

Ring magnetic susceptibilities in conjugated hydrocarbons

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In the context of an SCF π -electron theory an exact expression is derived which yields χ_{π}^{\perp} , the total π -electron contribution to the magnetic susceptibility perpendicular to the plane of a polycyclic conjugated hydrocarbon. Once given the first-order correction to the bond-order matrix of the molecule in question (which, in the present calculation, is obtained via a coupled Hartree-Fock procedure), this expression makes no further appeal to the London integral approximation. The terms which occur in the expression for χ_{π}^{\perp} due to the 'integrated current densities' correspond to those which would have arisen if the London approximation had been invoked, the remaining terms being, in general, non-zero if this approximation is not made. The relative 'integrated current densities' associated with the various constituent rings in 12 molecules agree well with the corresponding 'ring current' intensities estimated via the London-Pople-McWeeny method.

It is shown that for polycyclic conjugated systems which are predominantly diamagnetic, the total χ_{π}^{\perp} for a particular molecule can to a good approximation be partitioned into a sum of individual contributions from each of its constituent rings. Hence the intuitively appealing idea of a 'ring susceptibility' can be preserved, even when the whole of χ_{π}^{\perp} , and not just that part of it due to 'ring currents', is calculated. When an appropriate set of Pascal-type constants is derived from the experimental data and calculated χ_{π}^{\perp} for benzene substantial agreement with experiment is found for a wide range of benzenoid hydrocarbons. This is evidence for regarding π -electron 'ring susceptibility' as an additive property within each individual molecule of this type.

1. INTRODUCTION

A full *ab initio* calculation of the magnetic susceptibility of a general polycyclic conjugated molecule is not practicable at present; even when adequate ground-state wave functions are available, calculation of the paramagnetic part of the overall susceptibility is not possible since the required [1] excited-state wave functions are usually not known to the same accuracy [2, 3]. Resort has therefore been made to empirical and semi-empirical methods. In the most elementary of these it is assumed that the overall susceptibility of a given molecule may be broken down into atomic contributions, with extra terms accounting for certain special features such as double bonds [4, 5]. It has been realized for 50 years that this simple model produces poor results when applied to conjugated hydrocarbons, and it was suggested [6-11] that the large

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anisotropy of magnetic susceptibility observed in these molecules might be due effectively to their π -electron systems. Although some classical treatments have since been proposed [10–17], these ideas, and later extensions of them to N.M.R. chemical shifts, have mainly been formulated quantum-mechanically [18–32].

The starting point in some of the more recent SCF approaches is a calculation of the interaction of the current density [1, 33, 30, 28] induced in the π -electrons of the molecule by the external magnetic field, either with the field itself (to give the magnetic susceptibility), or with a nuclear magnetic dipole (to estimate an N.M.R. chemical shift). Using such an approach Amos and Roberts [30] made several approximations to reduce the current density in the π -electron system of a conjugated molecule to a sum over pairs of chemically bonded atoms. The ‘bond current densities’ so obtained depend on the first-order perturbation of the bond-order matrix. However, the uncoupled Hartree–Fock scheme they used did not give this directly and so it had to be estimated by the procedure of Feenberg and Goldhammer† [30, 34]. This latter approximation (which can be obviated by use of a coupled Hartree–Fock procedure [21]) need not be invoked in the case of a calculation on benzene. Even so, the calculated π -electron susceptibility (exclusive of certain terms considered to be ‘local’ in character) can vary over a range of *ca.* 25 per cent, depending on whether or not the London approximation is adopted. This approximation should therefore be avoided whenever possible, as has also been found in the calculation of proton chemical shifts [35, 29, 32].

Caralp and Hoarau [22] have recently developed a new perturbation approach for calculating π -electron susceptibilities, within a Goepfert-Mayer and Sklar [36] framework. They used Slater-type orbitals modified by a variational factor and their estimate of the π -electron contribution, χ_{π}^{\perp} , to the total susceptibility, χ^{\perp} , in the direction perpendicular to the molecular plane is arguably the best calculation so far for this type of molecule; it is also quite independent of the other methods discussed here. They also attempted to calculate the π -electron contribution to the susceptibility *in* the molecular plane, χ_{π}^{\parallel} . We have not tried to estimate this as we feel that the idea of a σ – π separation will not be valid in this case.

On a more prosaic level, since the most striking and obvious feature of a polycyclic hydrocarbon is that it contains *rings*, there has traditionally been a tendency to break down the total contribution of the ‘mobile’ π -electrons to χ_{π}^{\perp} (or to proton chemical shifts), into ring- rather than bond-terms and to talk of entities such as ‘ring currents’. It would, therefore, be of interest to see whether, in the context of a ‘semi-rigorous’ [30 a] SCF approach which makes as few traditional approximations as practicable, the overall χ_{π}^{\perp} for a given polycyclic molecule can be apportioned into ring contributions and hence to establish whether any quantitative credence can be given to the intuitively appealing idea of ‘ring susceptibilities’ as an additive property within each individual molecule. In principle, this concept appears reasonable, for the

† With reference to the extensive footnote on p. 1420 of [31], it now seems more likely that the non-conservation of ‘bond current densities’ reported in [30] is due to the use of the uncoupled Hartree–Fock procedure, with Feenberg–Goldhammer correction, rather than to a neglect of certain non-bonded terms. As is shown in § 2, however, entities of this sort are not strictly bound to obey any Kirchhoff type of conservation law.

expressions obtained in the current-density approach [1, 33, 30] can be interpreted as implying that each element of volume associated with the planar system makes its own contribution to the perturbation energy arising as a result of the presence of the external magnetic field. If, therefore, some sort of volume could be allotted to each ring, and if an integration were to be performed over that volume, then that ring's contribution to the total χ_{π}^{\perp} should be obtained. Alternatively, if we were to use the LCAO approximation, then omitting everything except the atomic orbitals of a particular ring, we would again obtain an estimate of that ring's contribution to χ_{π}^{\perp} .

The following considerations, therefore, were the stimulus for the present work.

(1) The separation between 'local' and 'non-local' π -electron effects seems largely arbitrary and it would therefore be more sound to calculate χ_{π}^{\perp} assuming σ - π separation.

(2) Some applications of the London integral approximation used previously [30] are avoidable and consequently an exact expression for χ_{π}^{\perp} may be derived (see § 2.2). It depends on a knowledge of the bond-order matrix for the molecule and its first-order perturbation; this may be estimated via the coupled Hartree-Fock procedure of Hall and Hardisson [21]†.

