



A FREE-ELECTRON MODEL FOR THE DELOCALIZATION ENERGIES OF ANNULENES

A one-dimensional free-electron theory with a harmonic potential is set up to calculate delocalization energies of cyclic polyenes. The only parameters in this theory are the harmonic-potential amplitude, V_0 , and the chain length, L . Delocalization energies of cyclic polyenes are calculated as the differences between their ground state energies and those of the analogous linear polyenes. Results are presented for the series of cyclic polyenes up to [40] annulene. These results are compared with those obtained by other authors with more elaborated methods. The use of these calculations to interpret the aromaticity of annulenes is discussed. It is concluded that the general trends of the aromatic and anti-aromatic properties of the annulenes may be explained to a considerable extent by means of the very simple model proposed.

1 — INTRODUCTION

A very considerable amount of work has been dedicated to the understanding of the concept of aromaticity, its experimental introduction and its theoretical background. The origin of the term is uncertain but by 1925 ROBINSON [1] had recognized clearly the need for the concept of aromaticity in order to explain the electronic properties of certain compounds. ROBINSON [1] considered that the enhanced stability shown by these compounds was due to the association of the six valence electrons in benzene and its derivatives, the "aromatic sextet". This idea of an aromatic sextet was later included in the famous Hückel $(4n + 2)$ rule [2] which states that those monocyclic, planar systems of trigonally hybridized atoms which contain $(4n+2)$ π -electrons will possess relative electronic stability. One of the recurring difficulties around the concept of aromaticity is the identification of precisely what experimental facts one is trying to explain. The chemical stability is, in itself, too vague a concept for any theory to be checked against it. DEWAR [3, 5] and BRESLOW [6, 7] interpreted this stability in terms of the heats of formation. A cyclic compound is then considered aromatic if the electronic delocalization brings about a negative contribution to the heats of formation. This will be discussed at greater length below.

The aromatic character of some cyclic conjugated hydrocarbons and especially the contrasting properties of $[4n]$ and $[4n + 2]$ annulenes produces some very striking effects in their magnetic properties [8, 9]. The magnetic susceptibility or the NMR chemical shift is best understood in terms of the ring current induced in the molecule by an external magnetic field [10-13].

When a molecule is placed in a magnetic field this perturbs the electron system in such a way as to create a flow of electronic currents which for cyclic conjugated hydrocarbons may usefully and simply be described by the ring current [12]. The current has two terms: the diamagnetic current corresponds to the classical Larmor precession of the whole π -electron cloud; the paramagnetic current depends on the contributions from the excited states of the molecule [14]. For $[4n + 2]$ annulenes there are no low-lying excited-states and hence the paramagnetic part of the ring current is small. This results in the molecule being strongly diamagnetic, which shows up as an exaltation of the diamagnetic susceptibility of the molecule as a whole and of the NMR chemical shifts of its constituent parts.

The link between this behaviour of the magnetic properties and the chemical stability discussed before is probably to be found in the fact that both correlate with the HOMO-LUMO separation (i.e. the energy difference between the Highest-Occupied Molecular-Orbital and the Lowest-Unoccupied Molecular-Orbital). In fact the HOMO-LUMO separation may be related to the reactivity of the molecule [15].

2 – DELOCALIZATION ENERGY

The idea that, in an aromatic hydrocarbon, the π -electrons cannot in any reasonable way be associated with individual bonds reflects itself in valence bond theory in the fact that several Kekulé structures may be written for each molecule. The energy gained from writing the wave function as a linear combination of the functions associated with each individual structure as compared with the energy of one of these structures is called resonance energy. This name comes from the fact that the simplified form of valence bond theory normally used in these calculations (involving *only* these 'singly-excited' Kekulé structures) is known as resonance theory. In molecular orbital theory this same fact is reflected in a set of molecular orbitals which in themselves, or after a transformation, cannot be clearly associated with individual bonds. Comparison of the energy of this system with that of a similar system but with localized bonds will lead to a delocalization energy. The immediate difficulty here is defining such a reference system for comparison which is close enough to the original system for the energy difference to be associated with the delocalization effect alone.

