

Anisotropy of Diamagnetic Susceptibility of Alternant Hydrocarbons

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The anisotropy of diamagnetic susceptibility of several hydrocarbons has been calculated with the use of the SC LCAO MO method with the London theory. The results for 10 hydrocarbons are compared with experiment and other known theoretical approaches. It is found that the SC LCAO MO method leads to a best agreement with experiment.

Die Anisotropie der diamagnetischen Suszeptibilität mehrerer Kohlenwasserstoffe wurde im Rahmen der Londonschen Theorie nach der SC LCAO MO-Methode berechnet. Für 10 Aromaten werden die Ergebnisse mit dem Experiment und anderweitig berechneten Werten verglichen. Die SC LCAO MO-Resultate zeigen die beste Übereinstimmung mit dem Experiment.

L'anisotropie de la susceptibilité diamagnétique de plusieurs hydrocarbures a été calculée par la méthode SC LCAO dans le cadre de la théorie de London. Pour 10 hydrocarbures on compare les résultats à l'expérience et aux résultats d'autres théories. La méthode SC LCAO MO rend le meilleur accord avec l'expérience.

Introduction

A characteristic property of aromatic hydrocarbons is their large anisotropy of diamagnetic susceptibility. For a planar aromatic molecule this anisotropy is usually defined as follows:

$$\Delta K = K_3 - \frac{1}{2}(K_1 + K_2), \quad (1)$$

where K_1 , K_2 and K_3 are the principal molar susceptibilities, K_1 and K_2 in the plane of the molecule and K_3 perpendicularly to it. A quantum-mechanical theory of the anisotropy of diamagnetic susceptibility of aromatic hydrocarbons was developed first by London [33]. His theory was based on the simple LCAO MO method in the Hückel approximation. According to London the anisotropy has its origin in π -electronic ring currents induced by the external magnetic field. This π -electronic contribution follows from formula (2),

$$\Delta\chi_\pi = - \sum_k^{\text{occ}} n_k \left(\frac{\partial^2 E_k}{\partial H_0^2} \right)_{H_0 \rightarrow 0}, \quad (2)$$

where n_k is the occupation number of the k -th m.o. in the ground state and E_k is the energy eigenvalue of this orbital. Within the standard Hückel approximation $\Delta\chi_\pi$ depends linearly on the value of resonance integral β_0 , an empirical parameter of the theory. Therefore, comparing the theory with experiment one usually considers a relative susceptibility,

$$\rho_{\text{molecule}} = \frac{\Delta\chi_\pi \text{ molecule}}{\Delta\chi_\pi \text{ benzene}}. \quad (3)$$

London's theory is not necessarily related to the Hückel approximation. It can be naturally extended to the SC LCAO MO basis [16, 19]. We recall that the SC LCAO MO method, to be referred to, is based on an exponential form of the resonance integral of nearest neighbours:

$$\beta_{kl} = \beta_0 \exp[-4.2(R_{kl} - 1.397)], \quad (4)$$

where R_{kl} is the appropriate bond length, and on a linear bond length – bond order relation,

$$R_{kl} = 1.517 - 0.180 p_{kl}. \quad (5)$$

This form of the SC method was also successful in discussing many other properties like reactivities, bond lengths, ionization potentials, electronic spectra, etc. [16, 17, 18, 42, 43].

In a previous paper [19] q_{molecule} of naphthalene, anthracene, naphthacene, chrysene and perylene were computed. The present work is an extension of these calculations to phenanthrene, pyrene, triphenylene, coronene and biphenyl, for which molecules new experimental data are now known. The calculations have been performed on the computer UMC-1 basing on a new mathematical technique elaborated earlier [19]. All the results are listed in Column 7 of Table 2.

The purpose of this work was not only to increase the material necessary for a statistical discussion. The aim was also to compare the many different estimations of the anisotropy, known in the literature.

Discussion

To find the principal diamagnetic susceptibility of a molecule it is necessary to determine the principal diamagnetic susceptibility of a unit cell of the crystal and to know the distribution of molecules in the unit cell. Therefore, determination of the anisotropy of diamagnetic susceptibility requires accurate measurements of the principal diamagnetic susceptibilities for the crystal and an accurate three-dimensional X-ray analysis. For this reason reasonably accurate data for the diamagnetic susceptibility have been obtained only recently [11, 23, 40, 45].