(3) Many recent formalisms effectively rely on a 'ring current' picture which, although conceptually useful, does represent a grossly incomplete physical picture—particularly with regard to the paramagnetic nature of the π -electron contribution in certain conjugated systems. Because of this and the fact that the induced currents have a far from simple pattern even in diatomic molecules [37, 38] it would seem more legitimate to describe these currents by their equivalent magnetic multipoles at a particular point (§ 2), rather than in terms of a model of linear currents which is classical and oversimplified.

(4) For the calculation of magnetic susceptibilities by this method, it is sufficient to obtain the magnetic dipole moment. As indicated, however, we should still like to preserve the idea of a 'ring susceptibility', and this can be achieved (as will be seen in § 4.1) if the appropriate moment is separately evaluated for each ring of the polycyclic conjugated molecule in question.

2. THEORY

2.1. General formulation

The current density at position \mathbf{r} is given by the familiar expression [1, 33]

$$\mathbf{j}(\mathbf{r}) = \sum_{k=1}^N \int \left[\frac{ie\hbar}{2m} (\psi^* \nabla_k \psi - \psi \nabla_k \psi^*) - \frac{e^2}{m} \mathbf{A}(\mathbf{r}_k) \psi^* \psi \right] \delta(\mathbf{r} - \mathbf{r}_k) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (1)$$

† It should be pointed out, however, that in deriving their coupled Hartree-Fock method for calculating \mathbf{p}^1 , the first-order correction to the bond-order matrix of the conjugated system in question, Hall and Hardisson invoked a series of assumptions which are tantamount to the London approximation. Furthermore, it is by no means an easy matter to calculate \mathbf{p}^1 without following this procedure. A similar philosophy was adopted by Edwards and McWeeny [28] in the context of magnetic susceptibilities and N.M.R. chemical shifts, although they employed the density-matrix form of SCF perturbation theory which is, however, mathematically equivalent to the fully coupled Hall-Hardisson approach (see [27]).

where ψ is the wave function describing the N -electron system and \mathbf{A} is the vector potential due to the constant, homogeneous, external magnetic field, \mathbf{B} . The term in the Taylor expansion of the energy which is second order in \mathbf{B} is

$$E^{(2)} = - \int \mathbf{A}(\mathbf{r}) \cdot \mathbf{j}^1(\mathbf{r}) d\mathbf{r} = \frac{e}{m} \langle 0 | \mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p} | 1 \rangle + \frac{e^2}{m} \langle 0 | A^2 | 0 \rangle, \quad (2)$$

where \mathbf{j}^1 is the component of \mathbf{j} which is first order in \mathbf{B} . With the z axis along the direction of \mathbf{B} , the zz -component of the magnetic susceptibility may be written

$$\chi_{zz} = \frac{N\mu_0}{B^2} \int \mathbf{A} \cdot \mathbf{j}^1 d\mathbf{r}. \quad (3)$$

The z -component of the term in the magnetic dipole moment first order in \mathbf{B} is

$$\begin{aligned} M_z^{(1)} &= \frac{1}{2} \int \mathbf{k} \cdot \mathbf{r} \wedge \mathbf{j}^1 d\mathbf{r} \\ &= \frac{1}{B} \int \mathbf{A} \cdot \mathbf{j}^1 d\mathbf{r}, \end{aligned} \quad (4)$$

where \mathbf{k} is a unit vector along the z -axis. Then from (3) and (4):

$$\chi_{zz} = \frac{N\mu_0}{B} M_z^{(1)}. \quad (5)$$

For the purpose of calculating the magnetic dipole moment, the system may formally be partitioned into any number of convenient sub-domains. The magnetic dipole moment of the whole molecule is independent of the point, \mathbf{Q} , at which this moment, $\mathbf{M}(\mathbf{Q})$, is calculated—although for each of the sub-domains, D_k , this is not in general true because \mathbf{J}_k (in equation (7)) is not zero. We then have

$$\begin{aligned} \mathbf{M} &= \mathbf{M}(\mathbf{Q}) = \frac{1}{2} \int (\mathbf{r} - \mathbf{Q}) \wedge \mathbf{j} d\mathbf{r} \\ &= \sum_{k=1}^N \mathbf{M}_k(\mathbf{Q}_k) + \sum_{k=1}^N \frac{1}{2} (\mathbf{Q}_k - \mathbf{Q}) \wedge \mathbf{J}_k \end{aligned} \quad (6)$$

with

$$\mathbf{J}_k = \int_{D_k} \mathbf{j}(\mathbf{r}) d\mathbf{r} \quad \text{and} \quad \mathbf{M}_k(\mathbf{Q}_k) = \frac{1}{2} \int_{D_k} (\mathbf{r} - \mathbf{Q}_k) \wedge \mathbf{j} d\mathbf{r} \quad (7)$$

and $D_1 \cup D_2 \cup D_3 \cup \dots \cup D_N =$ complete geometrical space.

In equation (6) we allow the dipole moment of each subdomain, D_k , to be calculated at any convenient point, \mathbf{Q}_k .

It is especially of interest to consider the choice of a particular set of sub-domains, D_k , such that the integrated currents, \mathbf{J}_k , are zero. In some cases this condition may be brought about by the assumption of virtual surface currents in the boundary between pairs of domains, whose effect in the overall integral vanishes. With such a set of sub-domains, equation (6) becomes

$$\mathbf{M} = \sum_k \mathbf{M}_k \quad (8)$$

and we thus have a simple law of additivity for the magnetic dipoles which will also hold for the magnetic susceptibility.

2.2. Application to conjugated molecules

The theory as it is developed in § 2.1 is largely formal since it assumes that $|0\rangle$ and $|1\rangle$ are *exact* solutions to the zero- and first-order equations. When non-exact wave functions are used one should therefore strictly ask whether the results of § 2.1 hold at each level of approximation. However, as we are about to apply an approximate analogy of this formalism in the context of a *semi-empirical* calculation, we do not consider these problems further.

The wave function, ψ , describing a planar conjugated molecule is, as usual [30], assumed to be of the form of a (closed-shell) Slater determinant of molecular orbitals (MO), ϕ_k , themselves taken as a linear combination of atomic orbitals (AO), χ_k . Two types of atomic orbitals have been used in minimal basis sets for molecules in the presence of magnetic fields: AO's which contain approximate terms of one-electron one-centre eigenfunctions as far as those first order, and second order, respectively, in B . In the first category are the so-called 'gauge-invariant' atomic orbitals (GIAO) obtained [18] by multiplying the usual field-free AO's, ω_s (p_z Slater functions in the present case), by a complex exponential factor

$$\chi_s(\mathbf{r}) = \omega_s \exp\left(-\frac{ie}{2\hbar} B\mathbf{k} \wedge \mathbf{R}_s \cdot \mathbf{r}\right) \quad (9)$$

with

$$\omega_s = \frac{1}{\sqrt{\pi}} \zeta^{5/2} \exp(-\zeta r_s), \quad (10)$$

\mathbf{R}_s being the vector relating the centre of orbital χ_s to the origin of coordinates, and $r_s = |\mathbf{r} - \mathbf{R}_s|$. The term 'gauge invariance' here is thus supposed to refer to the variational or perturbational procedure rather than the functions themselves (see also [39]). Caralp and Hoarau [22] used basis functions of the second type, in which an AO corrected up to second order in B , for a vector potential with gauge origin at the centre of the atom, is multiplied by the same exponential factor as above; since our present theory depends only on that term of the current density which is first order in the field, it is immaterial which type of function we choose. In fact, we take the first.

