this column are those from ref 88 when they have subsequently been divided by a benzene value of −11.5 ppm and expressed corrected to two decimal places. [f] From ref 153. [g] From ref 77. [h] From ref 256.


(**35**)   (**36**)
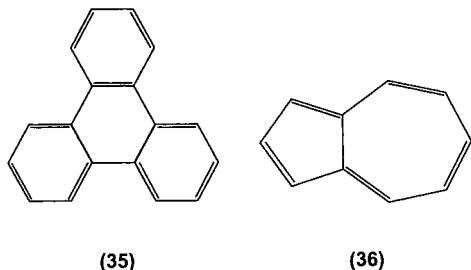
ref 88, were calculated there by a GIAO−SCF method with basis set 6-31G*; the absolute value for benzene with the latter method and basis set is[88] −11.5 ppm, and, accordingly, the values quoted in Table 1 for triphenylene (**35**) are those from ref 88 after they have been divided by *this* benzene value of −11.5 ppm and likewise expressed corrected to two places of decimals.

Although there is manifestly no close overall correlation between the two columns of ratios in Table

1, both models do at least agree qualitatively in that (a) they predict the same relative order of aromaticity (if indeed that is what these figures are measuring!) for the several rings within each of the six diatropic species considered and (b) for the last two hydrocarbons, **17** and **22**, which seem to involve paramagnetic rings, the two methods agree on which rings are paramagnetic and which are diamagnetic. The biggest quantitative discrepancy is in the case of azulene (**36**)—not surprising, perhaps, when it is recalled that **36** is a nonalternant hydrocarbon[204] and so, in the context of the simple noniterative HMO used by Pople[153] in his original paper to calculate the values we have quoted, it would notoriously fall foul of the Coulson−Rushbrooke Theorem.[204,326] Nevertheless, there is probably enough qualitative, or even semiquantitative, agreement in Table 1 to engender the feeling that relative ring-current intensities and NICS might, perhaps, be measuring the same kind of phenomenon, though whether this implies a scale for aromaticity or not is, inevitably, a more contentious matter.

In conclusion, it may be noted that we tried a similar exercise to the above by comparing relative ring-current intensities computed from the simplified topological version of eq 16, published in ref 211, for coronene (**37**)[257,260] and benzo[*ghi*]perylene (**38**)[264] with the recently published NICS values for these molecules due to Schulman and Disch.[318] (Energies

(**37**)   (**38**)
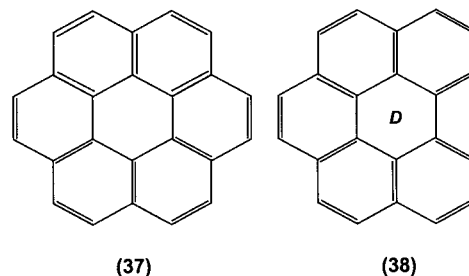
and geometries were calculated by these authors at the DFT level with basis set up to the standard of G-311G**. Magnetic susceptibilities were computed using Keith and Bader's[327,328] continuous-gauge formulation, and magnetic shieldings were evaluated with the classical GIAO method at HF 6-31G* level (see pp 230−247 of ref 3 for an explanation of this ab initio jargon)). Like von Ragué Schleyer et al.[88] in the case of their calculations on triphenylene (**35**), Schulman and Disch[318] used the GIAO method at the 6-31G* level. Once again, the same order of the aromaticity of the several rings within each molecule was predicted by both the NICS(0) and ring-current models, but NICS(0) predicted the central ring in coronene (**37**) and the most condensed ring in benzo-[*ghi*]perylene (**38**) (ring *D* on the labeling scheme adopted by Schulman and Disch[318]—see structure **38**) to be slightly paramagnetic, with relative NICS values of −0.07 and −0.21, respectively, whereas the corresponding relative ring currents are diamagnetic, at +1.04 and +0.68, respectively. (NICS(1)[88] does, however, make these two rings go diamagnetic,[318] assigning them (relative) NICS values[319] of +0.35 and +0.21, respectively.) This discrepancy could either be

attributed to crudeness of the calculated relative ring-current intensities,[257,260,264] or (more likely, we think) it could be a manifestation of Lazzeretti's criticism[4] (quoted above) that NICS's plausibility as an indicator of diamagnetic ring-current might be limited because of its potential propensity for introducing 'spurious information'[4] about local paramagnetism. However, these comparisons between relative ring-current intensities and relative NICS values—especially on very large, condensed benzenoid hydrocarbons of the type already extensively exploited[210,211,229,260−264,266] by the semiempirical approaches via our eq 16 of section V—do, we feel, merit further investigation by those with the will (and, of course, the computational facilities) to pursue them.

VII. Topological Analysis of the Current-Density Flow

A global description of the current-density field induced in a molecule by an external magnetic field may help the reader in identifying and conceptualizing the special features of aromatic molecules. Such a description, based on the techniques and concepts of differential topology, was introduced by one of the present authors.[329−333] Twenty years later, that analysis still stands. In recent years, it has become a standard method of examining the induced current-density fields (e.g., refs 4, 334, and 335) and it is providing a language for the discussion of the reaction of electron density to external magnetic fields. We give here a very brief and truncated account of it; the reader interested in further details is directed to the original references[329−333] (especially the review articles, refs 332 and 333, to recent applications (e.g., refs 334 and 335), to pp 230−245 of our earlier review,[3] and to an extensive and very detailed discussion in pp 28−80 of Lazzeretti's recent ring-current review).[4]

Consider an N-electron probability current density,[12,331] $\mathbf{j}(\mathbf{r})$. In the applications considered here, this current density is the electronic response to an external magnetic field but the theory is completely general and may be applied in other, possibly more complex, circumstances. The current density is a three-dimensional vector-field defined at any point in space. In a stationary situation, the fact that the time derivative of the charge density is zero requires the divergence of the current density also to vanish: $\nabla \cdot \mathbf{j} = 0$. This is a particular application of the continuity equation, i.e., the conservation of the electronic charge. For an N-electron system, when the state function is of the single-determinantal form, the total current density, $\mathbf{j}(\mathbf{r})$, may be broken down into additive orbital components,[11,336] $\mathbf{j}_k(\mathbf{r})$. However, these orbital currents are not, in general, conserved. The proposal has been made[11] that this orbital current should be supplemented by an exchange term, $\mathbf{j}_k^{\text{exch}}(\mathbf{r})$, so that the so-called 'complete' orbital current, $\mathbf{j}_k^c(\mathbf{r})$, given by the equation

$$\mathbf{j}_k^c(\mathbf{r}) = \mathbf{j}_k(\mathbf{r}) + \mathbf{j}_k^{\text{exch}}(\mathbf{r}) \tag{18}$$

is divergenceless, i.e.,

$$\nabla \cdot \mathbf{j}_k^c(\mathbf{r}) = 0 \tag{19}$$

These exchange currents will cancel when summed over all electrons

$$\mathbf{j}(\mathbf{r}) = \sum_k n_k \mathbf{j}_k(\mathbf{r}) = \sum_k n_k \mathbf{j}_k^c(\mathbf{r}) \tag{20}$$

where n_k is the occupancy of orbital k. The topological theory reviewed here for the total current, $\mathbf{j}(\mathbf{r})$, may also be applied to the complete orbital current, $\mathbf{j}_k^c(\mathbf{r})$, thus allowing a detailed discussion of the magnetic properties of molecules in terms of orbital components.

Lazzeretti[4] presented a very detailed review of the one-electron current-density theory, calling, in the process, on the constraints of magnetic point groups. This approach leads to the elegant prediction of the two types of vortices, axial and toroidal, also considered below. This is an example of how far the discussion of one-electron current-density theory may lead toward comprehending the magnetic properties of molecules. It is unfortunate, however, that this has not yet been explored to its full extent to deepen our understanding of current flows.

The most interesting features of the vector field, $\mathbf{j}(\mathbf{r})$, may be identified through the analysis of its singularities—i.e., an analysis of the shape of the field in the neighborhood of its stagnation points; (these are points where the magnitude of the current density vanishes: $\mathbf{j}(\mathbf{r}) = \mathbf{0}$). Looking at the space derivatives of the current at a stagnation point is a natural way of establishing its behavior in the neighborhood. Let us then consider the nine first derivatives, $\nabla \mathbf{j}(\mathbf{r})$, which may be organized into a (3×3) matrix $\mathbf{D}$. In the neighborhood of a stagnation point, $\mathbf{r}_0$, the current-density field may be approximated by

$$\mathbf{j}(\mathbf{r}) \approx \mathbf{D}(\mathbf{r} - \mathbf{r}_0) \tag{21}$$

The directions, $\{\mathbf{v}\}$, for which

$$\mathbf{D}\mathbf{v} = \lambda \mathbf{v} \tag{22}$$

are called *eigenvectors*, the scalars $\{\lambda\}$ being the corresponding *eigenvalues*. The number of nonzero eigenvalues is called the *rank* of the stagnation point. It is clear that a real (nonzero) eigenvalue λ is associated with a direction $\mathbf{v}$ along which the current density radiates inward (if $\lambda < 0$) or outward (if $\lambda > 0$) from the stagnation point. The *signature* of a stagnation point is the difference between the number of eigenvalues with a positive real part and the number with a negative real part. With the (rank, signature)-classification of stagnation points as introduced by one of us,[329−333] the following features have been identified.

(I) Isolated singularities that must be of the $(3, \pm 1)$-type (see Figure 9) and are associated with separatrices that are toplological spheres. A *separatrix* is a surface of zero flux; when this is a topological sphere (i.e., a closed surface that may be continually deformed into a sphere), it defines a region of space where charge circulation may occur but outside of
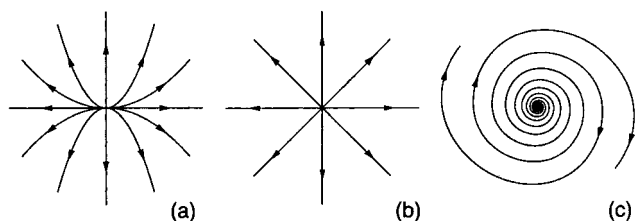
Figure 9. Circulation near isolated $(3, +1)$ singularities. The three planar cases depicted correspond to real eigenvalues $\lambda_1 > \lambda_2 > 0$ in case a and $\lambda_1 = \lambda_2 > 0$ in case b. In case c, the two eigenvalues are complex, $\lambda_1 = \lambda_2{}^*$ with $\text{Re}(\lambda_1) > 0$. The third eigenvalue, associated with the direction perpendicular to the plane of the drawing, is $\lambda_3 = -\text{Re}(\lambda_1 + \lambda_2)$.
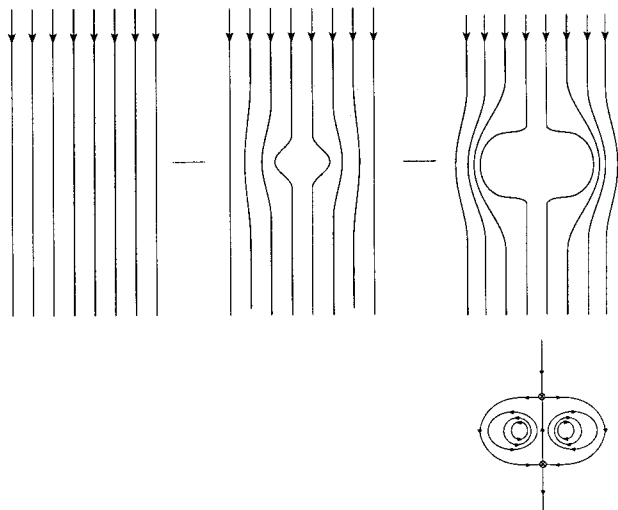

Figure 10. Formal process of insertion of a spherical separatrix (associated with two isolated singularities) into a (locally) homogeneous field. A local deformation of the lines of flow creates the space where the topologically spherical separatrix is located. This is shown in the lower part with the toroidal circulation that may exist inside.

which such charge circulation is forbidden. The type of charge circulation permitted inside these 'spheres' will be described below. Spheres such as these are topologically allowed at any point in the current-density field—i.e., they may be introduced at any point in the current-density field by continuously deforming it, thus opening up the necessary space. Formally, one may say that a line of flow may initiate one of these spheres, pushing out neighboring flow lines (see Figure 10). The spherical separatrix has two isolated singularities, one of the $(3, +1)$-type at the upper 'north pole' and the other of the $(3, -1)$-type at the lower 'south pole'.

(II) Stagnation graph. A set of singular points of type $(2, 0)$ together form a stagnation graph. By their very nature, $(2, 0)$-singular points are associated with a planar circulation having translational (local) symmetry along the direction of the zero eigenvalue (see Figure 11). The régime of circulation near the singularity depends on whether the two nonzero eigenvalues are real or imaginary, as shown in Figure 11.

A stagnation graph is composed of two types of lines, vortical lines (later called 'center stagnation lines' by Keith and Bader[334]) and saddle lines, interconversion being allowed at critical points where an index theorem is obeyed.[331] This states that on going
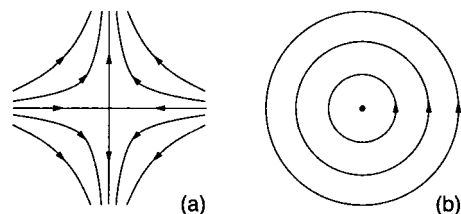

Figure 11. Circulation near a stagnation line, i.e., a $(2, 0)$ singular point in the plane of the drawing, perpendicular to the stagnation line: a saddle line when the two nonzero eigenvalues are real, $\lambda_2 = -\lambda_1$ in case a, and a vortical line when the two eigenvalues are imaginary, $\lambda_2 = -\lambda_1 = \lambda_1{}^*$, in case b.

through a critical point, the sum of the indices is conserved: if we assign the index -1 for vortical lines and $+1$ for saddle lines, the sum of the indices associated with the lines branching out of a critical point that occurs in a vortical line is equal to -1, and, for branching out of a critical point that arises in a saddle line, the corresponding sum is $+1$. The theorem was proved by Gomes[331] on very technical topological arguments. It may, however, be stated in very simple language that is easy to understand. As asserted above, vortical lines have an associated index of -1, and saddle lines have associated with them an index of $+1$. At certain points (the critical points with $(0, 0)$ as their (rank, signature)), this stagnation line may branch, conserving the index sum. A vortical line may branch into a saddle line and two vortical lines or into any set of n saddle lines and $(n + 1)$ vortical lines. A saddle line may branch into a vortical line and two saddle lines or into any set of n vortical lines and $(n + 1)$ saddle lines.

