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Heteroaromaticity. 12. A Group Additivity Method For The Derivation Of Diamagnetic Susceptibility Enhancements Of Aromatic Hydrocarbons And Azines†.

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Abstract: A group additivity approach has been devised for the prediction of the diamagnetic susceptibility enhancements of polycylic aromatic hydrocarbons and their aza derivatives. It is shown that this approach provides a useful tool for probing the thesis that some polycyclic systems prefer to exist as aromatic sub-units.

INTRODUCTION

The exaltation of diamagnetic susceptibility has long been recognised as a criterion of aromatic character[1,2] and the quantitative relationship between this and other criteria of aromaticity is an area of curent debate.[3-5] While there can be no doubt about the role of diamagnetic susceptibility enhancement as an extensive property, that is in general it increases with increasing molecular size,[6] inclusion of this criterion amongst a range of others subjected to principal component analysis according to ring size led to the conclusion[3] that aromaticity is a multi-dimensional phenomenon and in particular that the classical and magnetic concepts of aromaticity are almost completely orthogonal. This appears to run contrary to theoretical analyses[7,8] which indicate that there is a direct mathematical interdependency between resonance energies and diamagnetic exaltations. A principal problem in resolving this dispute is the very limited experimental measurements of diamagnetic susceptibilities for heterocycles, and at least one semiempirical method of estimating diamagnetic susceptibilities of aromatic molecules has been introduced.[9] Consequently, recourse has been made[10] to fully theoretically calculated values and excellent linear correlations have been reported between diamagnetic susceptibility exaltations and aromatic stabilisation energies for a series of five-membered C_4H_4X ring systems.

In view of the successful manner in which group additivity parameters can be applied to the prediction of another extensive property, namely the enthalpies of formation of polycyclic hydrocarbons[11] and heteroaromatic compounds,[12] it was decided to investigate whether a comparable approach could be applied to the estimation of diamagnetic susceptibility enhancements. Also it seemed likely that such an approach would provide a better basis for detecting and interpreting apparent anomalies between diamagnetic susceptibility exaltations and molecular structure than the variations in the average effective radius of the π-electron orbitals, $\sqrt{r^2}$, employed in earlier discussions.[13]

RESULTS AND DISCUSSION

Most of the diamagnetic susceptibility enhancements used in this study have been listed previously[6] and were

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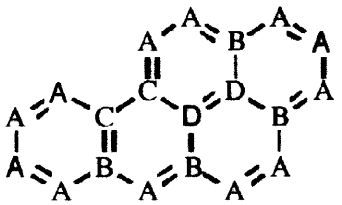

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Table 1. Diamagnetic Susceptibility Increments

Group*	Label	Λ -10^{-6}cm^3 mol^{-1}
C_B-(H)	A	2.42
C_{BF}-$(C_B)_2(C_{BF})$	B	4.02
C_{BF}-$(C_B)(C_{BF})_2$	C	3.88
C_{BF}-$(C_{BF})_2$	D	8.56
C_B-$(C_B)_2$(Ph)	E	0.45
C_{BF}-*$(C_B)(C_{BF})_2$	G	2.71
C_{BF}-$(C_B)(C_{BF})$(N)	Y	4.63
N_A-$(C_B)_2$	N_P	1.4
N_A-$(C_B)(N_A)$	N_{AZ}	2.21

* Group and label designations follow Benson, S.W., *Thermochemical Kinetics*, 2nd edition, Wiley, New York, 1976, and references 10 and 11.

obtained by subtracting diamagnetic susceptibilities calculated using the Haberditzl "Semi-Empirical Increment System" [2] from experimentally observed values.[2,12,13] The Haberditzl method assigns a susceptibility increment to each type of bond and electron grouping and these increments are then summed. It is important to note that other methods may give similar but not necessarily identical values. Analysis of the data in the light of earlier experience[10,11] led to the identification of the groups required and appropriate numerical values. For convenience both the formal and informal terminology used previously has been adopted here. The groups utilised are indicated on formulae **1** to **3**, and are listed along with recommended values in Table 1. The range and accuracy of the data available did not justify the use of such a wide variety of values as employed for the predicton of enthalpies of formation. The consequences of applying these values to the prediction of the diamagnetic susceptibilities of a range of polycyclic hydrocarbons and azines are shown in Table 2 where they are listed alongside the experimentally determined values. There is generally excellent concurrence between the two sets of data, particularly in view of the oft quoted accuracy of ±1 or 2 units. Of particular interest is its success in predicting exaltations for non-benzenoid hydrocarbons such as azulene and azupyrene, entries 9 and 17.