Now, the MO,

$$\phi_k = \sum_s a_{ks} \chi_s \quad (11)$$

may be expanded as a power series in the magnetic field.

After some manipulation, starting from equation (1), this LCAO formalism leads to the following expression for the first-order electronic current density:

$$\mathbf{j}^1 = -\frac{e^2 B}{2m} \sum_{st} \left\{ P_{st}^0 \mathbf{k} \wedge \left(\mathbf{r} - \frac{\mathbf{R}_s + \mathbf{R}_t}{2} \right) \omega_s \omega_t + \left[P_{st}^1 \mathbf{k} \wedge (\mathbf{R}_s - \mathbf{R}_t) \cdot \mathbf{r} - \frac{\hbar}{e} P_{st}^1 \right] (\omega_s \nabla \omega_t - \omega_t \nabla \omega_s) \right\}, \quad (12)$$

where P_{st}^n is the (s, t) element of the n th-order bond-order matrix [21, 30].

For the polycyclic conjugated systems of the type we consider, the relevant elementary sub-domains will be each single ring, whose total integrated current

will be seen (§ 4) to vanish by consideration of appropriate self-compensating currents along the boundaries between sub-domains. Expressions analogous to equation (8) will then apply, and we are left with the task of calculating the magnetic dipole, \mathbf{M}_k , of a single ring (the k th one); this moment is independent of the origin taken for the calculation.

In the present LCAO model the magnetic dipole moment first order in B becomes

$$\mathbf{M}^{(1)} = \sum_{s,t} \mathbf{M}_{st} \quad (13)$$

with

$$\mathbf{M}_{st} = \frac{1}{2} \int \mathbf{r} \wedge \mathbf{j}_{st}^1 d\mathbf{r} \quad (14)$$

in which the sum is over all combinations of atoms s and t in the conjugated system.

Considering the identity

$$\mathbf{r} = \frac{1}{2}(\mathbf{R}_s + \mathbf{R}_t) + [\mathbf{r} - \frac{1}{2}(\mathbf{R}_s + \mathbf{R}_t)] \quad (15)$$

leads to

$$\mathbf{M}_{st} = \frac{1}{2} \mathbf{k} \cdot \frac{1}{2}(\mathbf{R}_s + \mathbf{R}_t) \wedge \mathbf{J}_{st} + \mu_{st} \quad (16)$$

in which μ_{st} is the moment about the mid-point between centres s and t , and is given by

$$\mu_{st} = \frac{-e^2 B}{2m} \frac{1}{2} P_{st}^0 \left\{ (\omega_s, \rho^2 \omega_t) + |\mathbf{R}_s - \mathbf{R}_t|^2 \left(\omega_s, \frac{\zeta y^2}{r_t} \omega_t \right) \right\}, \quad (17)$$

where ρ is the cylindrical radius from an axis parallel with the z axis, (which is perpendicular to the molecular plane) through the mid-point of centres s and t ((f, g) denoting $\int f^* g d\tau$). \mathbf{J}_{st} in equation (16) is the integral of that term in the current density which is first order in B (equation (12)) and which involves centres s and t ; the expression for this is

$$\begin{aligned} \mathbf{J}_{st} &= \int \mathbf{j}_{st}^1 d\tau \\ \mathbf{J}_{st} &= -\frac{e^2 B}{2m} \left(\mathbf{k} \cdot \mathbf{R}_s \wedge \mathbf{R}_t P_{st}^0 - \frac{2\hbar}{e} P_{st}^1 \right) \left(\omega_s, \frac{\partial}{\partial x} \omega_t \right) \end{aligned} \quad (18)$$

along x , the axis directed from t to s . Equation (13) (together with (16)–(18)) is thus seen to be the LCAO analogy of equation (6) of the formal theory (§ 2.1) and it thus gives directly the component of the total magnetic dipole moment perpendicular to the molecular plane. Equation (16) also has the following interesting interpretation: the London integral approximation consists essentially in setting \mathbf{r} in equation (12) equal to $\frac{1}{2}(\mathbf{R}_s + \mathbf{R}_t)$ —that is to say, in making the second term (in square brackets) in the identity (15), exactly zero; now the *first* term of equation (16), involving \mathbf{J}_{st} , arises from the *first* term of identity (15) when the latter is substituted in equation (12), and it may therefore be thought of as corresponding in some way to the London contribution to χ_π^\perp . The second term, μ_{st} , of (16) may then be regarded as a ‘correction’ to the London estimate. Such a partition of the total π -electron effect allows us to compare (see § 4.3) the J_{st} terms calculated from equation (18) with the relative values of ‘bond current densities’ and ‘ring currents’ published elsewhere.

It is also important to emphasize that the integral of the current density, \mathbf{J}_{st} , is a pure vector which represents the rate of increase of electric dipole moment. It has dimension (electric current) \times (length) and units of C ms^{-1} or D s^{-1} . It is, therefore, a physical quantity which is different from an electric current and care must be taken to avoid confusion between these two concepts. However, a condition which must be satisfied by the entities \mathbf{J}_{st} is that

$$\sum_{s,t} \mathbf{J}_{st} \approx 0 \quad (19)$$

since this summation represents the rate of change of electric dipole moment of the molecule in question.

It should be noted that the current density itself satisfies the conservation condition $\nabla \cdot \mathbf{j} = 0$ when the wave function used to define it is exact or is at least an eigenfunction of some *effective* hamiltonian in which the potential energy operator is scalar and multiplicative. Such is not the case when (as here) a Roothaan-type of calculation is performed and quite extensive violations of $\nabla \cdot \mathbf{j} = 0$ may consequently occur—as has been observed previously by McWeeny (personal communication, 1974). However, even in these situations, $\sum_{s,t} \mathbf{J}_{st}$ in equation (19) is still exactly zero for molecules having at least C_{2v} symmetry when the principal axis is the direction of \mathbf{B} (assumed normal to the molecular plane); when this symmetry condition is not satisfied we find, however, that $\sum_{s,t} \mathbf{J}_{st}$ is still quite small (for details see § 4.1).