A closed-shell atom under an external magnetic field exhibits a simple rotation of its electronic charge (the so-called Larmor rotation). The stagnation graph of this system is a straight line of the vortical type parallel with the external magnetic field and going through the atomic nucleus. It is simply the axis of rotation of the charge (see Figure 12)

In molecular systems, at large distances from the nuclei the behavior of the current density is frequently similar to that pictured in Figure 12, so that the stagnation graph has associated vortical ends. This vortical line may branch out at critical points but the index theorem will be satisfied.[331]

Lazzeretti[4] supplemented this analysis by that of the magnetic point-group symmetry which helps in locating in space the components of the stagnation graph. This is of the utmost importance as stagnation graphs are frequently too complicated for easy three-dimensional visualization.

As stated earlier, toroidal circulations (associated with a pair of isolated singularities) may occur at any point in the vector field. This toroidal circulation has a stagnation subgraph that is a simple vortical line that closes upon itself forming a circle. The stagnation graph of a molecule is in general a disconnected graph, the main subgraph of the type displayed in Figure 13 being supplemented by disconnected vortical loops.

This topological analysis[329−333] has been used as a means of describing the calculated current fields which are difficult to visualize in their full detail and
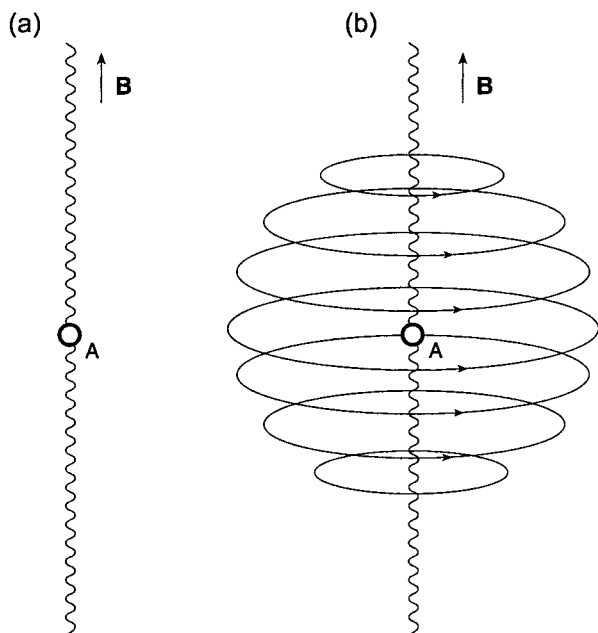
Figure 12. Stagnation graph (a) and the charge circulation (b) for a closed-shell atom under an external magnetic-field. The graph is a straight vortical line through the nucleus, the axis of Larmor rotation of the charge under the magnetic field.
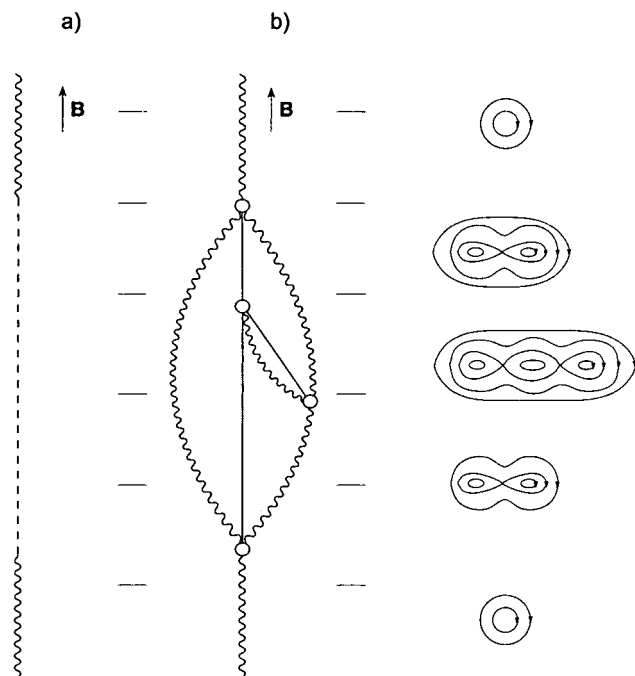

Figure 13. Stagnation graph of a molecular system. At long distance from the nuclei, there is a single vortical line (a) parallel with the external field that extends outward indefinitely. This vortical line may branch into new vortical and saddle lines, (b), forming a more-complicated stagnation graph in some cases and a less-complicated one in others. On the right-hand side of part b, a crude representation is shown of the current circulation on the perpendicular plane.

complexity. From the beginning,[329-333] this approach has been used to obtain a three-dimensional picture from the two-dimensional plots of the current in selected planes.

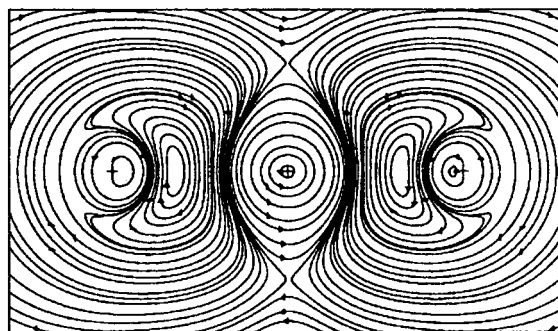The important question at this point is to what extent the above topological description helps in

Figure 14. Direction of the induced, first-order current density for the CO_2 molecule, in the molecular plane, obtained with the CTOCD-DZ method of Zanasi et al.[337] Note the outer diamagnetic circulation and the paramagnetic vortical circulation near the center of symmetry. (Adapted and reprinted with permission from ref 337. Copyright 1995 American Institute of Physics.)
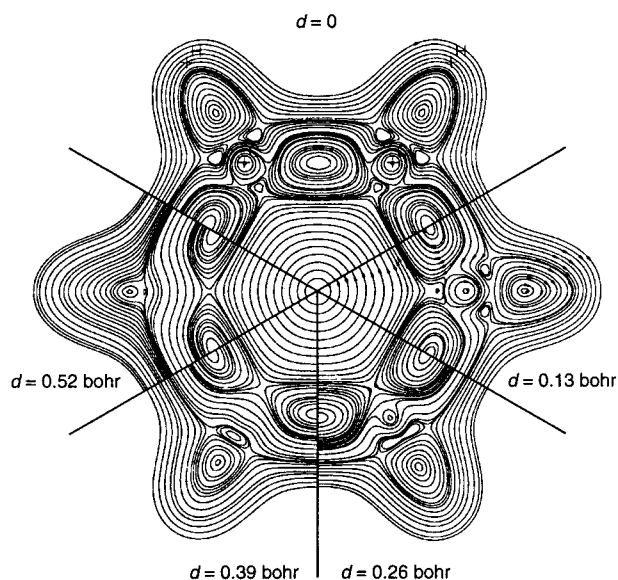

Figure 15. Projected direction of the induced, first-order, current-density field for benzene, in the molecular plane ($d = 0$) and in planes parallel with it at distances $d = 0.13$, 0.26, 0.39, and 0.52 bohr, obtained by the CTOCD-DZ method.[338] (Adapted and reprinted with permission from refs 4 and 338. Copyright 2000 Elsevier Science B.V.)

understanding the concept of ring current and the role played by ring currents in actual, extant molecules. It should be recalled that at large distances, the behavior of the current density is similar to that depicted in Figure 12, above. This means that an underlying diamagnetic behavior is to be expected, an example being shown in Figure 14 (see ref 337). When the molecule forms a topological loop, a charge circulation is to be expected in the outer region of the loop, giving rise to what may be called a ring current, as above, associated with the principal vortical line of the molecule that runs parallel with the external magnetic field (and will branch out in the region closer to the molecule). Two examples are recalled here: benzene (**3**) (Figure 15, condensed from refs 4 and 338), which has been extensively studied, and naphthalene (**4**) (Figure 16, condensed from ref 339).

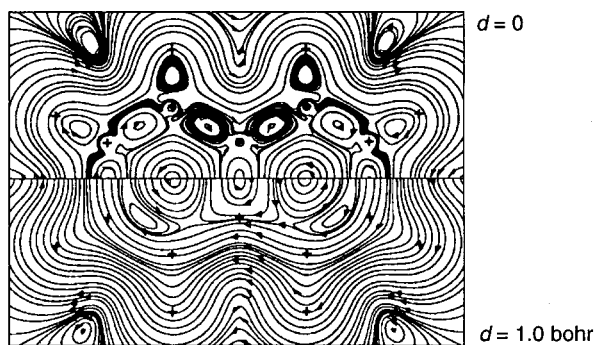A few comments may usefully be made at this stage about these plots and their relation to the ring-

Figure 16. Projected direction of the induced, first-order, current-density field for naphthalene[339] in the molecular plane ($d = 0$) and in a plane parallel with it at a distance of $d = 1$ bohr, obtained by the CTOCD-DZ2 method.[339] (Adapted and reprinted with permission from ref 339. Copyright 1997 Taylor & Francis Ltd. http://www.tandf.co.uk/journals.)
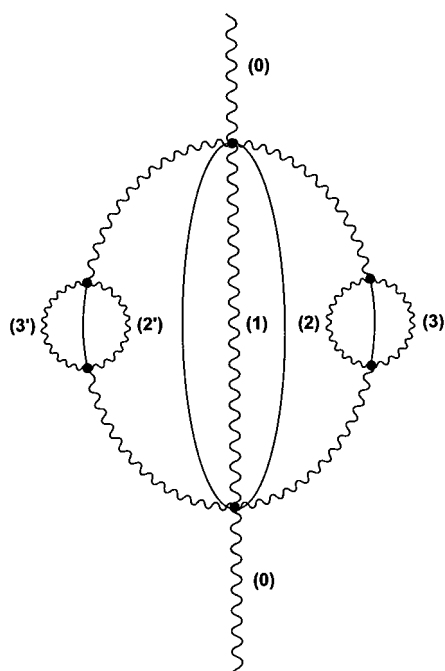

Figure 17. Stagnation graph of CO_2. The stagnation graph shown is compatible with the induced current density shown in Figure 14. The primary vortex (0), as well as vortices (2) and (2'), are diamagnetic; the inner vortex (1) corresponds to the paramagnetic circulation near the center of symmetry. Vortices (3) and (3') are the other paramagnetic circulations near the oxygen atoms.

current concept. (1) The current-density plots are relatively complex and difficult to interpret. When the *direction* plots in Figures 14−16 are supplanted by plots of *magnitudes*—as they should be—the interpretation is not made easier. There is at present no way of distinguishing the real physical features of these current-density fields from artifacts that arise because of the approximate nature of the calculations. (2) Identification of the topological features from the current-density plots is sometimes straightforward (see, for example, Figure 17 for the stagnation graph of CO_2) but it may often be difficult, especially where current-density plots on nonsymmetry planes are involved (see Figures 15 and 16). For benzene (**3**), the current-density plots of Malagoli[4,338] (condensed, in Figure 15, see also Figures 4−8,

on pp 48, 49, and 51−53 of ref 4) appear to be fully compatible with the stagnation graph proposed much earlier by one of us;[329] however, further and more-detailed study would be desirable. (3) A diamagnetic circulation is found in the outer region of the molecules, this being associated with the primary vortical line of the stagnation graph which runs parallel with the external magnetic field. (4) A paramagnetic circulation may be found around the center of symmetry of some molecules, CO_2 being an example of a simple one. (5) In benzene, the plots in Figure 15 show clearly the region around the center of the ring where a paramagnetic circulation occurs and the outer regions with their well-known diamagnetic circulation. It has been shown[4,336] that σ-electrons are responsible for this pattern of (inner) paramagnetic and (outer) diamagnetic circulations, while π-electrons give rise to a diamagnetic circulation over the molecule as a whole. (6) Further, from the plots for benzene in Figure 15, it is clear that the overall diamagnetism of the molecule is the result of cancellation of the effects of the paramagnetic circulation by the dominating diamagnetic part—and this should be evaluated not directly from Figure 15 but via the corresponding magnitude plots—together with important (mostly diamagnetic) contributions from local circulations. It should, accordingly, be emphasized that, at our present level of understanding, it is by no means obvious from an analysis of the current-density field that the overall relative diamagnetism of the condensed, benzenoid hydrocarbons—as well as that of certain members of the annulene series—can properly be estimated from the size of the associated ring current. (7) Naphthalene,[339] in Figure 16, shows features similar to those of benzene for each of its constituent rings. It may be noted that a diamagnetic, local vortex is now to be found near the center of symmetry between the paramagnetic vortices inside the two rings. The main diamagnetic circulation flows around the perimeter of the molecular skeleton.

In conclusion, we emphasize again that this topological analysis has been used as a means of describing the calculated current fields, which are difficult to visualize in their full detail and complexity, and that it has been used to obtain a three-dimensional picture from the two-dimensional plots of the current in selected planes. The present authors believe that the potential of this technique for the analysis of the magnetic properties of molecules has not yet been fully exploited.