The relative experimental values of the anisotropy of diamagnetic susceptibility are given in Column 2 of Table 1. For the further discussion, however, the values given in Column 4 (q_{exp}) have been accepted. There, of two or more measurements of a similar accuracy were known, the mean values were adopted. If, however, more accurate new results could be found, they have served for comparison. It should be noted that the accuracy of experimental data for naphthacene is the smallest one [3]. It follows from the recalculations carried out by the present author that the same can well be said about the accuracy of the data for triphenylene and coronene; the consistency between the structural data obtained by the magnetic measurements and the X-ray analysis is not satisfactory. Besides, these molecules are not strictly planar, the factor not taken into account in the present calculations.

The diamagnetic anisotropy can also be derived from the Cotton-Mouton effect [9, 10, 12, 13]. Recently, Le Fèvre and Murthy [32] applied this method to naphthalene, phenanthrene and pyrene. Their results are given in Column 3 of Table 1. These values are not basically different from those obtained from the crystal measurements, except for pyrene. However, in this case a mean diamagnetic susceptibility of a small accuracy was used by the authors.

Table 1. Experimental values of relative anisotropies of diamagnetic susceptibility

Molecule	Monocrystals	Cotton-Mouton effect	ϱ_{exp}	$\chi_m \cdot 10^6$ cgs emu	$K_3 \cdot 10^6$ cgs emu
1	2	3	4	5	6
Benzene	1 ^a [24]	1 ^b [5]	1	55.2 [4, 24]	94.6 [24]
Naphthalene	2.09 [36] 1.91 [25] 1.91 [34, 35]	2.05 [32]	2.00	92.2 [3]	169.0 [25]
Anthracene	3.02 [36] 3.06 [25, 34, 35] 2.93 [31]		2.93	130.3 [3]	250.7 [31]
Naphthacene	2.58 [8]		2.58	170.7 [3, 25]	270.7 [3, 8]
Phenanthrene	2.78 [25, 28, 34, 35]	2.83 [32]	2.78	127.9 [2, 4]	240.0 [28]
Chrysene	3.77 [25, 34, 35]		3.77	168.5 [3]	310.8 [25, 34, 35]
Pyrene	4.07 [25] 3.90 [34, 35]	3.44 [32]	4.07	148.6 [3]	315.5 [14]
Perylene	4.02 [8]		4.02	171.4 [25]	320.0 [8]
Triphenylene	3.07 [26] 3.13 [4, 27] 2.98 [1, 4]		2.98 ^c	156.6 [4]	275.1 [4]
Coronene	6.53 [41]		6.53	243.3 [3]	476.0 ^d
Biphenyl	2.02 [36] 1.99 [25, 30, 34, 35] 2.00 [29]		1.99	104.4 [30]	183.8 [30]

^a $\Delta K = -59.7 \cdot 10^{-6}$ cgs emu.

^b $\Delta K = -58.4 \cdot 10^{-6}$ cgs emu.

^c Calculated from the experimental data of diamagnetic susceptibility of a monocrystal [7], the X-ray data [1] and the mean diamagnetic susceptibility [4]; for this purpose the formulae given in Ref. [34] were used.

^d Calculated from the experimental data of diamagnetic susceptibility of a monocrystal [41], the mean diamagnetic susceptibility [3] and the X-ray data [15]; the formulae given in Ref. [34] were used with this purpose.

Table 2. Comparison of calculated and observed values of $\varrho = \frac{\Delta\chi_{\text{molecule}}}{\Delta\chi_{\text{benzene}}}$

Molecule	ϱ_{exp}	ϱ_J	ϱ_B	ϱ_{Ho}	ϱ_H	ϱ_{SC}	ϱ_G	ϱ_M	E_{H}^{D}	E_{SC}^{D}
1	2	3	4	5	6	7	8	9	10	11
Benzene	1	1	1	1	1	1	1	1	2.000	0.867
Naphthalene	2.00	1.94	2.07	1.94	2.19	2.00	1.96	1.98	3.683	1.676
Anthracene	2.93	2.94	3.33	2.94	3.45	2.89	3.00	2.96	5.314	2.350
Naphthacene	2.58	4.02	2.97	4.10	4.75	3.80	4.00	3.95	6.932	3.051
Phenanthrene	2.78	2.87	3.05	2.79	3.25	2.93	2.84	2.96	5.448	2.391
Chrysene	3.77	4.06	4.02	3.96	4.44	3.78	4.27	3.95	7.190	2.337
Pyrene	4.07	3.65	4.58	4.17	4.58	3.91	3.61	3.51	6.506	2.852
Perylene	4.02	3.57	3.87	3.55	4.12	3.98	3.97	4.60	8.245	3.723
Triphenylene	2.98	3.39	3.09	3.19	4.08	3.73	3.83	3.95	7.275	3.211
Coronene	6.53	7.20	7.18	6.99	9.79	8.12	5.62	5.89	10.572	4.790
Biphenyl	1.99	1.93	1.96	1.87	1.87	1.90	2.27	2.00	4.383	1.913