The postulate by Clar[14,15] that condensed aromatic hydrocarbons often prefer to behave as a combination of aromatic subunits has subsequently received both theoretical[16,17] and some experimental[18] support. The present study provides additional evidence for this diagnosis. Obviously, in the case of perylene **4** and *meso*-naphthodianthrene **5**, entries 29 and 30 in Table 3, the molecules behave essentially as two separate naphthalene/anthracene moieties as it is impossible to formulate a single Kekulé structure in which the a-bonds are double rather than single. Furthermore, X-ray crystallography establishes[19] the a-bond lengths in perylene as 1.476 Å. Consquently, it is not surprising that the diamagnetic susceptibility enhancements observed for **4**and **5** are in excellent accord with the values calculated assuming negligible conjugative interaction between the two naphthalene/anthracene moieties. In the case of dibenzocoronene **6**, entry 31, the X-ray crystal structure[20] shows that the lengths of the central bonds a and b are 1.47 and 1.49 Å respectively, in keeping with inspection

Table 2. Experimental and Calculated Diamagnetic Susceptibility Enhancements.

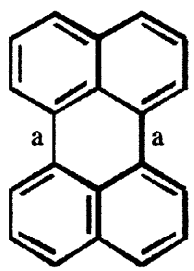
Λ -10^{-6}cm^3 mol^{-1}

Entry	Compound	Exptl.[2,12,13]	Calc.	Group Parameters	Error
1	Benzene	14.5	14.5	(6A)	0
2	Pyridine	13.5	13.5	(5A+N_p)	0
3	Pyridazine	14.1	14.1	(4A+2N_{AZ})	0
4	Pyrimidine	12.7	12.5	(4A+2N_p)	+ 0.2
5	1,3,5-Triazine	12.85	11.5	(3A+3N_p)	-1.35
6	Naphthalene	27.4	27.4	(8A+2B)	0
7	Quinoline	26.9	27.0	(7A+B+Y+N_p)	+0.1
8	Isoquinoline	24.8	26.3	(7A+2B+N_p)	+1.5
9	Azulene	26.5	27.4	(8A+2B)	+ 0.9
10	Biphenyl	25.1	25.1	(10A+2E)	0
11	Acenaphthylene	37.4	39.5	(8A+3C+D)	+ 2.1
12	Anthracene	42.4	40.3	(10A+4B)	-2.1
13	Acridine	40.75	40.5	(9A+2B+2Y+N_p)	-0.25
14	Phenanthrene	40.0	40.0	(10A+2B+2C)	0
15	Fluoranthrene	40.4	38.6	(10A+B+D+4E)	-1.8
16	Pyrene	57.4	57.4	(10A+4B+2D)	0
17	Azupyrene	53.4±4	57.4	(10A+4B+2D)	+3.0
18	Acepleiadylene	57.4±5	57.4	(10A+4B+2D)	0
19	p-Terphenyl	36.7	35.7	(14A+4E)	- 1.0
20	4,4'-Diphenylbiphenyl	48.6	46.3	(18A+6E)	-2.3
21	Tetracene	56.7	53.2	(12A+6B)	-3.5
22	Acenaphthanthracene	63	65.4	(12A+5B+2C+D)	+2.4
23	Chrysene	55.7	52.6	(12A+2B+4C)	-3.1
24	Benzo[a]pyrene	73	69.7	(12A+2B+4C+2D)	- 3.3
25	Pentacene	70.7	66.0	(14A+8B)	-4.7
26	Coronene	102.9	104.5	(12A+6B+6D)	+1.6
27	Violanthrene	118	124.9	(18A+4B+8C+4D)	+6.9
28	Isoviolanthrene	121.4	124.9	(18A+4B+8C+4D)	+3.5

of the various possible Kekulé structures which reveals that one of these bonds is always single. Allowance for this in estimating the diamagnetic exaltation leads to a predicted value in reasonable agreement with the observed one.