2.3. Possible models for ring susceptibilities

We now consider how the π -electron susceptibility (and, therefore, the magnetic dipole moment) normal to the plane of a given polycyclic molecule might be partitioned into individual contributions from each of its constituent rings. Division of the whole of space associated with some polynuclear molecule into fairly well-defined non-overlapping volumes followed by direct integration of the total current density (according to equation (6)), is generally too difficult. We shall, therefore, prefer to associate with each ring those terms in the double summation (13) which are more obviously related to that ring; for there occur in the summation terms referring to the atomic orbitals on centres s and t in one ring, and s - t terms which refer to atomic orbitals at centres in *two* rings. If the sizes of the terms in this second group were small, as we shall show to be the case in § 4, then we should be able to make a reasonable estimate of the contribution from each individual ring to the total summation (13); all that would be necessary would be to pick out those terms in the summation which involve AO's in the particular ring chosen, in order to obtain the contribution of that ring to χ_{π}^{\perp} .

It turns out that by far the most important terms in the summation of equation (13) are those arising from pairs of centres which are *chemically bonded* (as Amos and Roberts similarly observed [30]); from the form of equations (17) and (18) this is not unexpected since, as the distance between centres s and t increases, the integrals involving AO's on these centres decrease quickly and J_{st} and μ_{st} will do likewise. It would thus seem reasonable to start by assigning to each ring only those contributions from the chemically bonded centres around it and then to see how this initial approximation might be improved. As for

those terms which are shared by two or three rings, the following policy will be adopted: since we wish to simulate the result of an integration over an appropriate domain for each ring, it is logical to divide the μ_{st} (moment) terms in equation (17) equally between the two rings which share the bond $s-t$ ($s \neq t$) and, when $s=t$, between the two or three rings which share the vertex s . Furthermore, we find that if the (generally small) J_{st} terms (equation (18)) between non-bonded centres s and t are neglected, calculated values of these integrated currents between *chemically bonded* centres exhibit a very gratifying conservation (i.e. Kirchhoff-type laws are obeyed). We can, therefore, identify a certain integrated current with *each ring* (which will be a characteristic relating to all unshared bonds in that ring and, notionally at least, a characteristic of the shared ones) by postulating the association, with those bonds shared by two rings, of two opposite (and in general different) integrated currents whose sum equals the actual integrated current calculated for that bond from equation (18). In this way (as is shown quantitatively in § 4.1 and § 4.2) it is possible to divide the moment of a general polycyclic molecule into contributions from its individual constituent rings in such a way that each ring has a zero overall integrated current, thereby satisfying a condition analogous to what in our 'exact' treatment (§ 2.1) is represented by equation (6) with the J_k terms equal to zero (i.e. equation (8)). In this model all terms between non-bonded centres are neglected; however, allowance could easily be made for the two-centre 'moment' terms between those centres which are *not* chemically bonded but which are *situated in the same ring*, since the contribution of *these* non-bonded terms can just be added to the previously calculated moment of the corresponding ring.

The basic model, and the refinements to it just described, will now be tested quantitatively.

3. CALCULATIONS

Calculations were performed on eight alternant hydrocarbons ((I) to (VIII) in figure 1) and on four non-alternant ones ((IX) to (XII) in figure 2) chosen so as to provide a suitably wide range of molecules. For each hydrocarbon, the calculation was carried out in three stages:

- (i) A calculation of the ground state of the π -electron system. This was based on a Pariser-Parr-Pople SCF π -electron wave function with ζ exponent, in equation (10), set equal to the standard value of 31.8 nm^{-1} ; an idealized planar geometry of uniform carbon-carbon bond lengths of 0.140 nm was used throughout. The α core integrals were calculated via the Goepfert-Mayer and Sklar formalism [36]. Values of -2.39 eV (*ca.* -230 kJ mol^{-1}) and 11.08 eV (*ca.* 1101 kJ mol^{-1}) were taken for the β parameter, and the monocentric repulsion integrals, respectively, and these were used in conjunction with repulsion integrals estimated by the procedure of Mataga and Nishimoto [40]. Some initial calculations were also checked by Pariser's parametrization [41].
- (ii) A calculation of the perturbation induced by the external magnetic field perpendicular to the molecular plane. The first-order correction to the bond-order matrix was estimated via the coupled Hartree-Fock method [21], by means of the programme of Lazzeretti and Taddei [42].

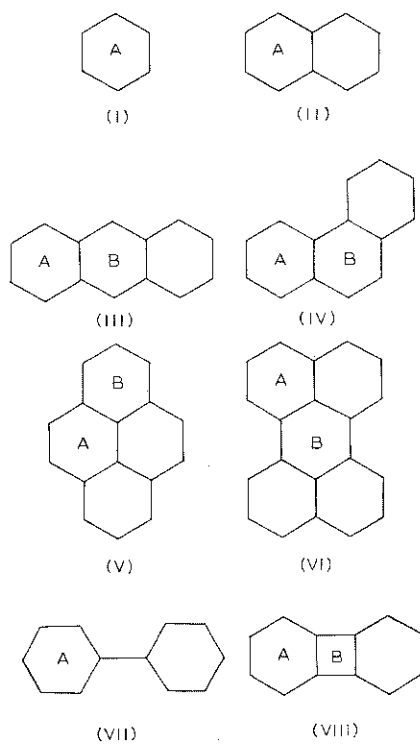


Fig. 1

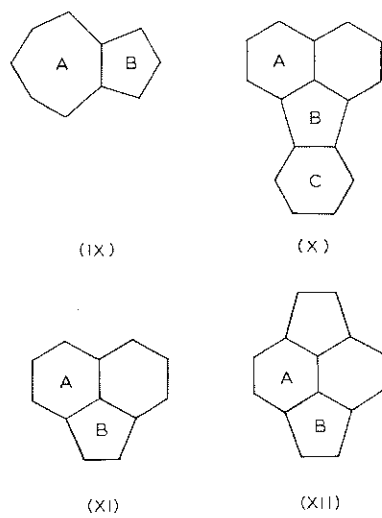


Fig. 2

- (iii) Calculation of magnetic moments and integrated currents. With the bond-order matrix produced in (i), and the first-order correction to it obtained in (ii), the moments, μ_{st} (equation (17)) and integrated currents, J_{st} (equation (18)) were calculated. All integrations were performed analytically and computations were carried out on the Oxford University ICL 1906A computer.