In the first two rows of Table 3 the mean deviation from experimental relative anisotropies is given, referring to results of the LCAO MO method in the Hückel approximation ϱ_H , and to results of the SC LCAO MO method, ϱ_{SC} . It follows that the application of the SC LCAO MO method reduces the mean deviation approximately twice in comparison to the Hückel method if all the 10 molecules are considered, and as much as six times, if the three less certain data for naphthacene, triphenylene and coronene are excluded. In the last case the deviation is the same as the experimental error (2%).

Table 3. Mean deviation of relative anisotropies^a (in %)

Type of experimental data	London's theory		Guha's method	Musher's method
	Hückel approximation	SCLCAO MO approximation		
1	2	3	4	5
ϱ_{exp} (10 molecules)	25	11	14	14
ϱ_{exp}^b (7 molecules)	12	2	7	6
ϱ_J	17	6	8	7
ϱ_B	16	10	15	12
ϱ_{H_0}	17	7	14	8

^a Calculated according to formula:

$$\Delta = 100 \frac{1}{n} \sum_{k=1}^n \frac{|(\varrho_{\text{calc}})_k - (\varrho_{\text{exp}})_k|}{(\varrho_{\text{exp}})_k}$$

^b Without the less certain values for naphthacene, triphenylene and coronene (see text).

Guha [20–22] paid recently attention to the fact that the sums of all bond-bond auto-polarizabilities calculated by the Hückel method correlate well with experimental anisotropies. The ratios of these sums relative to that for benzene, ϱ_G , are given in Column 8 of Table 2. It can be seen from the first two rows of Column 4 of Table 3 that the mean deviation following from this method is larger than following from the SC LCAO MO method.

In a recently presented article Musher [37] claimed that with a proper set of increments it is possible to reproduce the anisotropy in definitely a better agreement with experiment than by any theoretical approach based on the concept of ring currents. With this purpose he introduced four increments for the carbon atoms. Let \perp denote the direction perpendicular to the molecular plane and \parallel the direction parallel to it. If the carbon atom belongs to a single aromatic ring let us provide the increment with an upper index 1, otherwise with the index 2. Then, according to Musher,

$$\begin{aligned} \chi_{\parallel}^1 &= -3.0 \cdot 10^{-6} \text{ cgs emu}, \\ \chi_{\perp}^1 &= -12.5 \cdot 10^{-6} \text{ cgs emu}, \\ \chi_{\parallel}^2 &= -3.0 \cdot 10^{-6} \text{ cgs emu}, \\ \chi_{\perp}^2 &= -21.5 \cdot 10^{-6} \text{ cgs emu}. \end{aligned}$$

The values of relative anisotropies of diamagnetic susceptibility ϱ_M , calculated from these increments, are given in Column 9 of Table 2. The mean deviation from the experimental values is given in Column 5 of Table 3. The deviation is of the

same range as in the use of the auto-polarizability method and larger than in the case of the SC LCAO MO method. These results seem not to confirm Musher's viewpoint that the concept of ring currents is less effective than the concept of increments.

Because of many experimental difficulties in estimation of the accurate values of anisotropy (1) from direct crystal measurements, other definitions of anisotropy have been introduced by some authors.

For example according to Shiba, Hazato [44], Akamatu, Matsunaga and Kinoshita [2-4]:

$$\Delta K_{\pi} = 3(\chi_m - \Sigma \chi_{(C=)} - \Sigma \chi_{(H)}). \quad (6)$$

In this formula χ_m is the experimental value of the mean diamagnetic susceptibility, $\chi_{(C=)}$ is an increment for a carbon atom in the sp^2 state (equal to $-3.36 \cdot 10^{-6}$ cgs emu), $\chi_{(H)}$ is an increment for a hydrogen atom (equal to $-2.93 \cdot 10^{-6}$ cgs emu). The relative anisotropies (ρ_j) calculated according to this definition of ΔK_{π} and using the mean diamagnetic susceptibilities χ_m listed in Table 1 are given in Column 3 of Table 2.