Triphenylene **7**, entry 32, and hexabenzocoronene **8**, entry 33, have long been suspected as behaving as essentially three and seven separate benzene rings respectively as conveniently indicated by the Clar sextet formulations A suspicion supported by the inter-ring a-bond lengths reported for triphenylene[21] of 1.478Å. However, this bond is double in one of the ten contributing Kekulé structures and so it is convenient to introduce an additional group increment "G" for this situation. Application of this increment in calculating the predicted exaltation of hexabenzocoronene gives a value in excellent accord with the experimental one. For dibenz[a,h]anthracene **9**, anthanthrene **10** and dibenzopyrene **11**, entries 34,35 and 36, molecular orbital

calculations[22] indicate that the bonds labelled a are essentially pure double bonds and make little or no contribution to the global resonance energy, just like the central double bond in stilbene which makes no contribution to the diamagnetic exaltation of stilbene. In the case of **10** this conclusion receives additional



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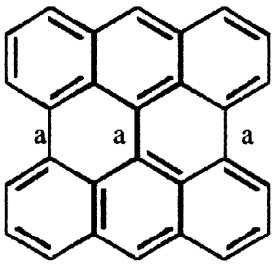

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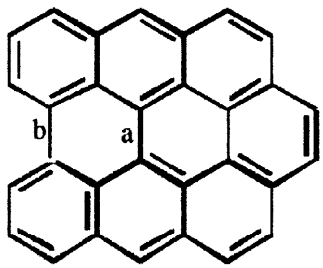

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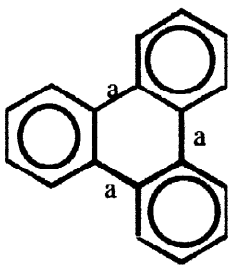

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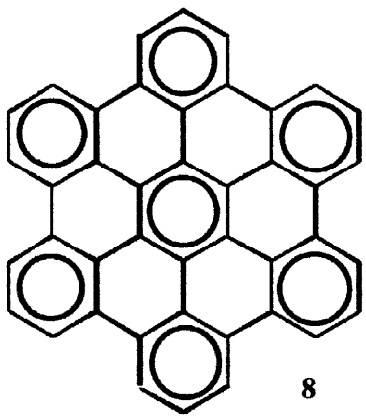

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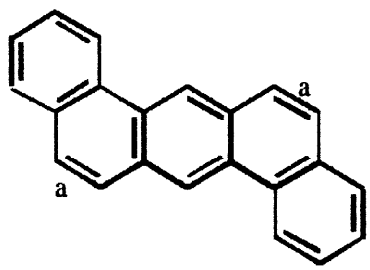

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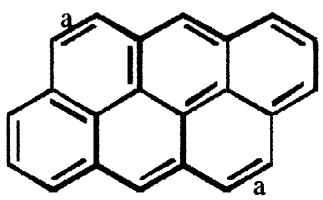

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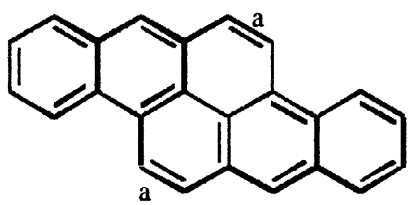

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support from the X-ray structure[23] of its 6,12-dimethyl derivative. Omission of contributions for these carbons as indicated for the second calculated values for compounds **9**,**10** and **11**, in Table 3 results in calculated diamagnetic exaltations very close to the observed values. The temptation to introduce another group value for the carbons adjacent to those omitted has been resisted. It is possible that the divergencies from calculated values for violanthrone and isoviolanthrone, entries 27 and 28 in Table 2, may be due to similar effects but no supporting evidence is available.