VIII. Aromaticity of the Fullerenes: Magnetic Evidence

As soon as the new, completely unexpected and beautifully aesthetic form of carbon C_{60}—instantly dubbed Buckminsterfullerene (**33**)—was diagnosed by Kroto et al.[340] in 1985 (being synthesized[341] in macroscopic quantities in 1990), there was naturally immediate speculation[340] about the possibility of its having a special aromaticity. The first theoretical treatment of its magnetic properties, by Elser and Haddon,[313] was avowedly and unashamedly semiempirical in nature. Despite the fact that one of us

reviewed[303] this paper in the 'News & Views' section of *Nature*, read several contemporary accounts[342−345] of the method from the school in question, and even had direct correspondence with Haddon himself on the matter, the present authors are still not entirely clear about how Elser and Haddon[313] did actually adapt the London method to accommodate the spherical nature of Buckminsterfullerene. Be that as it may, Elser and Haddon's[313] predicted ring-current susceptibility was "vanishingly small".[313] In a subsequent work,[282] however, the same group reported that "although the ring-current magnetic susceptibility is vanishingly small in C_{60}, there nevertheless exist remarkable ring currents." They claimed[282] that paramagnetic ring currents are found in the pentagons and diamagnetic ring currents flow around the equitorial region of Buckminsterfullerene. Pasquarello et al.[282] were of the view that "the latter are stronger in C_{70} (**39**) than in C_{60} (**33**)." Just before the
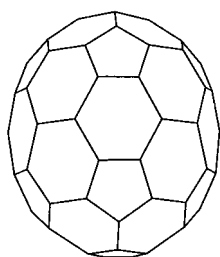
(39)

publication of ref 282 there had been (in the period 1990/1991) a diverting and lively debate about the calculated magnetic properties of Buckmisterfullerene that had been carried on through the columns of *Chemical Physics Letters.*[315,346−348] Later, Haddon[349] drew attention to the strains that exist in the fullerenes because of their curved geometries. Several authors (including the present ones) previously[267,282,303,313,345,350] and subsequently[307] performed calculations of the ring-current properties of molecules such as pyracylene (**17**) and corannulene (**34**)[267,307,345,350] which they considered as *fragments* to be found on the Buckminsterfullerene (**33**) surface. Indeed, Kroto himself [351] made such a suggestion very soon after his identification of C_{60}. Entertainingly, though, Haddon, in ref 349, doubted if, because of considerations of strain and nonplanarity, such molecules could ever properly be used as models for C_{60}, and he facetiously questioned[349] whether such suggestions should not be consigned to the same category as those from "The Flat Earth Society"! He observed that models of the electronic properties of C_{60} that rely on pyracylene (**17**) and other such substructures[267,282,303,307,313,345,350] focus on the *topology* of the fullerenes, whereas Haddon[349] was of the opinion that an analysis of the geometry of strain must primarily be concerned with what he termed the 'pyramidization' of the carbon atoms: this "is the factor that changes the character of the π-orbitals and can be viewed as a source of strain in the fullerene geometry ... although a rigorous separation of these two effects is not possible." Haddon claimed,[349] however, that "it is useful in a heuristic sense". He concluded[349] that

"the ring-current diamagnetism of the fullerenes is dwarfed by that of graphite." Haddon argued[349] that "the fullerenes cannot show aromatic chemistry in the conventional molecular sense because there is no periphery and [there are] no peripheral hydrogen atoms: they are molecules without boundaries." Haddon[349] reiterated his belief (also stated in refs 313 and 282) that strong diamagnetic ring currents in the six-membered rings and paramagnetic ones in the five-membered rings "cancel almost exactly in their contribution to the magnetic susceptibility." Haddon was adamant[349] that "the ring currents found in C_{60} militate against the pyracylene description of the molecule. The C_{60} molecule is of ambiguous aromatic character with anomalous magnetic properties but with the reactivity of a continuous aromatic molecule, moderated only by the tremendous strain inherent in the spheroidal structure." Haddon[349] was unequivocal in his view that "the use of planar conjugated molecules [e.g., our refs 267, 282, 303, 307, 313, 345, and 350] as primary reference points demonstrates a failure to capture the significance of the synthesis of the fullerenes for organic chemistry." He concluded[349] "If C_{60} is not to be considered aromatic, benzene will be condemned to a lonely existence"! Subsequently, Haddon's group[352] even offered a calculation of the ring-current magnetic properties of C_{60} based on the Pauling−Lonsdale[131,132] free-electron model (a task that, though unbeknown to Haddon, had actually been carried out previously, and independently, by the late Linus Pauling himself[353]). They arrived at a 'low χ_π value', just as they had on their London calculation,[313] and ascribed this to paramagnetic (Van Vleck[123]) contributions from the excited states "which almost completely cancel the diamagnetic contributions from the valence states".[352] The former "are dominated by matrix elements between the highest occupied molecular orbital and the lowest unoccupied molecular orbital" (cf. our discussion in section V and that given in refs 1, 77, and 303). In ref 352, Ramirez et al. also touched on the question of the large magnetic susceptibilities observed in carbon nanotubes. They suggested[352] that one possibility is that, because individual nanotubes are closed structures, "ring currents may flow around the waist of the tube in response to a field along the tube axis." By comparison, in graphite, "ring currents are confined to the planes and only flow when the field has a component normal to this direction."

The groups of Fowler et al. at Exeter and Lazzeretti et al. in Modena reported much work on the magnetic properties of the fullerenes; they both used well-defined, ab initio methods. In ref 354, for example, they applied a coupled-Hartree−Fock method using the SYSMO program in STO-3G, STO3-G*, 6-31G, and 6-31G* basis sets. They concluded[354] that their calculations were "broadly comparable with the picture of C_{60} as a molecule with a surface π system, with diamagnetic circulation induced within the faces of the truncated icosahedron by a magnetic field at right angles to them." However, they added, somewhat guardedly,[354] "Whether this constitutes a 'ring current' is difficult to say, since the pattern of anisotropy is common to several types of π system—

isolated, conjugated and aromatic." Furthermore,[354] "it would be premature to take the ^{13}C-NMR spectrum as decisive proof of aromaticity in C_{60}" (see also ref 355). In ref 356, Zanasi and Fowler addressed the whole question (embodied in their title) of ring currents and magnetizability in C_{60}. They used a distributed-origin coupled-Hartree–Fock method to compute the current density and hence to plot the π-electron ring currents and obtain ab initio values of the total magnetizability and nuclear-magnetic shielding. They observed that semiempirical calculations with the London model indicated that the π-electron ring currents would be small and paramagnetic in the five-membered rings[356] (cf. ref 282). Ab initio calculations of the total $(\sigma + \pi)$ magnetizability gave large diamagnetic values when small basis sets were used, but "even on extrapolation to the presumed basis-set limit a moderately large diamagnetism ... remained,[356] ... somewhat larger than the first measured value ... but not out of line with expectations for a molecule of this size with a conjugated π system." Zanasi and Fowler observed[356] that the size and sign of the measured[316] chemical shift of endohedral ^{3}He trapped in a C_{60} cage "was taken[316,317] to indicate significant diamagnetic ring currents in C_{60}, in apparent contradiction of the semiempirical picture of cancelling dia- and para-magnetic currents." Zanasi and Fowler[356] took up Haddon's suggestion[317] that a more sophisticated treatment of current flow in the C_{60} cage was required. They attempted to provide this in ref 356 by calculating π-electron ring currents in C_{60} using variants of the coupled-Hartree–Fock method with a 6-31G* basis. They admitted that the basis set employed was incomplete but claimed[356] that "the essential features of the results appear to be stable against extension of the basis set". In particular, they were able to confirm the paramagnetic ring currents in the pentagons, found semiempirically by Pasquarello et al.[282] However, Zanasi and Fowler[356] did hit a paradox: they found that the existence of these paramagnetic ring currents in the five-membered rings "did not of themselves force a small or near-vanishing" magnetic susceptibility. On the contrary, direct calculation from their newly computed current density still yielded a high diamagnetic magnetizability "coexisting with local paramagnetic circulations". Zanasi and Fowler pointed out[356] that ring currents may be sustained by the π-electrons of a planar conjugated system that has a suitable geometry, but that in the case of a pseudospherical cage such as the C_{60} system, "there is no strict symmetry-enforced distinction between σ and π orbitals, but an approximate separation persists between those orbitals locally tangential and those perpendicular to the curved surface passing through the nuclei." In calculations using the CTOCD-DZ and CTOCD-PZ approaches—see pp 230–247 of ref 3 and section IX of the present review for a discussion/description of these—Zanasi and Fowler[356] established that the shielding at the center of the cage was diamagnetic and the extrapolated ab initio result was found to be within 1 ppm of the experimentally measured shift[316,317,355] for entrapped ^{3}He in C_{60}. The conclusions concerning aromaticity that

Zanasi and Fowler[356] felt able to draw from this rather thorough investigation were, however, somewhat circumspect.[356] In what could be considered something of an understatement, they pointed out that "aromaticity is a term with different connotations, *not all of which are appropriate to the fullerenes*, [present authors' emphasis] in different parts of chemistry." They argued that if aromaticity is to be defined by means of some kind of diamagnetic exaltation, then a different reference molecule is going to have to be selected for the fullerenes. Using the Hameka model[357] that takes account of curvature would allow the conclusion that C_{60} is moderately aromatic. On the other hand, Zanasi and Fowler[356] considered that chemical arguments support a picture of C_{60} as "a mildly electron deficient olefin, rather than a three-dimensional version of benzene", something that they expect to be a "recurring motif in fullerene chemistry". In the end, therefore, they can only conclude—in all honesty after an extremely thorough investigation—that "the description of C_{60} as aromatic is thus problematic". They *are*, though, clear that C_{60} *is* diamagnetic, despite the paramagnetic effects of the five-membered rings, which are not sufficient to outweigh the main diamagnetic contributions to both magnetic susceptibility and shielding at the center of the sphere.

Bühl et al. considered the aromaticity and magnetic properties of a nitrogen analogue[358] of Buckminsterfullerene, $C_{54}N_6$, and a hydrogenated[359] C_{60}. Saunders et al.[360] examined isomers of the higher fullerenes by ^{3}He NMR spectroscopy (see also ref 320 for further details) with the intention of testing the ideas arising from the semiempirical calculations of Haddon et al.[282,313,317,349,352,355] They somewhat ingeniously[360] made the tantalizing and intriguing observation that if the paramagnetic five-membered rings quench the diamagnetism of the six-membered rings in C_{60}, as Haddon et al.[282,313,317,349,352,355] suggested, then, because, in the higher fullerenes, the number of five-membered rings remains at 12 whereas the number of six-membered rings increases from 20, C_{70} (**39**) would be expected to be more diamagnetic than C_{60} (**33**), while "in larger fullerenes ... the magnetic susceptibility would approach that of graphite." This nice and ingenious speculation was not, however, realized, for Saunders et al. noted[360] that "the bonding character of both the five- and six-membered rings changes from one structure to the other. The observed trend of the chemical shifts is a large jump upfield on going from C_{60} to C_{70}, and then downfield shifts as the size of the fullerene increases further."

We conclude this section on the fullerenes by drawing attention to an important recent paper by Bühl[320] in which he has applied the NICS method of von Ragué Schleyer et al.[88–100] (see section VI) to calculate chemical shifts at the centers of the pentagons and the hexagons for the fullerenes C_n (n = 32, 50, 60, 70, 76, 78, 84, 120, and 180). Bühl[320] performed ab initio calculations; geometries and energies were computed with the TURBOMOLE program using DFT.[320] The NICS calculations were performed by use of GIAO–SCF/DZP/BP86/3-21G

(see pp 230–247 of ref 3 for an explanation of the ab initio jargon; see also section IX of the present review). Bühl[320] considered that the NICS values reflect "the ring current flows in the polycyclic carbon framework" and thus "can help to identify areas of higher local aromaticity or antiaromaticity (usually associated with hexagons and pentagons, respectively) in each fullerene." He made the important point that even though corannulene (**34**) or coronene (**37**) patterns can be identified in some cases (e.g., refs 267, 307, 344, and 350), NICS values are *not* transferable from one species to another. (This observation is, in a sense, an echo of the one made in section V, in a semiempirical context, about peropyrene (**27**) and perylene (**28**) and about the two dibenzo derivatives, **30** and **31**, of zethrene (**29**), etc.) By use of a very simple, classical model, Bühl argued[320] that the endohedral chemical shifts at the center of the fullerenes "can to a large extent be attributed to the ring currents in the individual five- and six-membered rings, as assessed by their NICS values."

IX. The Latest ab Initio Work

In recent years a considerable effort has been applied to improve the rigorous ab initio methods of calculation of the magnetic properties of molecules.[3,4] The current-density field, being very sensitive to the quality of the calculation, is thus improved markedly. This may lead to a fresh insight into the concept of aromaticity, relating it to the reaction of certain molecules to an external magnetic field as evaluated from the features of the current-density field. All of this activity stems from previous efforts dating from the early 1980s and the early 1990s that were aimed at devising efficient ab initio methods for the calculation of magnetic properties. This was discussed in detail in pp 230–235 of our earlier review[3] and in Lazzeretti's recent *magnum opus*,[4] so we merely outline a brief summary of the developments here. We have already discussed the ab initio work of the von Ragué Schleyer school[59,82–100] during this recent period, in sections III.B and VI, when discussing (respectively) bulk magnetic properties and NICS diagnoses of aromaticity.

The initial work was by the group of Lazzeretti and Zanasi in Modena, in the period 1981–1984; they chose a coupled-Hartree–Fock method with a large basis set and used it to study electron current density.[361–366] At about the same time (1980–1983), Schindler and Kutzelnigg,[133–135] in Bochum, made a breakthrough by means of their method given the acronym IGLO (individual gauges for localized orbitals). Also during this period (1983–1984) was the work of Gomes,[329–333,336] in Porto, on the topological analysis of the current-density field, which we have briefly discussed in section VII. In the years 1992–1994, the McMaster team of Keith and Bader developed[327,328,334,367–369] their approaches called IGAIM (individual gauges for atoms in molecules) and CSGT (continuous set of gauge transformations). The period 1993–1995 was a time of much activity[335,337,356,370–374] from Fleischer, Kutzelnigg, and Mühlenkamp (Bochum), Lazzeretti, Zanasi, Malagoli, and Coriani (Modena), and Fowler (Exeter). These workers em-

ployed and devised various ab initio approaches, including their application to a study of Buckminsterfullerene that we already discussed at length in section VIII. The methods employed were given the acronyms CTOCD-DZ and CTOCD-PZ (standing for continuous transformation of origin of current density, diamagnetic [paramagnetic] contribution set to zero). Related to IGLO[133–135] and GIAO[136–140] is the method of Hansen and Bouman,[375] given the appellation LORG (local origin/localized orbitals) and the much earlier method of Okninski and Sadłej.[376] The mid-1990s saw a lively controversy about the merits of these several approaches between the Modena,[373,356] Bochum,[373] and Exeter[356] groups on one hand and the McMaster/Yale school of Bader and Keith[377] on the other. As we have discussed at some length in ref 3, the advantage of the IGAIM and CSGT methods[327,328,334,367–369] for calculating magnetic properties, over the conventional approaches that involve a simple gauge origin, seems to lie in the very large paramagnetic and diamagnetic contributions to χ_{zz}^{m} that arise in the conventional methods and which fail to cancel satisfactorily; in CSGT, on the other hand, the diamagnetic component of χ_{zz}^{m} is made to vanish identically. Furthermore, as we also emphasized in ref 3, the methods of IGLO,[133–135] LORG,[375] and GIAO[136–140] all share the advantage over the classical coupled-Hartree–Fock method[378,379] with simple gauge origin "that there is no necessity to rely on a felicitous cancellation of large, and often spurious, diamagnetic and paramagnetic contributions and that, consequently, the results are not very dependent on the size of the basis." (An excellent guide to, and summary of, many of the ab initio methods involved in the recent calculation of magnetic properties is to be found in the Introduction to the paper by Gauss that is cited in our list as ref 380.)