4. RESULTS AND DISCUSSION

4.1. *The model of π -electron 'ring susceptibilities'*

Since one of the main aims of the present work is to investigate the possibility of defining ring susceptibilities as an additive property within any given polycyclic conjugated hydrocarbon, the individual contributions to χ_{π}^{\perp} were separately evaluated for each ring in turn, for molecules (I)–(XII), as described in §§ 2 and 3, and the results are shown in table 1.

In columns (i)–(iv) of this table are entered the calculated π -electron contributions to the (perpendicular) magnetic dipole moment of each ring (proportional—via the factor $B/N\mu_0$ —to the 'ring susceptibility') as follows: (i) from the integrated currents around the ring (i.e. from J_{st} in equation (16), s, t bonded); (ii) from the 'bonded moments', μ_{sb} , of (16), (s, t bonded); (iii) from the 'one-centre' moments, μ_{ss} ; and (iv) from the 'non-bond' moments, μ_{st} (s, t non-bonded). All magnetic moments are in units of $10^{-9} B/N\mu_0 \text{ A m}^2$ (i.e. $1.321 \times 10^{-27} \text{ A m}^2 \text{ T}^{-1}$). Column (v) is the sum of columns (i)–(iv) and gives, therefore, the π -electron 'ring susceptibility' of each ring (in the direction perpendicular to the molecular plane) on the basis of the model discussed in § 2.3. The validity of this model, involving separation of χ_{π}^{\perp} into contributions from the individual rings, can now be tested by comparing the last two columns (Nos. (vi) and (vii)) of table 1, for column (vii) gives the result of an 'exact' calculation of the overall π -electron susceptibility of the molecule in question, in which the complete sum in equation (13) has been performed.

From the calculations on the 12 test molecules studied the following general conclusions are drawn concerning the 'ring susceptibility' model:

- (i) For molecules constructed entirely from six-membered rings ((I)–(VII)), the model is very good; the error introduced by the idea of 'ring susceptibilities' is in all cases less than 2 per cent and is usually well below this limit.
- (ii) For the one non-alternant hydrocarbon studied in which both constituent rings are unambiguously diamagnetic (azulene (IX)) the approximation still holds to high accuracy (better than 1 per cent).
- (iii) When some (or all) of the rings of a given molecule (whether alternant or non-alternant) display strong paramagnetic behaviour, however, the approximation is by no means as good. For example, in the case of the alternant hydrocarbon biphenylene (VIII) in which the four-membered ring is paramagnetic [43], the 'ring susceptibility' approximation introduces an error of 4.6 per cent; in the extreme case of pyracylene (XII)—which actually has an *overall* π -electron *para*-magnetism [44, 45], each one of its rings possibly being 'paratropic' [46]—the error is much larger (*ca.* 15 per cent).

Molecule	Ring	Integrated current moments				One-centre moments	Non-bond moments	Ring susceptibility	Sum over rings	'Exact' calculation
		(i)	(ii)	(iii)	(iv)					
Benzene (I)	A	-0.367	-0.109	-0.106	+0.005 ₂	-0.577	-0.577	-0.577	-0.577	
Naphthalene (II)	A	-0.394	-0.094	-0.089	+0.004 ₅	-0.572	-1.143	-1.140	-1.140	
Anthracene (III)	A	-0.387	-0.092	-0.089	+0.004 ₂	-0.563	-1.745	-1.732	-1.732	
	B	-0.471	-0.081	-0.071	+0.004 ₂	-0.619	-1.678	-1.663	-1.663	
Phenanthrene (IV)	A	-0.414	-0.095	-0.089	+0.004 ₇	-0.593	-1.678	-1.663	-1.663	
	B	-0.350	-0.075	-0.071	+0.003 ₄	-0.492	-2.247	-2.222	-2.222	
Pyrene (V)	A	-0.345	-0.069	-0.065	+0.003 ₂	-0.476	-2.314	-2.253	-2.253	
	B	-0.491	-0.085	-0.077	+0.004 ₄	-0.648	-1.122	-1.118	-1.118	
Perylene (VI)	A	-0.378	-0.084	-0.077	+0.004 ₃	-0.535	-0.477	-0.500	-0.500	
	B	-0.080	-0.049	-0.047	+0.001 ₈	-0.175	-1.186	-1.180	-1.180	
Diphenyl (VII)	A	-0.352	-0.108	-0.106	+0.005 ₁	-0.561	-1.625	-1.641	-1.641	
	B	-0.149	-0.099	-0.089	+0.004 ₉	-0.314	-1.084	-1.123	-1.123	
Biphenylene (VIII)	A	+0.249	-0.028	-0.035	0.000	+0.186	+0.691	+0.580	+0.580	
	B	-0.531	-0.100	-0.102	-0.000 ₉	-0.734	-1.186	-1.180	-1.180	
Azulene (IX)	A	-0.310	-0.074	-0.075	+0.007 ₈	-0.451	-1.625	-1.641	-1.641	
	B	-0.367	-0.085	-0.076	+0.004 ₁	-0.524	-1.084	-1.123	-1.123	
Fluoranthene (X)	A	+0.010	-0.041	-0.042	+0.003 ₉	-0.069	-0.061	-0.061	-0.061	
	C	-0.327	-0.097	-0.089	+0.004 ₈	-0.508	+0.407	+0.407	+0.407	
Accenaphthylene (XI)	A	-0.344	-0.084	-0.076	+0.003 ₈	-0.500	-1.084	-1.123	-1.123	
	B	+0.030	-0.059	-0.061	+0.006 ₀	-0.083	-0.691	-0.580	-0.580	
Pyracylene (XII)	A	+0.075	-0.075	-0.064	+0.003 ₃	-0.061	+0.407	+0.407	+0.407	
	B	+0.519	-0.057	-0.060	+0.005 ₀	-0.407	-0.580	-0.580	-0.580	

Table 1. Calculated π -electron susceptibilities (in units of 10^{-9} m³ mol⁻¹).

- (iv) As for what could be called the 'intermediate' cases of fluoranthene (X) and acenaphthylene (XI), in which the five-membered rings make only a small (diamagnetic) contribution to χ_{π}^{\perp} , the 'ring susceptibility' model again fares very well—its predictions differing from those of the 'exact' calculation by 1 per cent and 3 per cent, respectively.

Over the whole range of molecules considered, therefore, with the sole exception of the calculations on pyracylene (XII), the differences between the results of the 'exact' calculation and the predictions of the 'ring susceptibility' model are all well below a 'threshold' value of 5 per cent.