So far attempts to extend this group additivity approach to five-membered heterocycles has been unsuccessful. Inspection of the available diamagnetic exaltations listed in Table 4 fails to reveal any consistent patterns, for example replacement of a ring CH by nitrogen in going from furan to oxazole or from pyrrole to imidazole results in changes of +1.5 and +2.1 respectively, whereas the conversion of thiophene to thiazole results in a change of -1.4 in keeping with the behaviour observed in the six-membered ring series. However, the anticipated diminution is observed in the "nonlocal" contribution to the out-of-plane magnetic susceptibilities of all five-[24] and six-membered[25] ring nitrogen heterocycles but, while the "local" contributions to benzene and the six-membered azines stay virtually constant, the "local" values for pyrazole and imidazole increase and effectively offset the anticipated decrease in the magnetic susceptibility exaltation. Despite this inspection of the data in Tables 2 and 4 shows that fusion of a benzenoid ring to an existing system as in the formal conversion of furan to benzofuran or pyridine to quinoline results in an increase of diamagnetic susceptibility exaltation of 13±1 units. The only

Table 3. Some Special Cases of Diamagnetic Susceptibility Enhancement
Λ -10^{-6}cm^3 mol^{-1}

Entry	Compound	Exptl.[2,12,13]	Calc.	Group Parameters	Error
29.	Perylene **4**	45.8	69.7	(12A+2B+4C+2D)	+23.9
			46.9	(12A+4B+4E)	-0.1
30.	*meso*-Naphthodianthrene **5**	67.6	116.8	(14A+4B+4C+6D)	+49.2
			68.7	(14A+8B+6E)	+1.1
31.	Dibenzocoronene **6**	115.9	134.2	(14A+6B+2C+8D)	+18.3
			111.2	(14A+6B+6D+4E)	-4.7
32.	Triphenylene **7**	45.3	52.3	(12A+6C)	+7.0
			45.3	(12A+6G)	0.0
33.	Hexabenzocoronene **8**	106.3	192.8	(18A+12C+12D)	+86.5
			108.6	(18A+24G)	+2.3
34.	Dibenz[a,h]anthracene **9**	58.3	65.5	(14A+4B+4C)	+7.2
			60.6	(12A+4B+4C)	+2.3
35.	Anthanthrene **10**	73.5	87.5	(12A+6B+4D)	+14.0
			77.8	(8A+6B+4D)	+4.3
36.	Dibenzopyrene **11**	69.2	82.6	(14A+4B+4C+2D)	+13.4
			72.9	(10A+4B+4C+2D)	+3.7

exceptions are provided by benzimidazole and indazole. Here the diamagnetic susceptibilities were almost cetainly measured in the solid state where the very strong intermolecular hydrogen bonding[26,27] will greatly modify the electron distribution. Consequently, diamagnetic susceptibility exaltations of 26, 21.2 and 26 x -10^{-6}cm^3 mol^{-1} would be anticipated for benzothiophene, benzisoxazole and benzoxadiazole.

Table 4. Diamagnetic Susceptibility Exaltations of Heterocycles

Compound	Λ -10^{-6}cm^3 mol^{-1}	Compound	Λ -10^{-6}cm^3 mol^{-1}	Increment
Furan	8.9	Benzofuran	22.2	13.3
Thiophene	13.0	Benzothiophene	n/a	-
Pyrrole	10.2	Indole	24.2	14.0
Oxazole	10.4	Benzoxazole	22.2	11.8
Thiazole	11.6	Benzothiazole	26.1	14.5
Imidazole	12.3	Benzimidazole	16.6	4.3
Pyrazole	11.4	Indazole	18.1	6.7
Isoxazole	8.2	Benzisoxazole	n/a	-
1,2,5-Oxadiazole	11.0	Benzoxadiazole	n/a	-

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