We now review the major papers that have been produced in the past few years. The list is not exhaustive, but they are the ones which, in our opinion, have contributed the most to recent ab initio work that may have a bearing on the magnetic criteria for aromaticity. Fowler et al.[381] nicely updated our own work,[220,301] partly with Coulson,[77] of up to 25 years ago by examining the series pyracylene (**17**), acepleiadylene (**18**), and dipleiadiene (**19**) that were—at least superficially—candidates for being regarded as 'perturbed'[300,309] [4n]-, [4n + 2]-, and [4n]-annulenes, respectively.[1,77,220,301] Fowler et al.[381] produced aesthetic maps of the π-electron current density, by use of distributed-gauge methods (at an uncorrelated level of theory[381]) to examine the perturbed-annulene model[300,309] of these systems in a simple and very illuminating way. Their maps for **17**, **18**, and **19** are shown in our Figure 18. The plots show that "one can observe in each case a diamagnetic ring current flowing above the central naphthalenic carbons, which is very similar to that calculated for the isolated naphthalene molecule."[382,339] Fowler et al.[381] also had some interesting comments to make in light of the earlier semiempirical calculations on these molecules[1,77,220,301] by observing that "pyracylene (**17**) and dipleidiene (**19**) share the same magnetic behavior ... and that acepleiadylene (**18**)
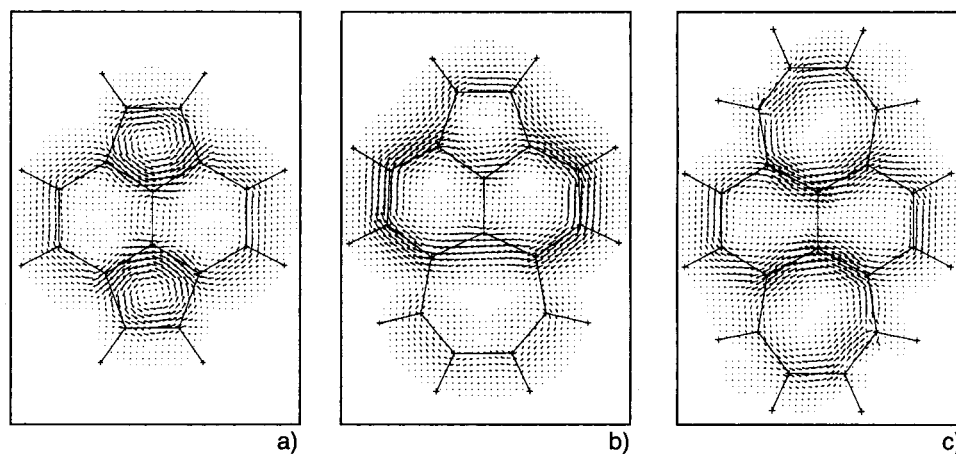
Figure 18. Induced current densities in (a) pyracylene (**17**), (b) acepleiadylene (**18**), and (c) dipleiadiene (**19**). The diagrams depict the direction and magnitude of the π-current, at 1 bohr above the molecular plane, induced by a perpendicular magnetic field of unit magnitude pointing out of the plane of the paper. The currents were computed in the 6-31G** basis by use of the CTOCD-DZ approach at the optimal geometries for that basis, as calculated in ref 381. (Reprinted with permission from ref 381. Copyright 1998 American Chemical Society.)

breaks the series." Concerning the ^{1}H and ^{13}C NMR of these species, Fowler et al.[381] also observed that "the paramagnetic ring currents located on the odd rings of pyracylene (**17**) and dipleiadiene (**19**) are sufficient to explain the observed upfield shift of the proton chemical shifts with respect to the naphthalenic protons, and the extended diamagnetic ring current in acepleiadylene (**18**) accounts for the small downfield shift found for the acepleiadylene protons." (However, it should perhaps be pointed out here that Fowler et al. gave no explicit consideration, in the course of their deliberations in ref 381, to possible contributions[22,163,265,383–386] that might arise because of nonuniform charge densities on the carbon atoms, guaranteed generally to be extant—by virtue of the Coulson–Rushbrooke Theorem[204,326]—in these non-alternant hydrocarbons.) Fowler et al.[381] further made another interesting observation—one that is fully consistent with our own previous, semiempirical work[1,77,220,301] on the dianions of **17**−**19**—when they stated that "the pyracylene (**17**) and dipleiadiene (**19**) *dianions* [our italics] display an extended diamagnetic ring current flowing above the external carbon atoms." In the paper that we are presently discussing (ref 381), these authors did not, however, fully endorse the semiempirical picture[1,77,220,301] but concluded instead that "the current maps do not support a perturbed-annulene model of these systems but rather a bridged-naphthalene picture, where the naphthalene core plays a fundamental role in determining the current flow." [381] In an earlier work,[387] though, the Modena–Exeter groups reported ab initio calculations, by the CTOCD method,[337,372,374] on pyracylene (**17**) (solely), the magnetic properties of which were, as Fowler et al. pointed out,[387] "much discussed in the classical literature of the ring-current model" [1,77,220] (see also ref 301). They concluded in ref 387 that "the classical ring-current model is predicated upon the dominance of the π electrons, and it is evident ... [from their calculations] ... that the prominent qualitative features of the total current density ... are indeed due to the π electrons. A strong, diamagnetic circulation runs around the perimeter of the central naphthalenoid hexagon pair, but the

circulation around the pentagons is in the opposite, paramagnetic sense." They further made the following (for us, rather agreeable) observation:[387] "Thus, the *ab initio* current density map is in qualitative accord with the early semi-empirical calculations of Coulson and Mallion [our ref 77] that predicted paramagnetic ring currents in the pentagons but not the hexagons."

Zanasi and Lazzeretti[339] presented a thorough study of the magnetic properties of naphthalene (**4**) at the coupled-Hartree–Fock level of accuracy, using the method of continuous transformation of the origin,[335,356,370,373] that yielded some current-density maps of extremely high quality; this study represents one of the first attempts at showing a rigorous stagnation graph (see section VII). They illustrated the first three-dimensional model for circulation of both σ- and π-electrons in naphthalene via diagrams showing streamlines, stagnation lines, and modules of the current density induced by a magnetic field perpendicular to the molecular plane. This followed earlier attempts at producing good-quality current-density maps for benzene;[361,363,364] a very recent accurate study of hexamethylbenzene, on similar lines, was published by Fowler et al.[388] Among the findings of Zanasi and Lazzeretti[339] in their study of naphthalene (**4**) was that "it can be reasonably concluded that ... the downfield shift of protons in naphthalene is due to deshielding of the perpendicular component of the proton magnetic shielding, which is essentially caused by π ring currents." However, "these findings seem to exclude [the possibility] that the chemical shift between nonequivalent naphthalenic protons is due to π ring currents." This conclusion does, of course, run counter to the findings of semiempirical investigations, such as, for example, that which one of the present authors and Haigh[210] published many years ago on the linear acenes benzene (**3**) to octacene (**10**). Zanasi and Lazzeretti[339] do, though, believe that their calculations show that "ring current effects are somewhat larger in naphthalene than in benzene." However, they emphasized that "the London–McWeeny–Pauling–Pople 'ring current' circulation [our refs 116–

118, 131, 132, 153, and 161] is much more evident than in the case of benzene (compare with our ref 335): a continuous pipe-line of currents, sustained by delocalized π electrons, passes through the circuit of the peripheral carbon nuclei... It is this special feature of the current density field which is responsible for the downfield shift of proton magnetic shielding in naphthalene."

A comparison of the current-density field among several members of the linear-acene series (benzene (**3**) to heptacene (**9**), with hexacene (**8**) omitted) as well as biphenylene (**22**) was offered by Steiner and Fowler.[382] They were of the opinion that "results of useful accuracy can be obtained with modest (6-31G**) basis sets by employing a continuous gauge transformation." They claimed[382] that their current-density maps "show that the strength of the π circulation in tetracene (**6**) is greatest within the central two-ring naphthalenic system, while that in pentacene (**7**) and heptacene (**9**) is greatest in the central three-ring anthracenic system." They added[382] that "in this picture, the greater π current in the central region of the longer molecules results in increased deshielding of the protons there, whereas the terminal protons [what we have called the Hβ protons, on Martin's terminology,[193] in our structure scheme depicting the homologous series **4**−**10**] have relatively constant shieldings throughout the series." We note that this latter conclusion is precisely that of the semiempirical study of Haigh and Mallion,[210] arrived at some 15 years earlier and clearly illustrated by Figure 1 in section IV.B.

Other members of the condensed, benzenoid hydrocarbon series whose current-density maps have recently been reported,[389] in a comparative study, are anthracene (**5**), phenanthrene (**1**), and triphenylene (**35**). Meanwhile, Fowler and Steiner[390] also presented a thorough and good-quality study of ring currents and aromaticity in monocyclic π-electron systems.[390] They used the coupled-Hartree−Fock method as programmed in the SYSMO package. They calculated magnetic susceptibility with gauge origin at the center of each molecule and computed the current-density field using the continuous-gauge formulation of Keith and Bader,[327,328,334,367−369] of the Modena−Bochum−Exeter groups,[335,337,356,370−374] and of Geertsen.[391−393] Fowler and Steiner[390] pointed out that ring currents themselves are not directly observable, but they can "nevertheless be obtained from theory by computing the response of a molecular system to an applied magnetic field." They concluded that "the component of the susceptibility ... perpendicular to the molecular plane ... can be used as a measure of aromaticity." Fowler and Steiner claimed that, at least for the six-membered-ring systems that they treated in ref 390, they "can give an unambiguous answer to the question, 'Is the molecule aromatic?'." They regarded the component of magnetic susceptibility at right angles to the molecular plane as being "a measure of freedom of circulation in the presence of a magnetic field in this direction." (It may be noted in passing that the latter remark is very much in accord[56] with the 25-year-old views of Benassi et al.[288] on magnetic criteria for aromaticity,

established, in ref 288, via semiempirical calculations.)

Burk et al.[394] used what is called a G2-MP2 computational method in order to optimize their geometries, and they then calculated magnetic susceptibilities and chemical shifts by use of an IGLO[133−135] ('92') program in a study of the aromaticity of substituted cyclopropenes. On chemical-shift criteria, they concluded that all the cyclopropenyl systems they investigated are aromatic, but these authors were, overall, pessimistic about the ability of magnetic criteria to establish aromaticity in this series because of what they call "very large structural changes" there extant.[394] In their investigation into the aromaticity of (benzene)Cr(Co)$_3$, Simion and Sorensen[395] used GAUSSIAN 94[141] for DFT calculations with the Becke3YLP hybrid method with a 6-311+G** basis-set for geometries and energies (see refs 3 and 4 for an explanation of this ab initio jargon). Magnetic shieldings were then computed both with traditional GIAO methods[136−140] and with variants of the continuous-gauge transformation.[327,328,334,335,337,352,367−374] They concluded, among other things, that "contrary to the usual assumptions, the in-plane shieldings of the complexed benzene ring are more important than the perpendicular (ring current) counterparts."

We conclude this section on recent ab initio work by focusing on an important paper by Bilde and Hansen,[232] with a (partial) title that demands attention: *Ab initio study of the Pauling−London−Pople (ring current) effect*. They used LORG[375] calculations and analyzed NMR shielding-tensors in what they called a 'Sondheimer aromatic annulene' (1,8-didehydro-[14]-annulene) and a 'nonaromatic analogue'. They pointed out that "contributions that represent diamagnetic and paramagnetic terms conforming to the Pauling−London−Pople formulation ... can be extracted ... retaining the possibility of decomposing the shielding tensors into sigma and pi contributions." They found that "the Sondheimer effect, i.e., the large difference between the isotropic shieldings measured for the inner proton ... and for the two outer protons ... in the aromatic annulene ... is reflected clearly in the calculations." However, for the π-electron contributions, Bilde and Hansen[232] again observed "an absence of ring-closure effects for the diagmagnetic part of the perpendicular shielding, whereas the perpendicular paramagnetic pi electron contributions experience a dramatic ring closure effect, reducing them almost to nothing." The final comments of Bilde and Hansen[232] concerning the ring-current effect and aromaticity were as follows: (a) "the characteristic shielding anisotropy observed for aromatic protons is caused solely by an absence of paramagnetic pi electron currents, all other shielding contributions being sensitive to local topology but indifferent to aromatic character"; (b) "the rationalization in terms of a diamagnetic ring current ... seems a misrepresentation of the observed effect and as suggested in the title of this communication we therefore advocate the term 'Pauling−London−Pople effect' for the unique magnetic anisotropy in aromatic systems, in honour of the original contributors." This

is a useful contribution to the discussion, but it should be noted that the terms 'aromatic character' and 'aromatic systems' that arise in the above quotation are *not* there explicitly defined: this, therefore, somewhat begs the question that we are attempting to discuss in this review. As we have seen throughout, this kind of difficulty has been a recurring theme that has continually bedogged our prospects of evaluating any alleged correlation between aromaticity and ring currents.

X. Conclusions and Future Directions

In this review, we have tried to bring together old and new ideas and methodologies associated with the ring-current concept and its relation to aromaticity—covering the entire spectrum of the subject from the original idea of a classical benzene magnetic ring current,[131,132] through the semiempirical methods[116–118,153,161] exemplified by our eq 16, through accurate current-density-field calculations (e.g., refs 361, 363, and 364) and their relations to ring current, to the most advanced methods currently available (e.g., sections VI, VII, and IX, and refs 3 and 4).

