

THE AROMATICITY OF HETEROCYCLES FROM MAGNETIC SUSCEPTIBILITY ANISOTROPY

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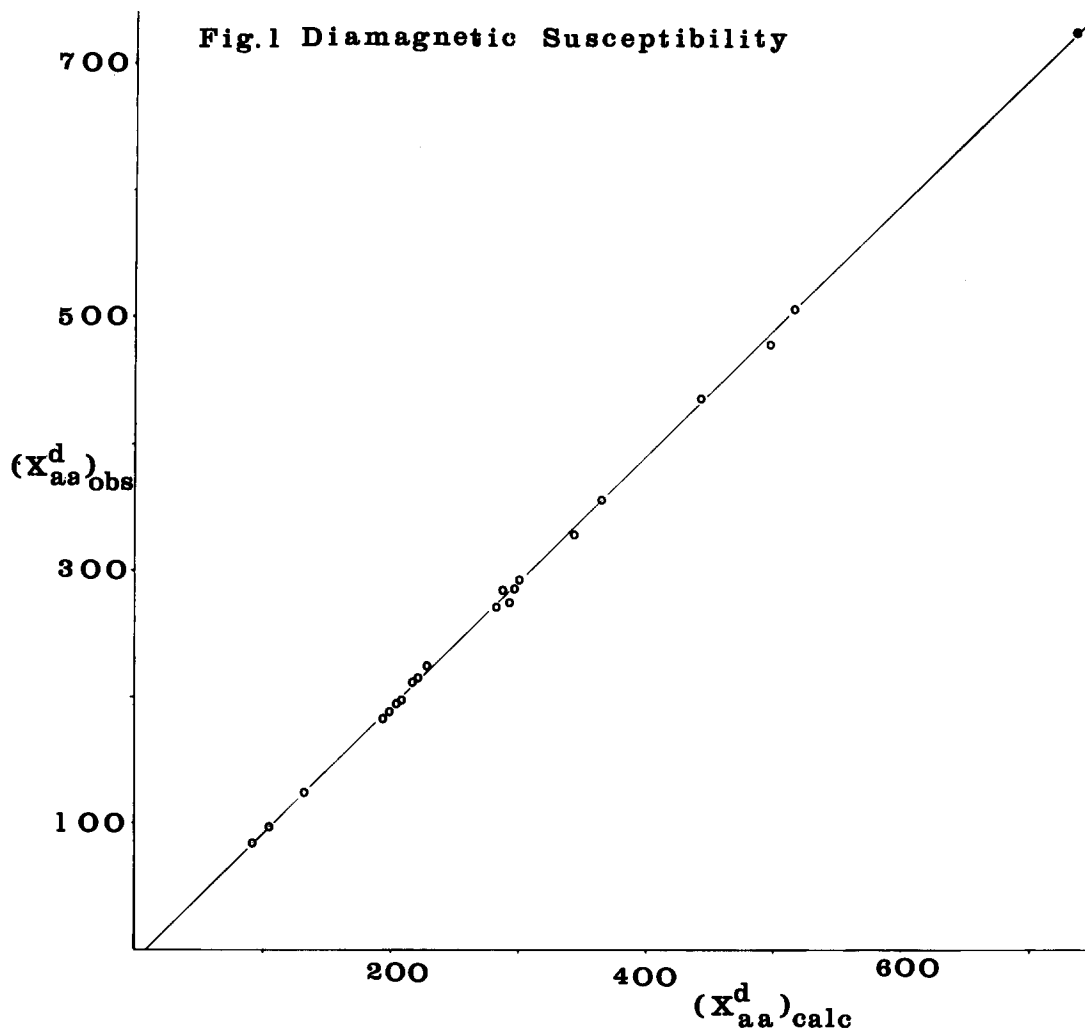
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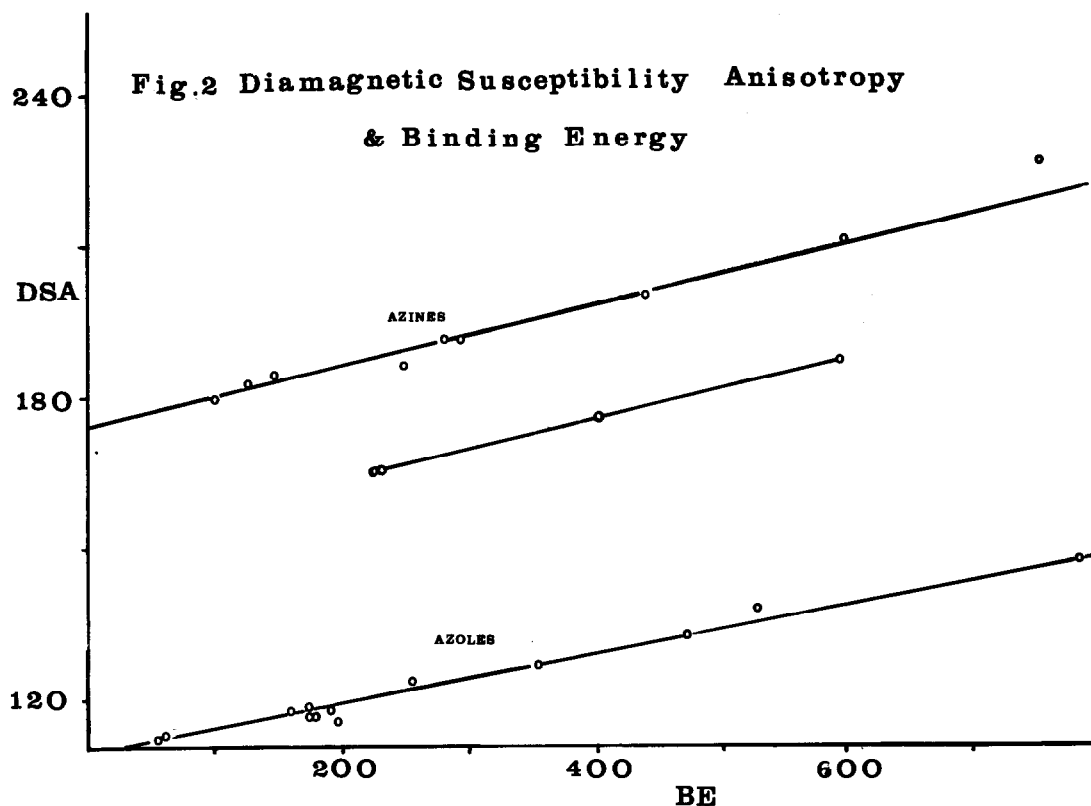
Recently magnetic susceptibility anisotropy (MSA), measured from the Zeeman splitting of microwave absorption spectra, was proposed<sup>1</sup> as a criterion of aromaticity. Owing to difficulties of interpretation almost all measurements of MSA to date have been on molecules of  $C_{2v}$  or higher symmetry.<sup>2-6</sup> MSA is defined for planar systems in terms of the in-plane and out-of-plane total susceptibilities as  $MSA = \chi_{oop}^T - (\chi_{ip}^T)_{av}$ , while the total susceptibility ( $\chi^T$ ) is a sum of diamagnetic ( $\chi^d$ ) terms involving the electronic ground state, and paramagnetic terms ( $\chi^P$ ) which include the nuclear geometry and electronic excited state wave-functions. We have previously reported<sup>7</sup> non-empirical wave-functions for a number of conjugated heterocycles, all calculated with the same basis set for comparison purposes. There are fundamental difficulties in calculating the total magnetic susceptibility as outlined below, but it is possible to evaluate the diamagnetic susceptibility term ( $\chi_{aa}^d$ ) (DSA) along axis aa from these functions, and since the wavefunctions can be readily evaluated for molecules of any symmetry calculated values of ( $\chi_{aa}^d$ ) may precede experimental data.