4.2. Comparison with other complete π -electron calculations

The present results for χ_{π}^{\perp} may be compared with the only other published calculations of this quantity, by Amos and Roberts [30 a] (for the special case of benzene) and by Caralp and Hoarau [22] (for several alternant hydrocarbons). Our results for benzene agree with those of Amos and Roberts [30 a] when our 'one-centre bond-moment' contributions (considered 'local' in the Amos-Roberts calculation) are subtracted from the benzene results presented in table 1. Caralp and Hoarau performed a special perturbation calculation, based also on a Goeppert-Mayer and Sklar formalism [36], with gauge-invariant field-modified atomic orbitals determined up to second order in the field. They obtained various contributions to χ_{π}^{\perp} which sum to totals differing by at most 1.5 per cent from the corresponding χ_{π}^{\perp} values (given in column (vii) of table 1) calculated by the present method, for the six molecules common to both studies. This good agreement between the two sets of calculations provides a reassuring check on Caralp and Hoarau's method, and on the present method, of calculating χ_{π}^{\perp} ; it also reflects well on Hall and Hardisson's coupled Hartree-Fock procedure for estimating the first-order bond-order matrices—in fact, the concordance between the two sets of calculations is probably a more reliable test of the validity of this latter procedure than comparison of predictions based on it with experimental data on total susceptibilities (see § 4.4).

In 'ring-current' calculations of π -electron susceptibilities one usually hopes that the contributions of the π -electron terms which have been neglected (which, like those from the σ terms, are considered, *a priori*, 'local' in nature) are rigorously proportional to the number of carbon atoms in a given molecule. From the results of the present calculation, this hypothesis may be tested by dividing the sum of the 'bond moments', and the 'one-centre' and 'non-bond moments' (columns (ii)–(iv), respectively, of table 1) by the number of carbon atoms in the corresponding molecule. Such an exercise does indeed verify that for all hydrocarbons which are made up of six-membered rings this ratio is practically constant (fluctuations well below 5 per cent). The apparent constancy of this ratio may thus be the reason for the good results often obtained by the policy of including the 'non-London' π -electron contributions with the 'local' terms; this procedure has been adopted in many previous calculations (e.g. [26]) which, by and large, have been concerned with condensed *benzenoid* hydrocarbons. The same cannot be said, however, for the other types of molecules considered here (e.g. (VIII) and (XII)) in which the corresponding ratios appear to fluctuate from molecule to molecule by up to 30 per cent. The

present method of calculation would therefore appear to be particularly appropriate when wider ranges of conjugated hydrocarbons, rather than simply condensed benzenoid molecules, are to be considered.

4.3. The integrated π -electron current densities ; comparison with 'ring currents'

Although, as we have emphasized in §§ 4.1 and 4.2, the contribution of the 'integrated π -electron current densities' (equation (18)) associated with the various bonds of the polycyclic network represents only a part of χ_{π}^{\perp} , the integrated π -electron current density associated with any unshared bond in a

Molecule	Ring	'Integrated π -electron current' †	'Ring current' §	Reference to 'ring current' calculation
Benzene (I)	A	1	1	
Naphthalene (II)	A	1.07 ₄	1.09 ₃	[20, 48]
Anthracene (III)	A	1.05 ₅	1.08 ₅	[48]
	B	1.28 ₅	1.28 ₀	
Phenanthrene (IV)	A	1.12 ₈	1.13 ₃	[48]
	B	0.95 ₂	0.97 ₅	
Pyrene (V)	A	0.94 ₀	0.96 ₄	[49]
	B	1.33 ₇	1.32 ₇	
Perylene (VI)	A	1.03 ₀	0.97 ₀	[49, 50]
	B	0.21 ₉	0.23 ₉	
Diphenyl (VII)	A	0.96 ₀	0.93 ₅	This work
Biphenylene (VIII)	A	0.40 ₅	0.25 ₀	This work
	B	-1.76 ₁	-1.80 ₇	
Azulene (IX)	A	1.03 ₅	1.06 ₉	[19]
	B	1.27 ₇	1.15 ₀	
Fluoranthene (X)	A	1.00 ₁	0.98 ₇	[52]
	B	-0.04 ₃	0.05 ₀	
	C	0.89 ₀	0.86 ₀	
Acenaphthylene (XI)	A	0.93 ₈	0.92 ₈	This work
	B	-0.14 ₅	0.10 ₇	
Pyracylene (XII)	A	-0.20 ₃	-0.38 ₆	[45]
	B	-2.15 ₆	-2.31 ₇	

† In a ring containing a bond between centres s and t which is *unshared* with any other ring, the 'integrated π -electron current' for that ring is the quantity J_{st} , the expression for which is given in equation (18); if the bond $s-t$ is shared between two rings, then J_{st} is the *algebraic sum* of the 'integrated π -electron currents' which characterize the two rings sharing the bond $s-t$ (as described in § 2.3).

‡ Values given as ratios to the 'integrated π -electron current' calculated, by the same method (equation (18)), for benzene (this value being $e^2 B/2m \times 0.946 \times 10^{-20}$ A m⁻²). A positive entry therefore indicates diamagnetic character, a negative one, paramagnetic character.

§ Values given as ratios to the π -electron 'ring current' calculated by the same method (Hückel-London-Pople-McWeeny [18-20, 31]), for benzene. Again, a positive entry indicates diamagnetic character, a negative one, paramagnetic character.

|| Via the programmes described in [51].

Table 2. Comparison between the 'integrated π -electron current' † around each ring, calculated as described in §§ 2.2 and 2.3, and the corresponding 'ring current' calculated by the London-Pople-McWeeny method [18-20, 31] based on a simple ('topological' [47, 45]) HMO.

particular ring is a quantity which is analogous to what the London–Pople–McWeeny method [18–20, 31] would identify with the ‘ π -electron ring current’ intensity in that ring (see § 2.2); and, in the case of a bond which is *shared* between two rings, the ‘integrated current density’ associated with that bond is comparable with the *algebraic sum* of the ‘ring current’ intensities which characterize the two rings flanking the given bond. It is, therefore, of some interest to compare computed values of the integrated π -electron current densities characteristic of the various non-equivalent rings in the 12 molecules studied, with the corresponding (and long-familiar) ‘ring currents’. Such a comparison is made in table 2, where the ‘integrated π -electron current densities’ and the ‘ring currents’ are expressed as ratios to the respective values for benzene. A regular, idealized geometry was again assumed in all cases and the calculations were based on a simple (‘topological’ [47, 45]) HMO wave function. Under these conditions, no subjective parameters whatever are involved in the ‘ring current’ *ratios* (expressed relative to the benzene value) given in table 2 [45, 47]; all are immediately and automatically determined (via, for example, equation (25) of [31]) once the molecular topology and the ring areas have been specified [47].