We have deliberately devoted considerable attention in our discussion to the semiempirical methods (especially sections IV.B and V). This is because we feel that, at one level, and contrary to fashionable belief, the semiempirical approaches still have something to contribute, at least conceptually. The problem with the ab initio formalisms is that the more complex they are, the more difficult they become to interpret and vizualize, and aromaticity, if it is to be of any use at all to chemists, has to be an essentially qualitative and intuitive idea. This, we think, is where the semiempirical theories can still be of service. As we have stated in concluding previous reviews,[2,3] the 'ring-current' picture "is so pictorial that one can almost *feel* what is happening when a molecule is subjected to a magnetic field" and this, we submit, is one of its inherent strengths. Another thing to bear in mind[3] is that the term 'ab initio', by its very grandiose sound, can induce a sense of false security: ab initio calculations—precisely *because* they *are* ab initio rather than semiempirical—are thereby apt to bludgeon the user or reader into feeling that conclusions based on them must be unassailable. This is in practice most emphatically not the case: as we have seen in section IX of the present review and is evident from refs 3 and 4, there have burgeoned in recent years an almost bewildering number of ab initio approaches and recipes for the wave functions on which they are based. It is vital, therefore, that present-day ab initio calculations are looked at as critically as the semiempirical ones used to be—especially when (as in the present context) *concepts* are to be based on deductions made from them. By contrast, the most basic of the semiempirical methods is embodied in eq 16; as emphasized in section V, when (i) eq 16 is based on a simple HMO with all resonance integrals equal (i.e., when all the $\eta_{(\omega)}$ terms in the equation are set equal to 1), (ii) all benzenoid hexagons in polycyclic benzenoid hydrocarbons are taken to have the same area as the unique ring in benzene, and (iii) all ring-current intensities, J_i, are expressed in the form (J_i/

J_{benzene}), then assumptions i–iii remove all further subjectivity (in the form of any subsequently adjustable parameters) from ring-current calculations on this class of molecules (the condensed, benzenoid hydrocarbons, the archetypal aromatic class). Relative ring-current intensities calculated in this way thus depend *solely* on molecular topology (in the graph-theoretical sense of this word—not in the sense in which it was used in the context of the current-density field, in section VII, and below.) Because of this, such topological ring currents are *entirely independent of any subjectively chosen parameters* or schemes of calculation; the numerical values of their relative intensities are latent—and are thus immediately, albeit only implicitly, predetermined—as soon as the carbon-atom connectivity of the condensed, benzenoid hydrocarbon in question has been written down.

At the other extreme, modern ab initio methods allow very accurate estimates of the magnetic properties of molecules and give good-quality current-density fields. These current fields have been shown to give some general understanding of the magnetic behavior of molecules, and in recent publications (e.g., refs 367–374) the topological analysis proposed by one of us[329–333] in the early 1980s (and outlined in section VII) has been used to give a fuller understanding of this vector field. The construction (and location in real space) of a stagnation graph as a means of achieving this goal is an attractive possibility but is fraught with major difficulties. The location of the stagnation points and stagnation lines with their critical points is a problem whose difficulty is comparable with that of studying a three-dimensional potential-energy surface or finding the topology of the charge density. New difficulties arise from examining a vector field and the considerable complexity of such fields found in some of the examples that have been studied in detail. The main connected subgraph could be constructed analytically by following the vortical line (see section VII) that comes down from infinity, parallel with the external magnetic field, and finding where its critical points are and the way in which it branches at those points. The magnetic point-group symmetry may help, but the task is still a major one, even for relatively simple molecules. It is, however, feasible, and a detailed study of its component circulations (defined by vortical lines and separated from others by separatrices) will clarify the behavior of the molecule.

We believe that great progress is still to be expected in the next few years by exploiting the general topological analysis of the current-density field (section VII) obtained by the most accurate methods and relating some features of this field to well-seasoned chemical concepts such as ring currents and aromaticity.

Another area which we think merits further investigation is a more-extended numerical comparison of relative NICS values with relative ring-current intensities, as exemplified by the data in our Table 1. Such an exercise may well be material to the problems of using magnetic criteria to define a quantitative scale for aromaticity.

In his comprehensive definitive work on the concept of ring currents, just published,[4] Lazzeretti quoted the recently stated opinion of Hoffman, Minkin, and Carpenter[396] (which, itself, echoes the earlier views of Labarre and Crasnier[14,15,64]) that "no single property exists whose measurement could be taken as a direct, unequivocal measure of aromaticity" and that, consequently, "the concept of aromaticity should be analysed in terms of ornate hypotheses, a multiplicity of measures." We are inclined to agree. Accordingly, therefore, despite all that we have reviewed here on the relevance of ring-current ideas to the concept of aromaticity, we feel that, in concluding, we have no option but to persist—even at the beginning of this 21st century—in maintaining (as one of us, with Coulson,[77,397] did a quarter of a century ago[1,77,397]) that we still ought to question the propriety of trustingly making sole appeal to the "rather obscure and somewhat esoteric ... index, ... the 'ring-current', concerned with a second-order magnetic-property" as a crucial and authoritative arbiter when "evaluating such a basic and intuitively *global* attribute of a molecule as its 'aromaticity'."

XI. Acknowledgments

XII. References

(1) Mallion, R. B. *Pure Appl. Chem.* **1980**, *52*, 1541–1548.
(2) Haigh, C. W.; Mallion, R. B. Ring current theories in nuclear magnetic resonance. In *Progress in Nuclear Magnetic Resonance Spectroscopy*; Emsley, J. W., Feeney, J., Sutcliffe, L. H., Eds.; Pergamon Press: Oxford, 1979/1980; Vol. 13, pp 303–344.
(3) Gomes, J. A. N. F.; Mallion, R. B. The concept of ring currents. In *Concepts in Chemistry: A Contemporary Challenge*; Rouvray, D. H., Ed.; Research Studies Press: Taunton, Somerset (U.K.), 1997; pp 205–253.
(4) Lazzeretti, P. Ring currents. In *Progress in Nuclear Magnetic Resonance Spectroscopy*; Emsley, J. W., Feeney, J., Sutcliffe, L. H., Eds.; Elsevier: Amsterdam, 2000; Vol. 36, pp 1–88.
(5) Musher, J. I. *J. Chem. Phys.* **1965**, *43*, 4081–4083.
(6) Musher, J. I. Theory of the chemical shift. In *Advances in Magnetic Resonance*; Waugh, J. S., Ed.; Academic Press: New York, 1966; Vol. 2, pp 177–224.
(7) Musher, J. I. *J. Chem. Phys.* **1967**, *46*, 1219–1221.
(8) Gaidis, J. M.; West, R. *J. Chem. Phys.* **1967**, *46*, 1218–1219.
(9) Nowakowski, J. *Theor. Chim. Acta* **1968**, *10*, 79–85.
(10) Kumanova, M. D.; Rebane, T. K. *Zh. Strukt. Khim.* **1971**, *12*, 552–553. Kumanova, M. D.; Rebane, T. K. *J. Struct. Chem.* **1971**, *12*, 507–508; *Chem. Abstr.* **1971**, *75*, 114236*k*.
(11) Atkins, P. W.; Gomes, J. A. N. F. *Mol. Phys.* **1976**, *32*, 1063–1074.
(12) Gomes, J. A. N. F. Some Magnetic Effects in Molecules, D.Phil. Thesis, University of Oxford (Linacre College), U.K., 1976. (a) *Appendix*; Chapter 5, pp 74–77. (b) Chapter 6, pp 78–91.
(13) Gomes, J. A. N. F. *Mol. Phys.* **1980**, *40*, 765–769.
(14) Labarre, J. F. *Bull. Soc. Chim. Fr.* **1970**, pp 2463–2467.
(15) Labarre, J. F.; Crasnier, F. *Top. Curr. Chem.* **1971**, *24*, 33–54.
(16) Hückel, E. *Grundzüge der Theorie ungesättigter und aromatischer Verbindungen*; Verlag Chemie: Berlin, 1938.
(17) Berthier, G. In *Les Théories Electroniques de la Chimie Organique*; Pullman, A., Pullman, B., Eds.; Maçon: Paris, 1952; Chapter 9.
(18) *Non-Benzenoid Aromatic Compounds*; Ginsburg, D., Ed.; Interscience: New York, 1959.
(19) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, 1964.
(20) Lloyd, D. M. G. *Carbocyclic, Non-Benzenoid Aromatic Compounds*; Elsevier: Amersterdam, 1966.
(21) Sondheimer, F. *Proc. R. Soc. London, Ser. A* **1967**, *297*, 173–204.
(22) Salem, L. *Molecular Orbital Theory of Conjugated Systems*; W. A. Benjamin: New York, 1966; especially Chapter 4.
(23) *Aromaticity*; Special Publication No. 21; The Chemical Society: London, 1967. (a) Longuet-Higgins, H. C. *Aromaticity*; Special Publication No. 21; The Chemical Society: London, 1967; pp 109–111. (b) Vogel, E. *Aromaticity*; Special Publication No. 21; The Chemical Society: London, 1967; pp 113–147. (c) Winstein, S. *Aromaticity*; Special Publication No. 21; The Chemical Society: London, 1967; pp 5–45. (d) Sondheimer, F.; Calder, I. C.; Elix, J. A.; Gaoni, Y.; Garratt, P. J.; Grohmann, K.; Di Maio,

G.; Mayer, J.; Sargent, M. V.; Wolovsky, R. *Aromaticity*; Special Publication No. 21; The Chemical Society: London, 1967; pp 75–107.

(24) Jones, A. J. *Rev. Pure Appl. Chem.* **1968**, *18*, 253–280.

(25) Garratt, P. J.; Sargent, M. V. *Adv. Org. Chem.* **1969**, *6*, 1–108.

(26) Badger, G. M. *Aromatic Character and Aromaticity*; Cambridge University Press: London, 1969.

(27) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969.

(28) Dewar, M. J. S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 761–776.

(29) Baird, N. C. *J. Chem. Educ.* **1971**, *48*, 509–514.

(30) *The Jerusalem Symposium on Aromaticity, and Pseudo-Aromaticity*; Bergmann, E. D., Pullman, B., Eds.; Israeli Academy of Sciences: Jerusalem, 1971, and Academic Press: New York, 1971.

(31) *Sendai International Symposium: The Chemistry of Non-Benzenoid Aromatic Compounds*; Oki, M., Ed.; I.U.P.A.C. Butterworth's: London, 1971.

(32) Snyder, J. P., Ed.; *Nonbenzenoid Aromatics*; Academic Press: New York, 1971; Vol. II.

(33) Haddon, R. C.; Haddon, V. R.; Jackman, L. M. *Top. Curr. Chem.* **1971**, *16*, 103–220.

(34) Clar, E. *The Aromatic Sextet*; Wiley: London, 1972.

(35) *Topics in Nonbenzenoid Aromatic Chemistry*; Nozoe, T., Breslow, R., Hafner, K.,; Ito, S., Murata, I., Eds.; Hirokawa: Tokyo, 1972; Vol. 1.

(36) Sondheimer, F. *Acc. Chem. Res.* **1972**, *5*, 81–91.

(37) Breslow, R. *Acc. Chem. Res.* **1973**, *6*, 393–398.

(38) Agranat, I. Recent developments in aromatic molecules. In *Med. Tech. Publ. Co. Int. Rev. Sci. Org. Chem., Ser. One*; Zollinger, H., Ed.; Butterworth's: London, 1973; Vol. 3, pp 139–178; *Chem. Abstr.* **1973**, *79*, 52409*r*.

(39) Binsch. G. *Naturwissenschaften* **1973**, *60*, 369–374.

(40) Cook, M. J.; Katritzky, A. R.; Linda, P. *Adv. Heterocycl. Chem.* **1974**, *17*, 255–356.

(41) Lewis, D.; Peters, D. *Facts and Theories of Aromaticity*; Macmillan: New York, 1975.

(42) Balaban, A. T. *Chemical Applications of Graph Theory*; Academic Press: London, New York, and San Francisco, 1976.

(43) Graovac, A.; Gutman, I.; Trinajstić, N. *Topological Approach to the Chemistry of Conjugated Molecules*; Springer-Verlag: Berlin (West), 1977.

(44) Perlstein, J. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519–534.

(45) Aihara, J.-I. *The Theory of Aromatic Stabilization: A Source Book 1974–1979*; Department of Chemistry, Faculty of Science: Hokkaido University, Japan, 1979.

(46) Graovac, A., Trinajstić, N., Eds.; *International Symposium on Aromaticity*, Dubrovnik, Croatia, Yugoslavia, Sept 3–5, 1979; *Pure Appl. Chem.* **1980**, *52*, 1399–1667.

(47) Balaban, A. T. *Pure Appl. Chem.* **1980**, *52*, 1409–1429.

(48) Aihara, J.-I. *J. Am. Chem. Soc.* **1981**, *103*, 5704–5706.

(49) Lloyd, D. M. G. *Nonbenzenoid Conjugated Carbocyclic Compounds*; Elsevier: Amsterdam, 1984.

(50) Garratt, P. J. *Aromaticity*; Wiley: New York, 1986.

(51) Balaban, A. T.; Bancin, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo Derivatives, and their Valence Isomers*; CRC Press: Boca Raton, FL, 1987; Vol. 1.

(52) Katritzky, A. R.; Barczynski, P.; Musumarra, G.; Pisano, D.; Szafran, M. *J. Am. Chem. Soc.* **1989**, *111*, 7–15.

(53) Lloyd, D. *The Chemistry of Conjugated Compounds: To Be or Not to Be like Benzene*; Wiley: New York, 1989.

(54) Kutzelnigg, W.; Schindler, M.; Fleischer, U. *N. M. R. Basic Principles and Progress*; Springer-Verlag: Berlin, 1990.

(55) Gorelik, M. V. *Usp. Khim.* **1990**, *59*, 197–228; *Chem. Abstr.* **1990**, *113*, 5324*v*.

(56) Zhou, Z. *Int. Rev. Phys. Chem.* **1992**, *11*, 243–261.

(57) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity: Electronic and Spectral Aspects*; Wiley: New York, 1994.

(58) Lloyd, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 442–447.

(59) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209–218.

(60) Glukhovtsev, M. *J. Chem. Educ.* **1997**, *74*, 132–136.

(61) Rouvray, D. H., Ed.; *Concepts in Chemistry: A Contemporary Challenge*, Research Studies Press: Taunton (U.K.), 1997.