Direct comparison between a cyclic polyene and its linear-polyene analogue is not straightforward since bond lengths change. For this reason DEWAR and co-workers [3-5] calculate their resonance energies from expressions in which a number of parameters representing energies associated with certain features of the molecule were adjusted to fit experimental results. In this way they compensated for the energy of compression and extension of single and double bonds relative to the bond lengths observed in cyclic polyenes.

FIGEYS [16, 17] has used the LCAO-BETA [18] method to calculate π -electron energies and σ -compression energies and from these has estimated the delocalization energies of annulenes by a method which has some resemblance to that of Dewar.

In the next section we show how a simple free-electron model may be applied in order to understand the delocalization energies of annulenes. We use simple free-electron models to calculate the energies of cyclic and linear polyenes and estimate delocalization energies as the difference between the two.

3 – FREE-ELECTRON MODEL FOR DELOCALIZATION ENERGIES

Simple one-dimensional, quasi-free-electron models for linear and cyclic polyenes are compared to estimate the gain in energy which results from cyclization. This gain in energy is identified with the delocalization energy of the cyclic polyene.

The alternating single and double bonds are simulated by a harmonic potential with negative lobes in the regions of double bonds. For linear polyenes, an extra bond length is added at each end. For cyclic polyenes (the annulenes), a periodic boundary condition is applied. The one-dimensional Schrödinger equation to be solved reads.

$$-\frac{\hbar^2}{2m_0} \frac{d^2 \psi}{ds^2} + (V_0 \cos \frac{2\pi}{L} m s - E) \psi = 0$$

where s is a length coordinate varying in $[0, L]$, m is the number of double bonds and V_0 is the amplitude of the harmonic potential. The wavefunction ψ_k (state k) is written as a linear combination of trigonometric functions,

$$\psi_k = \sum_{\nu=1} C_{\nu}^{(k)} \cos \nu \phi + \sum_{\nu'=1} S_{\nu'}^{(k)} \sin \nu' \phi$$

with

$$\psi \equiv \frac{s}{L} \pi, \quad \phi \in [0, \pi]$$

For annulenes, the coefficients $C_{\nu}^{(k)}$ are determined from the system of linear equations

$$\begin{cases} (q \mu^2 - E_k) C_{\mu}^{(k)} + V_0 \frac{1}{2} (C_{m-\mu}^{(k)} + C_{m+\mu}^{(k)}) = \nu & \mu < m \\ (q \mu^2 - E_k) C_{m}^{(k)} + V_0 \frac{1}{2} (2C_{2m}^{(k)} + C_{2m}^{(k)}) = \nu & \mu = m \\ (q \mu^2 - E_k) C_{\mu}^{(k)} + V_0 \frac{1}{2} (C_{\mu-m}^{(k)} + C_{m+\mu}^{(k)}) = \nu & \mu > m \end{cases}$$

with $q = \frac{\hbar^2}{2m_0} \left(\frac{2\pi}{L}\right)^2$ and E_k is the energy of the k -level. Similarly the coefficients $S_{\nu}^{(k)}$ are determined from

the system of linear equations

$$\begin{cases} (q \mu^2 - E_k) S_\mu^{(k)} + V_0 \frac{1}{2} (S_{m+\mu}^{(k)} - S_{m-\mu}^{(k)}) = 0 & \mu < m \\ (q m^2 - E_k) S_m^{(k)} + V_0 \frac{1}{2} S_{2m}^{(k)} = 0 & \mu = m \\ (q \mu^2 - E_k) S_\mu^{(k)} + V_0 \frac{1}{2} (S_{\mu-m}^{(k)} + S_{\mu+m}^{(k)}) = 0 & \mu > m \end{cases}$$

We get two families of solutions, cos- and sin-type functions, which alternate in the spectrum of energies.