It can be seen from the table that the two quantities compare well (to within 0.06 of these units) for molecules (I)–(VIII), all of which are constructed from hexagonal rings. For the strongly diamagnetic non-alternant hydrocarbon azulene (IX), however, the correspondence is less evident. As was the situation with the ‘ring susceptibility’ idea discussed in § 4.1, the most marked disaccord between the two quantities arises in the case of those hydrocarbons which have some (or all) of their constituent rings ‘paratropic’ [46] in character—pyracylene (XII), biphenylene (VIII), even acenaphthylene (XI) and, to a certain degree, fluoranthene (X).

4.4. Comparison with experiment : the effect of the σ -electrons

In order to compare the present theoretical predictions with experimental data, it is necessary to estimate the susceptibilities contributed by the σ -electrons in these molecules for, on the assumption of an exact σ - π separation, only the π -electron contribution to the total susceptibility has been calculated by the formalism so far outlined. There are, however, well-established empirical methods for predicting the susceptibility due to a framework of σ -bonded atoms, in terms of a scheme of additive Pascal constants [4, 5]. For example, Hoarau [5], from extensive experimental data on a large number of hydrocarbons, estimated atomic contributions of $-25 \times 10^{-12} \text{ m}^3 \text{ mol}^{-1}$ (-2.0×10^{-6} in c.g.s. e.m.u.) for a hydrogen atom, and $-93 \times 10^{-12} \text{ m}^3 \text{ mol}^{-1}$ (-7.4×10^{-6} c.g.s. e.m.u.) for a carbon atom†. Hoarau’s value for the hydrogen Pascal constant can quite properly be adopted here since any hydrogen contributions to the molecular susceptibility have been completely unaccounted for in the previous π -electron calculation (§ 4.1). The situation with respect to carbon, however, is different; *all* contributions from the $2p_z$ orbitals have been fully considered in the previous calculation of χ_π^\perp , given the assumption of a complete σ - π separation.

† Note that in the SI system χ_{molar} is taken to be rationalized, and in the c.g.s. e.m.u. system to be unrationalized. Thus

$$\chi_{\text{molar}}^{\text{(rational)}}/\text{m}^3 \text{ mol}^{-1} = 4\pi \times 10^{-6} \chi_{\text{molar}}^{\text{(irrational)}}/\text{cm}^3 \text{ mol}^{-1}.$$

Since there do not appear to be any Pascal-type constants available for a carbon atom depleted of its $2p_z$ electron, the estimation of such a quantity was attempted here solely from the experimental data on benzene [53], which appear more reliable than those on most other molecules. A suitable Pascal constant for carbon, exclusive of the contribution from its $2p_z$ orbital, and in the direction perpendicular to the plane of the ring, ($\chi_{\sigma}^{\perp}(\text{C})$), was taken as $-77 \times 10^{-12} \text{ m}^3 \text{ mol}^{-1}$. The carbon atom contribution to the 'in-plane' susceptibility ($\chi^{\parallel}(\text{C})$) was also estimated, yielding the value $-48 \times 10^{-12} \text{ m}^3 \text{ mol}^{-1}\dagger$.

In table 3 the following quantities are listed for each of the 12 molecules studied: (i) $\chi_{\pi \text{ calc}}^{\perp}$, the total χ_{π}^{\perp} calculated as described in §§ 2.3 and 4.1, from a summation over rings (and transcribed from column (vi) of table 1); (ii) $\chi_{\sigma \text{ calc}}^{\perp}$, the σ -electron contribution to the magnetic susceptibility perpendicular to the molecular plane, estimated from Pascal constants as described above; (iii) $\chi_{\text{calc}}^{\perp} = \chi_{\pi \text{ calc}}^{\perp} + \chi_{\sigma \text{ calc}}^{\perp}$; (iv) $\chi_{\text{calc}}^{\parallel}$, the 'in-plane' contribution to the magnetic susceptibility, calculated from Pascal constants; (v) $\bar{\chi}_{\text{calc}} = (\chi_{\text{calc}}^{\perp} + 2\chi_{\text{calc}}^{\parallel})/3$, the trace of the calculated susceptibility tensor; (vi) $\Delta\chi_{\text{calc}} = \chi_{\text{calc}}^{\perp} - \chi_{\text{calc}}^{\parallel}$, the calculated anisotropy of magnetic susceptibility. These are then compared in the next four columns of table 3 with corresponding quantities derived from the experimental data available [5, 11, 53-68], the appropriate references to which are given in the extreme right-hand column of the table. Some attempt was made to evaluate the large amount of experimental work to be found in the literature in order to select that which seems to be the most reliable; that considered the best (usually the most recent) is listed first.

The agreement between calculated and experimental susceptibilities is seen to be very satisfactory, again apparently justifying, *a posteriori*, the approximations inherent in a π -electron calculation, and in Hall and Hardisson's method [21] for obtaining the perturbed bond-order matrix. The present results, overall, also compare with experiment as well as, or better than, those of some other recent investigations [26, 42]. The relatively large error (5-11 per cent) which persists in the final χ^{\perp} values of Caralp and Hoarau [22] in spite of the rigor of their calculated χ_{π}^{\perp} terms (see § 4.2), may be attributed to their use of the theoretical estimates of Pascal constants due to Guy and Tillieu [69, 70] in computing the σ -electron contributions. (The Guy and Tillieu constants were not used in our work since they are known [69, 70] to be of low accuracy.)

In the present calculations all bond lengths were assumed to be uniform. Such an approximation is not an intrinsic feature of the method of calculation outlined in § 2, and it is possible that using real geometries might improve the agreement with experiment, although, in the case of the diamagnetic condensed benzenoid molecules, probably only marginally so (see [71]). Use of a 'variable bond-length' SCF LCAO- π -MO method [72] certainly seems to be necessary for a realistic treatment of strongly paramagnetic π -systems such as (VIII) and (XII) (see [72, 73, 45]). These various refinements were not, however, incorporated into the present calculations since our primary aim here has been

† It should be noted that the Pascal constants used by Amos and Roberts [26] were obtained by fitting $\chi^{\perp}(\text{C})$ and $\chi^{\perp}(\text{H})$ (as well as $\chi^{\parallel}(\text{C})$ and $\chi^{\parallel}(\text{H})$) to a set of experimental susceptibilities. In their investigation, $\chi^{\perp}(\text{C})$ includes a contribution not *just* from the σ -electrons (as does our $\chi_{\sigma}^{\perp}(\text{C})$) but also one from *some* π -electron effects (considered 'local' in that calculation). This is why it would not have been legitimate for us simply to have taken over the Pascal constants used by Amos and Roberts [26] for the purpose of comparing our (complete) π -electron calculations with experiment.