(62) Heilbronner, E. *The Jerusalem Symposium on Aromaticity, and Pseudo-Aromaticity*; Bergmann, E. D., Pullman, B., Eds.; Israeli Academy of Sciences: Jerusalem, 1971, and Academic Press: New York, 1971; p 21.

(63) Lloyd, D.; Marshall, D. R. *The Jerusalem Symposium on Aromaticity, and Pseudo-Aromaticity*; Bergmann, E. D., Pullman, B., Eds.; Israeli Academy of Sciences: Jerusalem, 1971, and Academic Press: New York, 1971; p 87.

(64) Labarre, J.-F. *The Jerusalem Symposium on Aromaticity, and Pseudo-Aromaticity*; Bergmann, E. D., Pullman, B., Eds.; Israeli Academy of Sciences: Jerusalem, 1971, and Academic Press: New York, 1971; p 55.

(65) Elvidge, J. A.; Jackman, L. M. *J. Chem. Soc.* **1961**, pp 859–866.

(66) Elvidge, J. A. *Chem. Commun.* **1965**, pp 160–161.

(67) Breslow, R. *Chem. Eng. News* **1965**, *43*, 90–99; *Chem. Abstr.* **1965**, *63* 6801*a*.

(68) Dauben, H. J.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 1991–1998.

(69) Winstein, S. *Q. Rev.* **1969**, *23*, 141–176.

(70) Poulter, C. D.; Boikess, R. S.; Brauman, J. I.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2291–2296.

(71) Forsén, S.; Norin, T. *Tetrahedron Lett.* **1964**, pp 2845–2849.

(72) Jackman, L. M.; Sternhell, S. *Applications of N. M. R. in Organic Chemistry*; Pergamon Press: Oxford, 1969; p. 94.

(73) Schenck, G. E.; Anet, F. A. L. *Tetrahedron Lett.* **1971**, pp 2779–2781.

(74) Anderson, J. E. *J. Chem. Soc. B* **1971**, pp 2388–2390.

(75) Schoeller, W. W. *Tetrahedron* **1973**, *29*, 929–931.

(76) Mallion, R. B. Nuclear shielding. In *Specialist Periodical Report on Nuclear Magnetic Resonance*; Harris, R. K., Ed.; The Chemical Society: London, 1975; Vol. 4, pp 1–66, especially p 44.

(77) Coulson, C. A.; Mallion, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 592–598.

(78) Katritzky, A. R.; Feygelman, V.; Musamarra, G.; Barczynski, P.; Szafran, M. *J. Prakt. Chem./Chem. Ztg.* **1990**, *332*, 853–869.

(79) Katritzky, A. R.; Karelson, M.; Malhotra, N. *Heterocycles* **1991**, *32*, 127–161.

(80) Katritzky, A. R.; Karelson, M.; Wells, A. P. *J. Org. Chem.* **1996**, *61*, 1619–1623.

(81) Jug, K.; Köster, A. M. *J. Phys. Org. Chem.* **1991**, *4*, 163–169.

(82) Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337–340.

(83) Schleyer, P. v. R.; Jiao, H.; Glukhovtsev, M. N.; Chandrasekhar, J.; Kraka, E. *J. Am. Chem. Soc.* **1994**, *116*, 10129–10134.

(84) Jiao, H.; Schleyer, P. v. R. *J. Chem. Soc., Perkin Trans. 2* **1994**, pp 407–410.

(85) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 334–337.

(86) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2383–2386.

(87) Schleyer, P. v. R.; Jiao, H.; Sulzbach, H. M.; Schaefer, H. F. *J. Am. Chem. Soc.* **1996**, *118*, 2093–2094.

(88) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

(89) Subramanian, G.; Schleyer, P. v. R.; Jiao, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2638–2641.

(90) Jiao, H.; Schleyer, P. v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075–7083.

(91) Subramanian, G.; Schleyer, P. v. R.; Jiao, H. *Organometallics* **1997**, *16*, 6, 2362–2369.

(92) Jiao, H.; Schleyer, P. v. R.; Beno, B. R.; Houk, K. N.; Warmuth, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2761–2764.

(93) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669–12670.

(94) Cyrañski, M. K.; Krygowski, T. M.; Wisiorowski, M.; Hommes, N. J. R. v. E.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 177–180.

(95) Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1945–1948.

(96) Jiao, H.; Schleyer, P. v. R. *J. Phys. Org. Chem.* **1998**, *11*, 655–662.

(97) Fokin, A. A.; Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1998**, *120*, 9364–9365.

(98) Mauksch, M.; Gogonea, V.; Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2395–2397.

(99) Cossío, F. P.; Morao, I.; Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1999**, *121*, 6737–6746.

(100) Nyulászi, L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1999**, *121*, 6872–6875.

(101) The Symbols Committee of the Royal Society. *Quantities, Units and Symbols*, 2nd ed.; The Royal Society: London, 1975.

(102) Chestnut, D. B. The ab initio computation of nuclear magnetic resonance chemical shielding. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1996; Vol. 8, Chapter 5, pp 245–297.

(103) Flygare, W. H. *Chem. Rev.* **1974**, *74*, 653–687.

(104) Ingold, C. K. *Structures and Mechanisms of Organic Chemistry*; Bell: London, 1953; pp 185–196.

(105) Hoarau, J. *Ann. Chim.* (*13ᵉ série*) **1956**, *1*, 544–587.

(106) Selwood, P. W. *Magnetochemistry*, 2nd ed.; Interscience: New York, 1956.

(107) Dorfman, Y. G. *Diamagnetism and the Chemical Bond*; Poole, C. P., Translation Ed.; Elsevier: New York, 1965; pp 15 and 16.

(108) Haberditzl, W. *Magnetochemie*; Akademie-Verlag: Berlin (East), 1966.

(109) *Diamagnetic Susceptibilities*; Landolt-Börnstein, New Series, II/16; Hellwege, K.-H., Hellwege, A. M., Eds.; Springer-Verlag: Berlin (West), 1986.

(110) Pascal, P. *Ann. Chim.* (*8ᵉ série*) **1910**, *19*, 5–70.

(111) Haberditzl, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 288−298.
(112) Pacault, A. *Ann. Chim.* (*12e série*) **1946**, *1*, 527−587.
(113) Bergmann, E. D.; Hoarau, J.; Pacault, A.; Pullman, A.; Pullman, B. *J. Chim. Phys. Phys.-Chim. Biol.* **1952**, *49*, 474−480.
(114) Pacault, A.; Hoarau, J.; Marchand, A. Aspects récents du diamagnétisme. In *Advances in Chemical Physics*; Wiley: New York, 1961; Vol. 3, pp 171−238.
(115) Pacault, A. *Bull. Soc. Chim. Fr.* **1949**, *16 Documentation*, 371−376.
(116) London, F. *C. R. Hebd. Scéances Acad. Sci.* **1937**, *205*, 28−30.
(117) London, F. *J. Phys. Radium* (*7e série*) **1937**, *8*, 397−409.
(118) London, F. *J. Chem. Phys.* **1937**, *5*, 837−838.
(119) Dauben, H. J.; Wilson, J. D.; Laity, J. L. In *Non-Benzenoid Aromatics*; Snyder, J. P., Ed.; Academic Press: New York, 1971; Vol. 2.
(120) Benson, R. C.; Norris, C. L.; Flygare, W. H.; Beak, P. *J. Am. Chem. Soc.* **1971**, *93*, 5591−5593.
(121) Norris, C. L.; Tigelaar, H. L.; Flygare, W. H. *Chem. Phys.* **1973**, *1*, 1−8.
(122) Dauben, H. J.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 811−813.
(123) Van Vleck, J. H. *The Theory of Electric and Magnetic Susceptibilities*; Oxford University Press: Oxford, 1932.
(124) Benson, R. C.; Flygare, W. H. *J. Am. Chem. Soc.* **1970**, *92*, 7523−7529.
(125) Schmalz, T. G.; Norris, C. L.; Flygare, W. H. *J. Am. Chem. Soc.* **1973**, *95*, 7961−7967.
(126) Sutter, D. H.; Flygare, W. H. *J. Am. Chem. Soc.* **1969**, *91*, 4063−4068.
(127) Schmalz, T. G.; Gierke, T. D.; Beak, P.; Flygare, W. H. *Tetrahedron Lett.* **1974**, pp 2885−2888.
(128) Pople, J. A. *J. Chem. Phys.* **1964**, *41*, 2559−2560.
(129) Ferguson, A. F.; Pople, J. A. *J. Chem. Phys.* **1965**, *42*, 1560−1563.
(130) Dailey, B. P. *J. Chem. Phys.* **1964**, *41*, 2304−2310.
(131) Pauling, L. *J. Chem. Phys.* **1936**, *4*, 673−677.
(132) Lonsdale, K. *Proc. R. Soc. London, Ser. A* **1937**, *159*, 149−161.
(133) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193−200.
(134) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919−1933.
(135) Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1983**, *105*, 1360−1970.
(136) Hameka, H. F. *Mol. Phys.* **1958**, *1*, 203-215.
(137) Ditchfield, R. *J. Chem. Phys.* **1972**, *56*, 5688−5691.
(138) Epstein, S. T. *J. Chem. Phys.* **1973**, *58*, 1592−1595.
(139) Mallion, R. B. *Mol. Phys.* **1973**, *25*, 1415−1432.
(140) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789−807.
(141) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Mongomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanôf, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision B2; Gaussian, Inc.: Pittsburgh, PA, 1994.
(142) Cremer, D.; Reichel, F.; Kraka, E. *J. Am. Chem. Soc.* **1991**, *113*, 9459−9466.
(143) Cremer, D.; Svensson, P.; Kraka, E.; Ahlberg, P. *J. Am. Chem. Soc.* **1993**, *115*, 7445−7456.
(144) Cremer, D.; Svensson, P.; Kraka, E.; Konkoli, Z.; Ahlberg, P. *J. Am. Chem. Soc.* **1993**, *115*, 7457−7464.
(145) Myers, A. G.; Finney, N. S. *J. Am. Chem. Soc.* **1992**, *114*, 10986−10987.
(146) Sondheimer, F. *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1968**, (published 1969), *12*, 125−169; *Chem. Abstr.* **1971**, *74*, 12867d.
(147) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High-Resolution Nuclear Magnetic Resonance*; McGraw-Hill: London, 1959.
(148) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High-Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: Oxford, 1965; Vol. 1.
(149) Memory, J. D. *Quantum Theory of Magnetic Resonance Parameters*; McGraw-Hill Series in Advanced Chemistry; McGraw-Hill: New York, 1968; especially Chapters 5 and 6 and Appendices 5D and 6B.
(150) Bovey, F. A. *Nuclear Magnetic Resonance Spectroscopy*; Academic Press: London, 1969.
(151) Pople, J. A. *J. Chem. Phys.* **1956**, *24*, 1111−1111.
(152) Bernstein, H. J.; Schneider, W. G.; Pople, J. A. *Proc. R. Soc. London, Ser. A* **1956**, *236*, 515−528.
(153) Pople, J. A. *Mol. Phys.* **1958**, *1*, 175−180.
(154) Waugh, J. S.; Fessenden, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 846−849; *Corrigendum: ibid. idem* **1958**, *80*, 6697−6698.
(155) Johnson, C. E.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012−1014.
(156) Mayo, R. E.; Goldstein, J. H. *Mol. Phys.* **1965/1966**, *10*, 301−307.