For linear polyenes an infinite-potential boundary condition is applied. When the origin of the coordinates is taken at one end of the potential well, only sin-type functions are allowed. The coefficients $S_\nu^{(k)}$ and the energies E_k are obtained from the system of linear equations

$$(q \mu^2 - E_k) S_\mu^{(k)} - \sum_\nu \frac{8 \mu \nu (2m+1) V_0/\pi}{1 - \mu^2 - (2m+1)^2 - \nu^2 - 4\nu^2 (2m+1)^2} S_\nu^{(k)} = 0, \quad \mu = 1, 2, \dots$$

where the summation \sum' extends over all ν of the same parity as μ , m is the number of double bonds and q' is a parameter, $q' = (\hbar^2 \pi^2 / 2m_0 L^2)$.

The standard bond-length for a cyclic polyene was taken, $\ell = 140$ pm. Hence, the parameter L for cyclic polyenes is given the value $m \times 2\ell$. From previous experience [19, 20] it was expected that a reasonable value for the harmonic potential V_0 was 2.40 eV. The choice of the bond lengths for the linear polyenes is arbitrary to a point. Typical values may be obtained from the bond lengths in butadiene [21], $\ell_2 = 133.7$ and $\ell_1 = 148.3$ pm, but these values change slightly from molecule to molecule.

For propylene it is [22] $\ell_1 = 150.1$ pm and $\ell_2 = 133.6$ pm. In free-electron models for linear polyenes it is common practice to extend the potential well at each end of the hydrocarbon chain. To appreciate the effects of varying the extensions of the hydrocarbon chains and of varying the harmonic potential V_0 , some trial calculations of the first (vertical) excitation energies of a number of linear polyenes were run. The results are shown in Table I, along with the respective experimental values.

As a result of comparing the calculated values listed in the last six columns of Table I with their respective experimental values, it was decided to adopt $V_0 = 2.40$ eV with a chain-length increase of one bond length at each end. To achieve the finer tuning of the calculated values, an average bond-length of $2\ell = 283$ pm was assumed, which is well within the expected distension of the bonds in linear polyenes when compared with the assumed $2\ell = 280$ pm for the

cyclic polyene.

The free-electron theory outlined above, with the choice of parameters described, is now applied to linear and cyclic polyenes with a number, m , of double bonds running from 2 to 20.

4 - RESULTS AND DISCUSSION

We define the delocalization energy of a cyclic polyene as the difference between its ground-state energy and that of the associated linear polyene. These energies are calculated by use of free-electron models as described in section 3, with such simple models we avoid introducing fitting parameters which make the theoretical interpretation of the results less certain. The choice of magnitudes for the few parameters required in our model was described above. The value adopted for the harmonic potential is not crucial as the same value is used for both the linear and cyclic models.

Probably more important for the fine analysis of the results is the choice of the amount of bond compression. From known experimental geometries it was expected that this compression (of single bond-length plus double bond length) would be of the order of 2 to 4 pm.

The final choice of 3 pm was made for best fit to the experimental excitation-energies of a large number of linear polyenes, as discussed above (see Table I).

Table II lists the results of such energy calculations for polyene systems containing up to 40 π -electrons.

For the annulenes lower in the series it is clear that they are predicted to satisfy the $[4n+2]$ -Hückel rule. On the other hand $[4n]$ annulenes are predicted to have a negative delocalization energy ("anti-aromaticity"), i.e., the annulene is predicted to have an electronic energy higher than its linear polyene analogue. For the annulenes higher in the series definite conclusions are more difficult to draw. Molecules in the $[4n+2]$ -category still have delocalization energies above those in the $[4n]$ -family, but the differences become small. For practical purposes the only result which might be tentatively derived from these results is that the contrast in the behaviour of $[4n+2]$ and $[4n]$ annulenes becomes less marked as one goes up in the series.

This should be related with the bond alternation observed for the $[4n]$ annulenes due to Jahn-Teller or, more correctly, RENNER [24]-type distortion and also for the higher $[4n+2]$ annulenes [25, 27].

