Kerr Constants, Cotton–Mouton Constants, and Magnetic Anisotropies of Pyridazine, Pyrimidine, and Pyrazine

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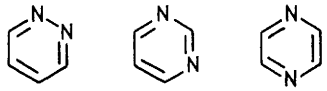
Experimental dipole moments, molar Kerr constants, and molar Cotton–Mouton constants obtained at 298 K and 633 nm are reported for pyridazine, pyrimidine, and pyrazine as solutes in dioxan and cyclohexane. Analysis of the Kerr-effect data yielded the effective polarisability anisotropies, which were then used to evaluate the molecular magnetic anisotropies from the Cotton–Mouton constants. The magnetic criterion of aromaticity was applied by estimating for each diazine the non-local contribution to the out-of-plane component of the magnetisability. Progressive replacement of –CH= by –N= causes a considerable reduction inelectron delocalisation and, by inference, aromaticity in the order benzene > pyridine ≈ pyridazine ≈ pyrazine > pyrimidine > *s*-triazine.

THE structures, properties, and reactions of the diazines (1)—(3) have attracted much attention,[1] and there have been several attempts to determine their relative aromaticities, mainly through considerations of delocalisation energies and other energetic criteria.[2-4] It has been shown [5-8] that the molecular magnetic anisotropy



(1) (2) (3)

can also provide a quantitative measure of electron delocalisation and, by inference, of aromatic character. The usefulness of the Cotton–Mouton effect (magnetic birefringence) as a route to magnetic anisotropies is well established.[9-14] In this paper we report and analyse the experimental dipole moments and the infinite-dilution Kerr and Cotton–Mouton constants at 298 K and 633 nm of the three diazines as solutes in dioxan and cyclohexane.

EXPERIMENTAL

Materials.—Samples of pyridazine (1), pyrimidine (2), and pyrazine (3) were purified by vacuum distillation or vacuum sublimation. Dioxan and cyclohexane, used as solvents, were prepared as previously described.[13]

Apparatus, Procedures, and Results.—A description was given recently [13] of improved equipment for measuring magnetic and electric birefringence in liquids and solutions. The photometric detection system incorporates a He–Ne laser (λ 632.8 nm) and Faraday effect polarisation modulator interfaced to a PAR 122 lock-in amplifier, and is similar to that described by Buckingham *et al.*[10] (Cotton–Mouton effect) and Myers and Robinson [15] (Kerr effect). It provides much greater sensitivity and precision in measurements of the Cotton–Mouton effect than apparatus previously used in these laboratories.[9,12] Procedures for obtaining infinite-dilution dipole moments, molar Kerr constants, and molar Cotton–Mouton constants were as developed and explained by Le Fèvre and his collaborators.[9,16] Other details (symbols, solvent constants, *etc.*) are as in ref. 13.

The results are summarized in Table 1. Factors for conversion of numerical data to the c.g.s. e.s.u., or e.m.u. system are as follows: 1 C m = $0.299\,8 \times 10^{30}$ D (dipole moment); 1 $m^5\ V^{-2}\ mol^{-1} = 0.898\,8 \times 10^{15}$ e.s.u. mol^{-1} (Kerr constant); 1 $m^5\ A^{-2}\ mol^{-1} = 0.633\,3 \times 10^{10}$ e.m.u. mol^{-1} (Cotton–Mouton constant); 1 C $m^2\ V^{-1} = 0.898\,8 \times 10^{16}$ cm^3 (polarisability); 1 J $T^{-2} = 10^{-1}$ e.m.u. (magnetisability).