A slightly different definition was proposed by Bailey [6]:

$$\Delta K_{\pi} = K_3 - \Sigma \chi_C - \Sigma \chi_H, \quad (7)$$

where K_3 is the experimental molar susceptibility perpendicularly to the molecular plane, χ_C is an increment for a carbon atom (equal now to $-7.4 \cdot 10^{-6}$ cgs emu), χ_H is an increment for a hydrogen atom (equal to $-2.0 \cdot 10^{-6}$ cgs emu). The relative anisotropies (ρ_B) calculated according to this definition of ΔK_{π} and using the experimental K_3 values from Table 1 are given in Column 4 of Table 2.

Still another definition of the diamagnetic anisotropy was introduced by Horou [25, 39]:

$$\Delta K_{\pi}^* = \chi_m - (\Sigma \chi_C + \Sigma \chi_H + \Sigma \chi_{(C=C)}). \quad (8)$$

Here χ_m is the mean diamagnetic susceptibility, $\chi_C = -7.36 \cdot 10^{-6}$ cgs emu is the increment for a carbon atom, $\chi_H = -2.00 \cdot 10^{-6}$ cgs emu is the increment for a hydrogen atom, $\chi_{(C=C)} = 5.50 \cdot 10^{-6}$ cgs emu is the structural increment for a double bond between carbon atoms. In Column 5 of Table 2 the values of appropriate relative anisotropies ρ_{H_0} are given.

It follows that for all the cases the SC LCAO MO method yields a best agreement with experiment.

In a search for improving the correlation between the experimental and calculated relative anisotropies of diamagnetic susceptibility Hoarau [25] and Pacault, Hoarau and Marchand [39] proposed an artificial relation which includes a dependency on the delocalisation energy E_H^D ,

$$\Delta K_{\pi}^* = \frac{1}{3} \Delta K_L + A E_H^D, \quad (9)$$

where ΔK_L is the diamagnetic susceptibility according to the London theory [33]. The parameter A was fitted to ensure a best agreement with experiment and the value 0.776 for the case of the Hückel basis was found. Recently, Nakajima and Kohda [38] proposed a different value for A , $A = 0.940$. However, in both papers (based on ρ_{H_0} -type experimental data) rather inaccurate values of the mean diamagnetic susceptibility were taken into account. Moreover, not all the molecules had been considered which are discussed in the present article. Reconsidering

their procedure with the use of the more recent values of the mean diamagnetic susceptibilities χ_m given in Table 1 and the Hückel delocalisation energies E_H^D given in Table 2 one obtains a different least square fit:

$$\varrho_H^t = 0.489 \varrho_H + 0.256 E_H^D. \quad (10)$$

ϱ_H is the value of the relative anisotropy of diamagnetic susceptibility according to the Hückel basis, given in Table 2.

It seems interesting to make a similar comparison for the SC basis. A least square procedure yields the equality:

$$\varrho_{SC}^t = 0.934 \varrho_{SC} + 0.075 E_{SC}^D, \quad (11)$$

where ϱ_{SC} is a relative anisotropy of diamagnetic susceptibility as calculated by the SC LCAO MO method. Comparing formulae (10) and (11) one notices that the delocalisation energy term is now much less important and almost negligible. This is particularly true if one notices that E_{SC}^D is in β_0 units about 2.5 times smaller than the appropriate value of E_H^D . The E_H^D term contributes to ϱ_H^t in about 53%, while the contribution of E_{SC}^D is as small as 3%. It can be concluded that in the SC LCAO MO method the delocalisation energy effect is internally contained.

Conclusion

This was a comparative study of four theoretical approaches to the anisotropy of diamagnetic susceptibility of aromatic hydrocarbons:

- i) the London theory based on the Hückel method,
- ii) the London theory based on the SC LCAO MO method,
- iii) Guha's auto-polarizability method,
- iv) Musher's increments method.

As a test of utility served four sets of experimental data, depending on the definition of anisotropy according to Londsdale, Eq. (1), Shiba, Hazato, Akamatu, Matsunaga and Kinoshita, Eq. (6), Bailey, Eq. (7) and according to Horoau, Eq. (8).

It follows from the study that the London theory based on the SC LCAO MO is in best agreement with experiment whatever experimental set of data is compared with.

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