(157) Farnum, D. G.; Wilcox, C. F. *J. Am. Chem. Soc.* **1967**, *89*, 5379−5383.
(158) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* **1960**, *257*, 445−456.
(159) Haddon, R. C. *Tetrahedron* **1972**, *28*, 3613−3633.
(160) Haddon, R. C. *Tetrahedron* **1972**, *28*, 3635−3655
(161) McWeeny, R. *Mol. Phys.* **1958**, *1*, 311−321.
(162) Hall, G. G.; Hardisson, A. *Proc. R. Soc. London, Ser. A* **1962**, *268*, 328−338.
(163) Veillard, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1962**, *59*, 1056−1066.
(164) Amos, A. T.; Roberts, H. G. Ff. *J. Chem. Phys.* **1969**, *50*, 2375−2381.
(165) Roberts, H. G. Ff. *Theor. Chim. Acta* **1969**, *15*, 63−72.
(166) Roberts, H. G. Ff. *Theor. Chim. Acta* **1971**, *22*, 105−108.
(167) McWeeny, R. *Chem. Phys. Lett.* **1971**, *9*, 341−342.
(168) Edwards, T. G.; McWeeny, R. *Chem. Phys. Lett.* **1971**, *10*, 283−286.
(169) Amos, A. T.; Roberts, H. G. Ff. *Mol. Phys.* **1971**, *20*, 1073−1080.
(170) Roberts, H. G. Ff.; Amos, A. T. *Mol. Phys.* **1971**, *20*, 1081−1087.
(171) Roberts, H. G. Ff.; Amos, A. T. *Mol. Phys.* **1971**, *20*, 1089−1098.
(172) Haigh, C. W.; Mallion, R. B. *Mol. Phys.* **1971**, *22*, 955−970.
(173) Haigh, C. W.; Mallion, R. B. *Org. Magn. Reson.* **1972**, *4*, 203−228.
(174) Roberts, H. G. Ff. *Mol. Phys.* **1974**, *27*, 843−852.
(175) Lazzeretti, P. *Mol. Phys.* **1974**, *28*, 1389−1395.
(176) Ege, G.; Vogler, H. *Mol. Phys.* **1975**, *30*, 1511−1519.
(177) Smith, B. H. *Bridged Aromatic Protons*; Academic Press: London, 1964.
(178) Memory, J. D.; Parker, G. W.; Halsey, J. C. *J. Chem. Phys.* **1966**, *45*, 3567−3570.
(179) Cobb, T. B.; Memory, J. D. *J. Chem. Phys.* **1967**, *47*, 2020−2025.
(180) Cobb, T. B. High-Resolution Nuclear Magnetic Resonance of Polycyclic Aromatic Hydrocarbons and Polycyclic Heterocyclic Compounds, Dissertation, State University of North Carolina, Rayleigh, NC, 1968; *Diss. Abstr.* **1968**, *29*, 1463−1463.
(181) Mallion, R. B. Nuclear Magnetic Resonance: a Theoretical and Experimental Study of the Spectra of Condensed, Benzenoid Hydrocarbons, Ph.D. Thesis; University of Wales (University College, Swansea), U.K., 1969.
(182) Haigh, C. W.; Mallion, R. B.; Armour, E. A. G. *Mol. Phys.* **1970**, *18*, 751−766.
(183) Mallion, R. B. *J. Chem. Soc. B* **1971**, pp 681−686. (see also the *Corrigendum* on the last page [unnumbered] of the 'Index Issue' (No. 13), 1971).
(184) Lazzeretti, P.; Taddei, F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 839−845.
(185) Lazzeretti, P.; Taddei, F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1825−1832.
(186) Mallion, R. B. Empirical Appraisal and Graph-Theoretical Aspects of Simple Theories of the 'Ring-Current' Effect in Conjugated Systems, D.Phil. Thesis; University of Oxford (Christ Church), U.K., 1979.
(187) Mallion, R. B. *J. Chem. Phys.* **1981**, *75*, 793−797.
(188) Haigh, C. W.; Mallion, R. B. *J. Mol. Spectrosc.* **1969**, *29*, 478−485.
(189) Haigh, C. W.; Mallion., R. B. *Mol. Phys.* **1970**, *18*, 737−750.
(190) Memory, J. D.; Wilson, N. K. *N.M.R. of Aromatic. Compounds*; Wiley: New York, 1982.
(191) Bartle, K. D.; Smith, J. A. S. *Spectrochim. Acta, Part A* **1967**, *23*, 1689−1714.
(192) Bartle, K. D.; Mallion, R. B.; Jones, D. W.; Pickles, C. K. *J. Phys. Chem.* **1974**, *78*, 1330−1334.
(193) Martin, R. H. *Tetrahedron* **1964**, *20*, 897−902.
(194) Reid, C. *J. Mol. Spectrosc.* **1957**, *1*, 18−23.
(195) Cheney, B. V. *J. Am. Chem. Soc.* **1968**, *90*, 5386-5390.
(196) O'Reilly, D. E., Chemical shift calculations. In *Progress in Nuclear Magnetic Resonance Spectroscopy*; Emsley, J. W., Feeney, J., Sutcliffe, L. H., Eds.; Pergamon Press: Oxford, 1967; Vol. 2, pp. 1−61, especially pp 27−31.
(197) Coulson, C. A. *Electricity*, 5th ed.; Oliver & Boyd: London, 1958; p 104.
(198) Blustin, P. H. *Mol. Phys.* **1978**, *36*, 1441−1448.
(199) Blustin, P. H. *Chem. Phys. Lett.* **1979**, *64*, 507−510.
(200) Blustin, P. H. *Mol. Phys.* **1980**, *39*, 565−586.
(201) Kuthan, J. *Z. Chem.* **1966**, *6*, 150−151.
(202) Kuthan, J. *Collect. Czech. Chem. Commun.* **1968**, *33*, 1220−1228.
(203) Kuthan, J. *Collect. Czech. Chem. Commun.* **1970**, *35*, 714−720.
(204) Coulson, C. A.; O'Leary, B.; Mallion, R. B. *Hückel Theory for Organic Chemists*; Academic Press: London, 1978.
(205) Bartle, K. D.; Jones, D. W. *J. Phys. Chem.* **1969**, *73*, 293−298.
(206) Mallion, R. B. *Org. Magn. Reson.* **1973**, *5*, 91−94.
(207) Bartle, K. D. *Org. Magn. Reson.* **1973**, *5*, 95−97.
(208) Mekenyan, O.; Bonchev, D.; Balaban, A. T. *Chem. Phys. Lett.* **1984**, *109*, 85−88.
(209) Westermayer, M.; Häfelinger, G.; Regelmann, C. *Tetrahedron* **1984**, *40*, 1845−1854.
(210) Haigh, C. W.; Mallion, R. B. *J. Chem. Phys.* **1982**, *76*, 4063−4066.

(211) Mallion, R. B. *Proc. R. Soc. London, Ser. A* **1975**, *341*, 429−449.
(212) Newman, M. S.; Lednicer, D. *J. Am. Chem. Soc.* **1956**, *78*, 4765−4770.
(213) Martin, R. H.; Defay, N.; Figeys, H. P.; Flammang-Barbieux, M.; Cosyn, J. P.; Gelbcke, M.; Schurter, J. J. *Tetrahedron* **1969**, *25*, 4985−4998.
(214) Martin, R. H.; Morren, G.; Schurter, J. J. *Tetrahedron Lett.* **1969**, pp 3597−3598.
(215) Haigh, C. W.; Mallion, R. B. *Mol. Phys.* **1971**, *22*, 945−953.
(216) Ōsapay, K.; Case, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 9436−9444.
(217) Kao, Y.-H.; Lecomte, J. T. J. *J. Am. Chem. Soc.* **1993**, *115*, 9754−9762.
(218) Mallion, R. B. Some comments and comparisons concerning the use of 'ring-current' calculations in elucidating molecular conformations. In *Nuclear Magnetic Resonance Spectroscopy in Molecular Biology. Proceedings of the 11th Jerusalem Symposium on Quantum Chemistry and Biochemistry*, Jerusalem, Israel, April 3−7, 1978; Pullman, B., Ed.; Reidel: Dordrecht, The Netherlands, 1978; pp 183−191.
(219) Martin, N. H.; Allen, N. W.; Moore, K. D.; Vo, L. *J. Mol. Struct. (THEOCHEM)* **1998**, *454*, 161−166.
(220) Gomes, J. A. N. F.; Mallion, R. B. *J. Org. Chem.* **1981**, *46*, 719−727.
(221) Roberts, H. G. Ff. *Chem. Phys. Lett.* **1971**, *11*, 259−262.
(222) Godfrey, R. *J. Chem. Soc., Perkin Trans. 2* **1978**, pp 1019−1025.
(223) O' Sullivan, P. S.; Hameka, H. F. *J. Am. Chem. Soc.* **1970**, *92*, 1821−1824.
(224) Davies, D. W. *Trans. Faraday Soc.* **1961**, *57*, 2081−2088.
(225) Davies, D. W. *The Theory of Electric and Magnetic Properties*; Wiley: New York, 1967.
(226) Jiao, H.; Schleyer, P. v. R., Aromaticity: evidence from magnetic criteria. In *First European Conference on Computational Chemistry: Federation of European Chemical Societies' Conference, AIP Proceedings*, Bernardi, F., Rivail, J.-L., Eds.; American Institute of Physics Press: Woodbury, NY, 1995; Vol. 330, pp 107−128.
(227) Mallion, R. B. *J. Chem. Soc., Perkin Trans. 2* **1973**, pp 235−237.
(228) Maoche, B.; Gayoso, J.; Ouamerali, O. *Rev. Roum. Chim.* **1984**, *29*, 613−620.
(229) Haigh, C. W.; Mallion, R. B. *Croat. Chem. Acta* **1989**, *62*, 1−26.
(230) Brooks, H. *J. Chem. Phys.* **1940**, *8*, 939−949.
(231) (a) London, F. *Superfluids, Macroscopic Theory of Superconductivity*; Wiley: New York, 1952; Vol. 1. (b) London, F. *Superfluids, Macroscopic Theory of Superconductivity*; Wiley: New York, 1954; Vol. 2.
(232) Bilde, M.; Hansen, Aa. E. *Mol. Phys.* **1997**, *92*, 237−250.
(233) Coulson, C. A. An initially unpublished, hand-written account (now available in print as ref 236), dated May 16, 1953, extant in File No. B. 38.6 of the Coulson Papers that are part of the Contemporary Scientific Archives Collection to be found in the Department of Western Manuscripts of the Bodleian Library, University of Oxford, U.K. R.B.M. is deeply grateful to the late Mrs. Eileen Coulson for kindly allowing his privileged access to this document in 1974, before its actual deposition in the Bodleian Library.
(234) Mizoguchi, N. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2005−2010.
(235) Coulson, C. A. *Proc. Cambridge Philos. Soc.* **1940**, *36*, 201−203.
(236) O'Leary, B.; Mallion, R. B. *J. Math. Chem.* **1989**, *3*, 323−342. (It should be noted that, despite the authorship, the main part of this article—designated by the journal as a 'Special Paper'—was by the late Professor Coulson, based on the material in the archival documents described in ref 233).
(237) Mallion, R. B. *Biochimie* **1974**, *56*, 187−188.
(238) Ege, G.; Vogler, H. *Z. Naturforsch., B: Chem. Sci.* **1972**, *27*, 1164−1165.
(239) Ege, G.; Vogler, H. *Tetrahedron* **1975**, *31*, 569−573.
(240) Vogler, H.; Ege, G. *Tetrahedron* **1976**, *32*, 1789−1792.
(241) Vincent, E. J.; Phan-Tan-Luu, R.; Metzger, J. *Bull. Soc. Chim. Fr.* **1966**, pp 3537−3540.
(242) Figeys, H. P. *Tetrahedron Lett.* **1966**, pp 4625−4630.
(243) Figeys, H. P. *Chem. Commun.* **1967**, pp 495−496.
(244) Figeys, H. P.; Defay, N.; Martin, R. H.; McOmbie, J. F. W.; Ayres, B. E.; Chadwick, J. B. *Tetrahedron* **1976**, *32*, 2571−2578.
(245) Gayoso, J.; Boucekkine, A. *C. R. Hebd. Séances Acad. Sci.* **1971**, *C272*, 184−187.
(246) Boucekkine, A.; Gayoso, J. *C. R. Hebd. Séances Acad. Sci.* **1972**, *C274*, 358−361.
(247) Gayoso, J. Contribution aux Méthodes Empiriques et Semi-Empiriques de la Chimie Quantique, Thèse, Docteur Ès Sciences: Université de Paris, 1973.
(248) Chausse, J.-P.; Hoarau, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1969**, *66*, 1062−1072.
(249) Nakajima, T.; Kohda, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 804−809.
(250) Yamaguchi, H.; Nakajima, T. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 682−686.

(251) Nakajima, T. *Pure Appl. Chem.* **1971**, *28*, 219−238.
(252) Mikami, Y.; Miyai, S.; Nakajima, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 787−790.
(253) Coulson, C. A.; Gomes, J. A. N. F.; Mallion, R. B. *Mol. Phys.* **1975**, *30*, 713−732.
(254) Wilcox, C. F.; Uetrecht, J. P.; Grantham, G. D.; Grohmann, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 1914−1920.
(255) Wilcox, C. F.; Farley, E. N. *J. Am. Chem. Soc.* **1984**, *106*, 7195−7200.
(256) Wilcox, C. F.; Farley, E. N. *J. Org. Chem.* **1985**, *50*, 351−356.
(257) Jonathan, N.; Gordon, S.; Dailey, B. P. *J. Chem. Phys.* **1962**, *36*, 2443−2448.
(258) Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811−4815.
(259) Jung, D. E. *Tetrahedron* **1969**, *25*, 129−134.
(260) Maddox, I. J.; McWeeny, R. *J. Chem. Phys.* **1962**, *36*, 2353−2354.
(261) Memory, J. D. *J. Chem. Phys.* **1963**, *38*, 1341−1343.
(262) Memory, J. D. *Biochim. Biophys. Acta* **1963**, *66*, 168−169.
(263) Memory, J. D.; Cobb, T. B. *J. Chem. Phys.* **1963**, *39*, 2386-2387.
(264) Haigh, C. W.; Mallion, R. B. *Mol. Phys.* **1970**, *18*, 767−772.
(265) Mallion, R. B. *J. Mol. Spectrosc.* **1970**, *35*, 491−493.
(266) Mallion, R. B. *J. Med. Chem.* **1971**, *14*, 824−826.
(267) Mallion, R. B. Ring currents in corannulene, a prototype molecule for Buckminsterfullerene. In *Studies in Physical and Theoretical Chemistry, Vol. 63. Proceedings of an International Course and Conference on the Interfaces between Mathematics, Chemistry and Computer Science*, Dubrovnik, Yugoslavia, June 20−25, 1988; Graovac A., Ed.; Elsevier: Amsterdam, 1989; pp 505−510.
(268) Mallion, R. B. *Chem. Phys. Lett.* **1975**, *36*, 170−174.
(269) Gomes, J. A. N. F.; Mallion, R. B. *Rev. Port. Quím.* **1979**, *21*, 82−89.
(270) Gutman, I.; Mallion, R. B.; Essam, J. W. *Mol. Phys.* **1983**, *50*, 859−877.
(271) Brown, T. J. N.; Mallion, R. B.; Pollak, P.; Gomes, J. A. N. F.; de Castro, B. R. M. *J. Comput. Chem.* **1991**, *12*, 1118−1124.
(272) John, P.; Mallion, R. B. *J. Math. Chem.* **1994**, *15*, 261−271. (See also *Corrigendum: ibid. idem* **1994**, *16*, 389−390).
(273) Brown, T. J. N.; Mallion, R. B.; Pollak, P.; Roth, A. *Discrete Appl. Math.* **1996**, *67*, 51−66.
(274) John, P. E.; Mallion, R. B. *Int. J. Quantum Chem.* **1996**, *60*, 59−66.
(275) John, P. E.; Mallion, R. B.; Gutman, I. *J. Chem. Inf. Comput. Sci.* **1998**, *38*, 108−112.
(276) Trianjstić, N.; Mihalić, Z.; Harris, F. E. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1994**, *28*, 525−527.
(277) Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; p 127.
(278) Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1947**, *191*, 39−60.
(279) Mallion, R. B.; Rouvray, D. H. *Mol. Phys.* **1978**, *36*, 125−128.
(280) Mallion, R. B. *Croat. Chem. Acta* **1983**, *56*, 477−490.
(281) Harary, F.; Mallion, R. B. *Nanta Math.* **1974**, *7*, 96−101.
(282) Pasquarello, A.; Schlüter, M.; Haddon, R. C. *Science (Washington, D.C.)* **1992**, *257*, 1660−1661.
(283) De Jongh, H. A. P.; Wynberg, H. *Tetrahedron* **1965**, *21*, 515−533.
(284) Abraham, R. J.; Sheppard, R. C.; Thomas, W. A.; Turner, S. *Chem. Commun.* **1965**, pp 43−44.
(285) Davies, D. W. *Chem. Commun.* **1965**, pp 258−258.
(286) Abraham, R. J.; Thomas, W. A. *J. Chem. Soc. B* **1966**, pp 127−131.
(287) Corradi, E.; Lazzeretti, P.; Taddei, F. *Mol. Phys.* **1973**, *26*, 41−47.
(288) Benassi, R.; Lazzeretti, P.; Taddei, F. *J. Phys. Chem.* **1975**, *79*, 848−851.
(289) Ashe, A. J.; Sharp, R. R.; Tolan, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 5451−5456.
(290) Hess, B. A.; Schaad, L. J.; Nakagawa, M. *J. Org. Chem.* **1977**, *42*, 1669−1670.
(291) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722−1728.
(292) Baer, F.; Kuhn, H.; Regel, W. *Z. Naturforsch., A: Phys. Sci.* **1967**, *22*, 103−112.
(293) Mayot, M.; Berthier, G.; Pullman, B. *J. Phys. Radium* **1951**, *12*, 652−658.
(294) Pullman, B.; Pullman, A.; Bergmann, E. D.; Berthier, G.; Fischer, E.; Hirshberg, Y.; Pontis, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1952**, *49*, 24−28.
(295) Mayot, M.; Berthier, G.; Pullman, B. *J. Chim. Phys. Phys.-Chim. Biol.* **1953**, *50*, 176−182.
(296) Wagnière, G.; Gouterman, M. *Mol. Phys.* **1962**, *5*, 621−627.
(297) Aihara, J.-I. *J. Am. Chem. Soc.* **1979**, *101*, 558−560.
(298) McWeeny, R. *Phys. Rev.* **1962**, *126*, 1028−1034.
(299) McWeeny, R. *Chem. Phys. Lett.* **1968**, *1*, 567−568.
(300) Trost. B. M.; Bright, G. M.; Frihart, C.; Brittelli, D. *J. Am. Chem. Soc.* **1971**, *93*, 737−745.
(301) de Castro, B. R. M.; Gomes, J. A. N. F.; Mallion, R. B. *J. Mol. Struct. (THEOCHEM)* **1992**, *260*, 123−132.