Recently, the bond alternation observed for higher

Table I
First excitation energies of linear polyenes (nm)

Number of double bonds m	Experimental (†)	Adopted Parameters (#)	Calculated					
			Half bond length at each end (2ℓ = 280 pm)			One bond length at each end (2ℓ = 280 pm)		
			V ₀ =1.20 eV	V ₀ =2.40 eV	V ₀ =3.60 eV	V ₀ =1.20 eV	V ₀ =2.40 eV	V ₀ =3.60 eV
2	217-235	228.2	187	169	152	292.6	265.5	241.5
3	260-282	282.0	283	264	206	393.9	334.4	302.7
4	295-308	323.1	368	296	243	487.0	410.8	349.8
5	326-348	355.0	442	339	268	572.6	466.5	386.1
6	352-371	380.0	508	372	286	651.2	513.3	414.2
7	374-403	400.0	565	397	298	723.2	552.6	436.1
8	396-422	414.4	615	417	307	789.3	585.7	453.2
9	413-447	430.3	658	433	314	849.8	614.0	467.7
10	432-461	437.3	697	445	319	902.7	632.4	472.0
11	449-473	448.7	730	455	323	956.2	657.2	486.3
12	461-482	456.3	759	464	326	1002.8	674.3	493.5

(†) see ref. [23]

(‡) V₀ = 2.40 eV; bond length, 2ℓ = 283.3 pm

Table II
Free-electron-model energies for linear and cyclic systems (eV)

m	Total energy		Delocalization energy	Delocalization energy per electron
	cyclic	linear		
2	6.8204	5.6380	- 1.1824	- 0.2956
3	7.1796	8.1718	+ 0.9922	+ 0.1654
4	10.8280	10.6990	- 0.1290	- 0.0161
5	12.8022	13.2252	+ 0.4230	+ 0.0423
6	15.7620	15.7522	- 0.0098	- 0.0008
7	18.1434	18.2822	+ 0.1388	+ 0.0099
8	20.8820	20.8208	- 0.0612	- 0.0038
9	23.4002	23.3918	- 0.0084	- 0.0005
10	26.0576	25.9404	- 0.1172	- 0.0059
11	28.6270	28.5224	- 0.1046	- 0.0047
12	31.2528	31.1166	- 0.1362	- 0.0057
13	33.8422	33.7172	- 0.1250	- 0.0048
14	36.4552	36.3224	- 0.1328	- 0.0048
15	39.0542	38.9306	- 0.1236	- 0.0041
16	41.6616	41.5412	- 0.1204	- 0.0038
17	44.2620	44.1538	- 0.1082	- 0.0032
18	46.8674	46.7670	- 0.1004	- 0.0028
19	49.4702	49.3802	- 0.0900	- 0.0023
20	52.0746	51.9894	- 0.0852	- 0.0021

[4n+ 2]-annulenes has been related to the instability [28] of the Hartree-Fock solutions for the π-electron model. FENTON [29] suggests that bond alternation is due to an Overhauser charge density wave.

HARRIS and FALIKOV [30], however, contend that, when the physical values are taken for the input parameters, charge density wave ground states do not exist and that spin density wave functions do not exhibit bond alternation. Bond alternation, but a very weak one, is found only for the normal ground states wave functions whose energies are higher than the spin density wave ones. More recently, the work of TOYOTA et al. [31] appears to indicate that the presence of a charge density wave will necessarily lead to bond alternation, i.e., the lattice of conjugated hydrocarbons is sufficiently soft to feel that effect.

Notice that in the current model a decrease in the delocalization energies of the higher annulenes is obtained *without* forcing the bond alternation by, for example, appropriate adjustment of the one-electron potential. These general trends of the calculated delocalization energies are more easily seen in fig. 1 where the [4n+ 2]- and [4n]- series are drawn separately. For comparison, results reported by DEWAR and GLEICHER [4] and by FIGEYS [17] are also plotted. The more important disagreement between these different calculations