A correlation of the experimental with our calculated data of  $\chi_{aa}^d$  on benzene, fluorobenzene, pyridine, pyrrole, furan, thiophene, cyclopentadiene and ethylene oxide includes all the data available on aromatic molecules and some which are of low or no aromaticity. The correlation (Fig. 1) is  $\chi_{Obs}^d = 1.002 \chi_{Calc}^d - 8.00 \text{ erg/gauss}^2 \text{ mole}$  with an average value of scatter <1%. In Table 1 we thus extend the calculated values of  $\chi_{aa}^d$  to a range of other heterocycles.

It is interesting to note that the diamagnetic susceptibility anisotropy (DSA) (a) declines as the number of nitrogen atoms increases in the rings, (b) that the 5-membered rings yield lower values than the azines and that both these factors do suggest some connection with aromaticity. However, the values for the long known 1, 3, 5-triazine and 1, 2, 4, 5-tetrazine are lower than those of some unknown isomers in each series. A further disturbing feature is the observation that DSA is linearly related to the binding energy (BE) of the molecule (heat of atomisation), but only among isoelectronic species. Thus (Fig. 2) the correlation lines (BE in kcal/mole) are (i) azines:  $\chi_{oop}^d - (\chi_{ip}^d)_{av} = 0.062 \text{ BE} + 173$ , (ii) Azoles and oxadiazoles:  $\chi_{oop}^d - (\chi_{ip}^d)_{av} = 0.048 \text{ BE} + 109$ , (iii) thiophene, thiazole, thiadiazoles



$\chi_{oop}^d - (\chi_{ip}^d)_{av} = 0.062 \text{ BE} + 151$ . Now it is clear that binding energy is not in itself a measure of aromaticity; for example, the calculations on benzene, fulvene and 1, 2-dimethylene cyclobutene<sup>8,9</sup> carried out with very similar basis sets to the present work lead to binding energies of 663.0, 618.5 and 584.6 kcal/mole, after correction of a systematic error in the free atom energies.<sup>10</sup> At least part of the BE difference between the BE of benzene and the others must arise from additional  $\pi$ -bond strain. Thus the last two compounds are normally regarded as non-aromatic, and Fig. 2 then leads to the unacceptable conclusion that most of the azines and all of the azoles are totally non-aromatic. It is well established that they show some aromatic character.<sup>11</sup> This suggests that DSA is not related to aromaticity. Finally we note that DSA and BE are related via the Schrodinger Equation



through the eigenvectors and eigenvalues respectively and that these two factors are not directly connected in any other way. The paramagnetic susceptibility ( $\chi_{aa}^P$ ) consists of a term derived purely from the molecular geometry,<sup>12</sup> together with a term in which the only electronic factor is the rotational g-value ( $g_{aa}$ );<sup>13</sup> since this is evaluated over excited state wavefunctions only, it seems unlikely that this and hence  $\chi_{aa}^P$  and  $\chi_{aa}^T$  can be associated with aromaticity, for this is a ground state phenomenon. Investigations into the nature of the MSA phenomenon are continuing.

#### Footnotes and References

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Table 1. Calculated Diamagnetic Susceptibility of ( $\chi_{aa}^d$ ) of Heterocyclic Systems.

Formula <sup>a</sup>	$-\chi_{oop}$	$(-\chi_{ip})_{av}$	Formula <sup>b</sup>	$-\chi_{oop}$	$(-\chi_{ip})_{av}$
$C_6H_6$	525.5	303.5	$C_5H_6$	363.9	218.2
$C_6H_5F$	738.9	408.3	$C_5H_5$	357.5	210.5
$C_5H_5N$	492.0	386.9	$C_4H_4O$	328.4	196.0
1,2- $C_4H_4N_2$	471.1	271.7	$C_4H_4NH$	342.8	205.1
1,3- $C_4H_4N_2$	468.3	270.1	$C_4H_4S$	444.8	258.4
1,2,4- $C_3H_3N_3$	446.2	258.9	1,2- $C_3H_4N_2$	308.8	187.5
1,3,5- $C_3H_3N_3$	426.9	247.0	1,3- $C_3H_4N_2$	315.3	189.6
1,2,3- $C_3H_3N_3$	447.5	257.8	1H-1,2,3- $C_2H_3N_3$	288.8	174.2
1,2,3,4- $C_2H_2N_4$	425.9	244.7	1H-1,2,4- $C_2H_3N_3$	290.8	174.6
1,2,3,5- $C_2H_2N_4$	429.9	246.6	1H- $CH_2N_4$	278.1	166.7
1,2,4,5- $C_2H_4N_4$	418.4	240.8	2H- $CH_2N_4$	274.8	164.4
$C_2H_4O$	132.3	98.3	1,2,5- $C_2H_2N_2O$	290.3	172.7
1,3- $C_3H_3NS^b$	409.5	243.0	1,2,3- $C_2H_2N_2O$	288.4	174.8
1,2,5- $C_2H_2N_2S^b$	494.0	287.5	1,2,4- $C_2H_4N_2O$	286.6	173.0

Footnotes: a. Azines;

b. Azoles, Oxadiazoles, Thiazoles and Thiadiazoles.

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