(302) de Castro, B. R. M.; Gomes, J. A. N. F.; Mallion, R. B. *J. Mol. Struct.* (*THEOCHEM*) **1992**, *260*, 133−142.
(303) Mallion, R. B. *Nature* (*London*) **1987**, *325*, 760−761.
(304) Wilcox, C. F.; Farley, E. N. *J. Am. Chem. Soc.* **1983**, *105*, 7191−7192.
(305) Vogel, E.; Neumann, B.; Klug, W.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1046−1048.
(306) Clar, E. Personal communications to R.B.M.: (a) May 25, 1971. (b) December 31, 1970.
(307) Anusooya, Y.; Chakrabarti, A.; Pati, S. K.; Ramasesha, S. *Int. J. Quantum Chem.* **1998**, *70*, 503−513.
(308) Kuwajima, S.; Soos, Z. G. *J. Am. Chem. Soc.* **1987**, *109*, 107−113.
(309) Trost, B. M.; Kinson, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 2438.
(310) Hunadi, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6889−6895.
(311) Pascal, R. A.; Winans, C. G.; Van Engen, D. *J. Am. Chem. Soc.* **1989**, *111*, 3007−3010.
(312) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776−8789.
(313) Elser, V.; Haddon, R. C. *Nature* (*London*) **1987**, *325*, 792−794.
(314) Zanasi, R.; Lazzeretti, P.; Fowler, P. W. *Chem. Phys. Lett.* **1997**, *278*, 251−255.
(315) Fowler, P. W.; Lazzeretti, P.; Zanasi, R. *Chem. Phys. Lett.* **1990**, *165*, 79−86.
(316) Saunders: M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Mroczkowski, S.; Freedberg, D. I.; Anet, F. A. L. *Nature* (*London*) **1994**, *367*, 256−258.
(317) Haddon, R. C. *Nature* (*London*) **1994**, *367*, 214−214.
(318) Schulman, J. M.; Disch, R. L. *J. Phys. Chem. A* **1997**, *101*, 9176−9179.
(319) Matzger A. J.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1998**, pp 6791−6794.
(320) Bühl, M. *Chem. Eur. J.* **1998**, *4*, 734−739.
(321) Choi, H. S.; Kim, K. S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2256−2258.
(322) Aihara. J.-I. *J. Am. Chem. Soc.* **1992**, *114*, 865−868.
(323) Aihara, J.-I. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 57−60.
(324) Malkin, V. G.; Malkina, O. L.; Eriksson, L. A.; Salahub, D. R. In *Modern Density Functional Theory*; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995; p 273.
(325) Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898−5908.
(326) Mallion, R. B.; Rouvray, D. H. *J. Math. Chem.* **1990**, *5*, 1−21 (see also *Postscript*: *ibid. idem* **1991**, *8*, 399−400).
(327) Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1992**, *194*, 1−8.
(328) Keith, T. A.; Bader, R. F. W. *Chem. Phys. Lett.* **1993**, *210*, 223−231.
(329) Gomes, J. A. N. F. *Mol. Phys.* **1982**, *47*, 1227−1230.
(330) Gomes, J. A. N. F. *J. Chem. Phys.* **1983**, *78*, 4585−4591.
(331) Gomes, J. A. N. F. *Phys. Rev. A*: At., Mol., Opt. Phys. **1983**, *28*, 559−566.
(332) Gomes, J. A. N. F. *J. Mol. Struct.* (*THEOCHEM*) **1983**, *93*, 111−127.
(333) Gomes, J. A. N. F. The qualitative theory of the current density in molecules. In *Local Density Approximations in Quantum Chemistry and Solid State Physics*; Dahl, J. P., Avery, J., Eds.; Plenum Press: New York, 1984; pp 145−153.
(334) Keith, T. A.; Bader, R. F. W. *J. Chem. Phys.* **1993**, *99*, 3669−3682.
(335) Lazzeretti, P.; Malagoli, M.; Zanasi, R. Electronic current density induced by magnetic fields and magnetic moments in molecules. In *Nuclear Magnetic Shieldings and Molecular Structure*; Tossell, J. A., Ed.; NATO Advanced Study Institute Series C; Kluwer: Dordrecht, The Netherlands, 1993; pp 163−190.
(336) Gomes, J. A. N. F. *J. Chem. Phys.* **1983**, *78*, 3133−3139.
(337) Zanasi, R.; Lazzeretti, P.; Malagoli, M.; Piccinini, F. *J. Chem. Phys.* **1995**, *102*, 7150−7157.
(338) Malagoli, M. Studio Teorico della Risposta Molecolare a Perturbazioni Elettromagnetiche. Ph.D. Thesis, Facoltà di Scienze M. F. N., Università di Modena, Italy, 1993.
(339) Zanasi, R.; Lazzeretti, P. *Mol. Phys.* **1997**, *92*, 609−617.
(340) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* (*London*) **1985**, *318*, 162−163.
(341) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* (*London*) **1990**, *347*, 354−358.
(342) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137−142.
(343) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *131*, 165−169.
(344) Haddon, R. C. *Chem. Phys. Lett.* **1986**, *125*, 231−234.
(345) Haddon, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 1676−1785.
(346) Haddon, R. C.; Elser, V. *Chem. Phys. Lett.* **1990**, *169*, 362−364.
(347) Schmalz, T. G. *Chem. Phys. Lett.* **1990**, *175*, 3−5.
(348) Fowler, P. W.; Lazzeretti, P.; Malagoli, M.; Zanasi, R. *Chem. Phys. Lett.* **1991**, *179*, 174−180.
(349) Haddon, R. C. *Science* (*Washington, D.C.*) **1993**, *261*, 1545−1550.
(350) de Castro, B. R. M.; Gomes, J. A. N. F.; Mallion, R. B. *Croat. Chem. Acta* **1993**, *66*, 49−58.
(351) Kroto, H. *Nature* (*London*) **1987**, *329*, 529−531.
(352) Ramirez, A. P.; Haddon, R. C.; Zhou, O.; Fleming, R. M.; Zhang, J.; McClure, S. M.; Smalley, R. E. *Science* (*Washington, D.C.*) **1994**, *265*, 84−86.
(353) Pauling, L. Unpublished calculation, 1987.
(354) Fowler, P. W.; Lazzeretti, P.; Malagoli, M.; Zanasi, R. *J. Phys. Chem.* **1991**, *95*, 6404−6405.
(355) Pasquarello, A.; Schlüter, M.; Haddon, R. C. *Phys Rev A*: At., Mol., Opt. Phys. **1993**, *47*, 1783−1789.
(356) Zanasi, R.; Fowler, P. W. *Chem. Phys. Lett.* **1995**, *238*, 270−280.
(357) Hameka, H. F. *J. Chem. Phys.* **1961**, *34*, 1996−2000.
(358) Bühl, M. *Chem. Phys. Lett.* **1995**, *242*, 580−584.
(359) Bühl, M.; Thiel, W.; Schneider, U. *J. Am. Chem. Soc.* **1995**, *117*, 4623−4627.
(360) Saunders: M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Billups, W. E.; Gesenberg, C.; Gonzalez, A.; Luo, W.; Haddon, R. C.; Diederich, F.; Herrmann, A. *J. Am. Chem. Soc.* **1995**, *117*, 9305−9308.
(361) Lazzeretti, P.; Zanasi, R. *J. Chem. Phys.* **1981**, *75*, 5019−5027.
(362) Lazzeretti, P.; Zanasi, R. *Chem. Phys. Lett.* **1981**, *80*, 533−536.
(363) Lazzeretti, P.; Rossi, E.; Zanasi, R. *Nuovo Cimento Ital. Phys. D* **1982**, pp 70−80.
(364) Lazzeretti, P.; Rossi, E.; Zanasi, R. *J. Chem. Phys.* **1982**, *77*, 3129−3139.
(365) Lazzeretti, P.; Rossi, E.; Zanasi, R. *J. Am. Chem. Soc.* **1983**, *105*, 12−15.
(366) Lazzeretti, P.; Rossi, E.; Zanasi, R. *Int. J. Quantum Chem.* **1984**, *25*, 929−940.
(367) Bader, R. F. W.; Keith, T. A. *J. Chem. Phys.* **1993**, *99*, 3683−3693.
(368) Bader, R. F. W. *Phys. Rev. B*: Condens. Matter **1994**, *49*, 13348−13356.
(369) Bader, R. F. W.; Popelier, P. L. A.; Keith, T. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 620−681.
(370) Lazzeretti, P.; Malagoli, M.; Zanasi, R. *J. Mol. Struct.* (*THEOCHEM*) **1991**, *234*, 127−145.
(371) Coriani, S.; Lazzeretti, P.; Malagoli, M.; Zanasi, R. *Theor. Chim. Acta* **1994**, *89*, 181−192.
(372) Lazzeretti, P.; Malagoli, M.; Zanasi, R. *Chem. Phys. Lett.* **1994**, *220*, 299−304.
(373) Fleischer, U.; Kutzelnigg, W.; Lazzeretti, P.; Mühlenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298−5306.
(374) Lazzeretti, P.; Malagoli, M.; Zanasi, R. *J. Chem. Phys.* **1995**, *102*, 9619−9625.
(375) Hansen, A. E.; Bouman, T. D. *J. Chem. Phys.* **1985**, *82*, 5035−5047.
(376) Okninski, A.; Sadłej, A. J. *Acta Phys. Pol., A* **1972**, *42*, 709−719.
(377) Keith, T. A.; Bader. R. F. W. *Can. J. Chem.* **1996**, *74*, 185−200.
(378) Lipscomb, W. N. The chemical shift and other second-order magnetic and electric properties of small molecules. In *Advances in Magnetic Resonance*; Waugh, J. S., Ed., Academic Press: New York, 1966; Vol. 2, pp 137−176.
(379) Lazzeretti, P.; Zanasi, R. *J. Chem. Phys.* **1980**, *72*, 6768−6776.
(380) Gauss, J. *J. Chem. Phys.* **1993**, *99*, 3629−3643.
(381) Fowler, P. W.; Steiner, E.; Cadioli, B.; Zanasi, R. *J. Phys. Chem. A* **1998**, *102*, 7297−7302.
(382) Steiner, E.; Fowler, P. W. *Int. J. Quantum Chem.* **1996**, *60*, 609−616.
(383) Fraenkel, G.; Carter, R. E.; McLachlan, A.; Richards, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 5846−5854.
(384) Spiesecke, H.: Schneider, W. G. *Tetrahedron Lett.* **1961**, pp 468−472.
(385) Heffernan, M. L.; Jones, A. J.; Black, P. J. *Aust. J. Chem.* **1967**, *20*, 589−593.
(386) Cobb, T. B.; Memory, J. D. *J. Chem. Phys.* **1969**, *50*, 4262−4282.
(387) Fowler, P. W.; Zanasi, R.; Cadioli, B.; Steiner, E. *Chem. Phys. Lett.* **1996**, *251*, 132−140.
(388) Fowler, P. W.; Steiner, E.; Zanasi, R.; Cadioli, B. *Mol. Phys.* **1999**, *96*, 1099−1108.
(389) Ligabue, A.; Pincelli, U.; Lazzeretti, P.; Zanasi, R. *J. Am. Chem. Soc.* **1999**, *121*, 5513−5518.
(390) Fowler, P. W.; Steiner, E. *J. Phys. Chem. A* **1997** *101*, 1409−1413.
(391) Geertsen, J. *J. Chem. Phys.* **1989**, *90*, 4892−4902.
(392) Geertsen, J. *Chem. Phys. Lett.* **1991**, *179*, 479−482.
(393) Geertsen, J. *Chem. Phys. Lett.* **1992**, *188*, 326−331.
(394) Burk, P.; Abboud, J.-L. M.; Koppel, I. A. *J. Phys. Chem.* **1996**, *100*, 6992−6997.
(395) Simion, D. V.; Sorensen, T. S. *J. Am. Chem. Soc.* **1996**, *118*, 7345−7352.
(396) Hoffman, R.; Minkin, V. I.; Carpenter, B. K. *HYLE*: Int. J. Philos. Chem. **1997**, *3*, 3−28.
(397) Coulson, C. A. Personal communication to R.B.M., 1973 (now in File No. B. 41.27 of the Coulson Papers in the Contemporary Scientific Archives Collection, Department of Western Manuscripts, Bodleian Library, University of Oxford, U.K.).