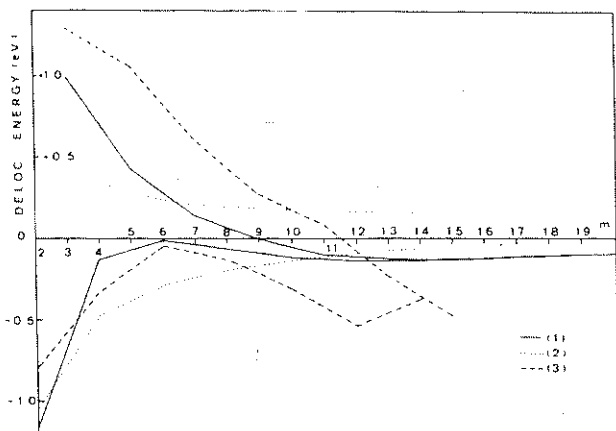


Fig. 1

Delocalization energies of $[4n+2]$ - and $[4n]$ -annulenes as a function of the number of double bonds; m .
(1) This work; (2) FIGEYS [13]; (3) SPO method, DEWAR and GLEICHER [4]

concerns the behaviour of $[4n+2]$ annulenes higher in the series. FIGEYS [17] method predicts a steady delocalization energy while DEWAR and GLEICHER [4] and the work reported here do not allow such a conclusion to be drawn. It is very difficult to find hard experimental evidence to decide on the validity of these results for our calculations refer to model systems with idealized geometries and experimentalists have to deal with real molecules. These may be non-planar or conclusions may have to be drawn from some of their derivatives when the annulene itself is too hard to synthesize and isolate.

For benzene SALEM [32] gives a resonance energy of 1.56 eV while DEWAR and DE LLANO [33] give a value of 0.869 eV, both results being derived from thermochemical data. This compares with the value of 0.992 eV calculated by the method reported here. It should be noted that, if the calculation of DEWAR and GLEICHER [4] referred to above and plotted for comparison in fig.1 were repeated using DEWAR and DE LLANO'S [33] more recent estimate for the resonance energy of benzene, a correction of $m \times (-0.150)$ eV would be introduced into those results, thereby changing completely the appearance of this figure. This is a good example of the effects which may be obtained by fitting parameters, especially when they are adjusted to quantities which are not immediately attainable experimentally as is the case with resonance energies. Thermochemical data on [18] annulene [34] suggest an important delocalization

energy which was estimated by DEWAR and DE LLANO [33] to be 0.12 eV. Our model predicts a delocalization energy close to zero for this molecule while the estimates of FIGEYS [16] and DEWAR and GLEICHER [4] vary from 0.185 eV to 0.382 eV.

5 - CONCLUSIONS

On the strength of the calculations reported, it is concluded that the aromatic or anti-aromatic properties of cyclic polyenes may be interpreted in a semi-quantitative way via a simple model of quasi-free-electrons. The model adopted involves no parameters which have been adjusted to fit any of the delocalization energies being calculated.

Excitation energies of linear annulenes are used to select the bond distention of linear vs. cyclic polyenes. A standard bond length of 140 pm is used for the cyclic polyenes while 141.5 pm is assumed for the linear ones. A conventional value of 2.40 eV for the harmonic potential V_0 is used throughout. The delocalization energies calculated by this method compare very favourably with those obtained by DEWAR and GLEICHER [4] by use of a number of parameters which were fitted to experimental heats of formation.

Discrepancies that remain are difficult to evaluate for lack of the reliable experimental data.

ACKNOWLEDGMENTS

The author wishes to thank Dr. R. B. Mallion for helpful discussions and comments on the contents of an earlier draft of the present manuscript.

Financial support from INIC (Lisboa) is gratefully acknowledged.

(Received 16. Oct. 1978)

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RESUMO

Propõe-se uma teoria unidimensional de electrões livres sob um potencial harmónico para o cálculo de energias de deslocalização de políenos cíclicos. Os únicos parâmetros desta teoria são o potencial harmónico V_0 e o comprimento de cadeia, L . As energias de deslocalização dos políenos cíclicos são calculadas pela diferença entre as energias dos seus estados fundamentais e as dos correspondentes políenos lineares. Apresentam-se os resultados dos cálculos para a série de anulenos até ao [40] anuleno e comparam-se com resultados obtidos por outros autores, com métodos mais elaborados. Discute-se a aplicação destes cálculos na interpretação da aromaticidade dos anulenos. Conclui-se que as tendências gerais da aromaticidade e anti-aromaticidade dos anulenos podem ser razoavelmente bem explicadas por um modelo tão simples como o que aqui é proposto.