	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	(ix)	(x)	Reference to experimental work
	$\chi_{\sigma}^{\perp \text{ calc}}$	$\chi_{\sigma}^{\perp \text{ calc}}$	$\chi^{\perp \text{ calc}}$	$\chi^{\parallel \text{ calc}}$	$\bar{\chi}^{\text{ calc}}$	$\Delta\chi^{\text{ calc}}$	$\chi^{\perp \text{ exp}}$	$\chi^{\parallel \text{ exp}}\dagger\dagger$	$\bar{\chi}^{\text{ exp}}$	$\Delta\chi^{\text{ exp}}$	
Benzene (I) ¶	-0.577	-0.612	-1.189	-0.438	-0.688	-0.751	-1.188	-0.439	-0.689	-0.750	[53] [54]
Naphthalene (II)	-1.143	-0.970	-2.11	-0.68	-1.16	-1.43	-2.11	-0.67	-1.15	-1.43	[55]
							-2.18	-0.67	-1.18	-1.51	[56]
							-2.12	-0.69	-1.16	-1.43	[57] [58]
Anthracene (III)	-1.745	-1.328	-3.07	-0.92	-1.64	-2.15	-3.09	-0.91	-1.63	-2.17	[59]
							± 0.03	± 0.02	± 0.04	± 0.04	
							-3.15	-0.95	-1.69	-2.19	[60]
							-3.13	-0.97	-1.69	-2.16	[57]
							-3.16	-0.87	-1.63	-2.29	[61] [58]
Phenanthrene (IV)	-1.678	-1.328	-3.01	-0.92	-1.62	-2.08	(-3.02)	(-0.93)	-1.61	(-2.09)	[54] [11]‡
Pyrene (V)	-2.247	-1.482	-3.73	-1.02	-1.92	-2.71	-3.83	-0.90	-1.88	-2.93	[55] [57]
Perylene (VI)	-2.314	-1.840	-4.15	-1.26	-2.22	-2.89	(-3.94)	(-1.01)	-1.95	(-2.93)	[11]‡
									-2.10	[62]	§
									-2.21		

M.P.	Diphenyl (VII)	-1.122	-1.174	-2.30	-0.83	-1.32	-1.47	-2.31 -2.25 (-2.29)	-0.81 -0.87 (-0.80)	-1.31 -1.33 -1.29	-1.50 -1.37 (-1.49)	[64] [65] [11]†
	Biphenylene (VIII)	0.477	-1.124	-1.60	-0.78	-1.05	-0.82			-1.11 ± 0.04		[66]
	Azulene (IX)	-1.186	-0.967	-2.15	-0.68	-1.17	-1.47			-1.14 -1.24		[67] [5]
Fluoranthene (X)	-1.625	-1.482	-3.11	-1.02	-1.71	-2.09				-1.73	(-2.22)	[5]
Acenaphthylene (XI)	-1.084	-1.124	-2.21	-0.78	-1.25	-1.43						[5]
Pyracylene (XII)	+0.580†	-1.278	-0.63	-0.70	-0.65	-0.07						

† Value taken from the exact calculation; for this molecule additivity of the ring susceptibilities is by no means rigorously displayed (see text).

‡ Data given in parentheses are only approximate estimates, as explained in [11].

§ Revised calculation based on the experimental work of [63], in which we have selected naphthalene as the standard and have assigned its mean susceptibility the more recent value of $-1.15 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ [55].

|| Data given in parentheses are only approximate estimates, from [68].

¶ The experimental values, $\chi^{\perp}_{\text{exp}}$ and $\chi^{\parallel}_{\text{exp}}$, for benzene were used for calibration (see text, § 4.4).

†† For almost all these molecules, the two principal in-plane values of the susceptibility tensor are distinct; in the case of particularly 'long' molecules, the two terms can differ markedly; however, in all cases, an average value for χ^{exp} is given in the present table.

Table 3. Comparison of calculated susceptibilities with experiment (units of $10^{-9} \text{ m}^3 \text{ mol}^{-1}$).

to test quantitatively the legitimacy of general physical concepts, such as the 'ring susceptibility' model proposed in §2.3, rather than to provide very accurate estimates of experimentally measurable magnetic quantities. Even so, the results in table 3 (admittedly, for the most part, on predominantly diamagnetic molecules) are very satisfactory.

5. CONCLUSIONS

- (1) In the context of an SCF π -electron theory, an exact expression has been devised which yields the total χ_π^\perp of a conjugated polycyclic hydrocarbon (§§2.2 and 2.3). Once given the first-order correction to the bond-order matrix of the molecule in question, this expression (equations (13)–(18)) does not rely on the London integral approximation.
- (2) It has been pointed out that certain terms which occur in the expression for χ_π^\perp (namely those due to J_{st} of equation (18)) correspond to those which would have arisen if the London approximation had been invoked; the remaining terms (due to the μ_{st} defined in (17)) are, in general, non-zero (§2.2). The relative integrated current densities associated with the various constituent rings are in a very close numerical correspondence with the previously calculated 'ring currents' estimated via the London–Pople–McWeeny method (§4.3).
- (3) Even when the whole of χ_π^\perp is calculated, and not just that part of it which is due to what most previous treatments have regarded as 'ring currents', it is indeed still possible (§§2.3 and 4.1) to break down the total π -electron contribution to χ^\perp into terms associated with the individual constituent rings of the molecule concerned and hence to preserve the intuitively appealing idea of a 'ring susceptibility'. However, whereas additivity of 'ring current' contributions within a given molecule gave only *part* of χ_π^\perp , the 'ring susceptibility' contributions sum to the *total* χ_π^\perp for that molecule.
- (4) Previous calculations have often sought to incorporate those π -electron contributions to χ_π^\perp which are lost by application of the London approximation with the empirically determined 'local' σ -contributions. This procedure has been shown (§4.2) to have some justification when applied to condensed benzenoid hydrocarbons, but it is less valid for other types of conjugated systems.
- (5) Finally, when an appropriate set of Pascal-type constants is derived from a calibration involving the calculated χ_π^\perp and the various susceptibility components measured experimentally for *just one* reference molecule (benzene), very satisfactory agreement with experiment is obtained for a wide range of conjugated hydrocarbon systems (§4.4). The comparisons detailed in table 3 are as good as, and in the case of some molecules better than, those arising from previous calculations.

Since the calculated χ_π^\perp entries in table 3 were obtained by a summation over rings, as described in §§2.3 and 4.1, this again emphasizes the quantitative nature of the concept of π -electron 'ring susceptibilities' as an additive property within individual conjugated polycyclic hydrocarbons which are predominantly diamagnetic.

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