DISCUSSION

Dipole Moments.—The non-zero dipole moments of pyridazine and pyrimidine as solutes in dioxan or cyclohexane (Table 1) are close to previously reported solution results [17,18] and, in the case of pyrimidine, to that from a microwave Stark-effect study (7.79×10^{-30} C m).[19] Apparent values obtained with dioxan as solvent slightly exceed those from benzene or cyclohexane solutions, an effect which has been attributed to the formation of weak $n \longrightarrow \pi^*$ charge-transfer complexes between dioxan and the diazines.[20] The observed moments of pyridazine and pyrimidine are close to those which might be predicted from the moment of pyridine (7.44×10^{-30} C m),[13]

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[17] A. L. McClellan, ' Tables of Experimental Dipole Moments,' Freeman, San Francisco, 1963; Rahara, California, 1974.
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[20] A. E. Lutskii and V. V. Prezhdo, *Russ. J. Phys. Chem.*, 1971, **45**, 723.

but a detailed analysis is not straightforward. Calculations of the dipole moments of the diazines have been made by using VESCF [21] and *ab initio* [22] molecular orbital theory.

Anisotropic Polarisabilities.—The polarisability anisotropies of the diazines can be derived from the measured Kerr effects and dipole moments in a manner similar to that described for benzene and pyridine.[13] Since the diazines, like pyridine, lack a three-fold or higher-order rotation axis, the two in-plane components (α_{11}, α_{22}) of the polarisability are not identical In consequence the three diagonal elements (α_{11}, α_{22}, α_{33}; 3-direction perpendicular to molecular plane) cannot be evaluated uniquely from the two available equations involving the experimental molar refraction and the molar Kerr constant, ham and Pople's [23] general expression for the zero-density molar Kerr constant can be written as equation (1), in which γ^k and β^k are the mean first and second Kerr hyperpolarisabilities; $\Delta\alpha^o$ ($= \alpha^o_{33} - \alpha^o_{11}$) and $\Delta\alpha$ ($= \alpha_{33} - \alpha_{11}$) are the anisotropies in the static and optical frequency polarisabilities; and p is the molecular dipole moment. In order to evaluate $\Delta\alpha$ from this equation it was further assumed that γ^k is the same as found for benzene,[24] and β^k was taken as zero. The analyses of the Kerr constants to yield values of $\Delta\alpha$ (and the Cotton–Mouton constants to give the magnetic anisotropies, $\Delta\chi$) are summarised in Table 2. The Kerr constants, dipole moments, and apparent polarisability anisotropies show some solvent dependence, as has been emphasised previously.[13]

$$ {}_mK = (N_A/81\varepsilon_o)\{\gamma^k + (kT)^{-1}[(2/3)p\beta^k + (1/5)(\Delta\alpha^o/\Delta\alpha)(\Delta\alpha)^2] - (10k^2T^2)^{-1}p^2\Delta\alpha\} \quad (1) $$

TABLE 1

Molar polarisations and refractions, dipole moments,[a,b] molar Kerr constants,[a] and molar Cotton–Mouton constants [a] of solutes at 298 K and 633 nm from observations of incremental relative permittivities, densities, refractive indices, electric birefringences, and magnetic birefringences of solutions in dioxan or cyclohexane

Solute	Solvent [c]	Solutions [d]	$\alpha\varepsilon_1$	β	γ	δ	δ'	$_\infty P_2$/ cm^3	R_D/ cm^3	$10^{30}p$/C m	$10^{27}{}_\infty({}_mK_2)$/ m^5 V^{-2} mol^{-1}	$10^{27}{}_\infty({}_mC_2)$/ m^5 A^{-2} mol^{-1}
Pyridazine	D	6.1—15.9,6	27.0	0.11 [f]	0.073	401	−42.2	378	21.8	13.9 ± 0.1	426 ± 14	31.3 ± 0.8
	CH	*e*	18.2	0.20 [g]	0.00	335	*e*	373	21 [g]	13.8 ± 0.1	388 ± 12	*e*
Pyrimidine	D	2.1—15.4,8	8.54	0.14 [f]	0.053	144	−35.5	133	20.0	7.77 ± 0.1	154.1 ± 3.8	26.2 ± 2.5
	CH	4.9—12.1,3	5.70	0.29 [g]	0.031	133.9	−40.5	128	21 [g]	7.59 ± 0.1	156.3 ± 0.7	26.6 ± 1.8
Pyrazine	D	1.1—7.6,7	0.16	0.151	0.061	7.47	−47.8	21.5	20.3	0	8.96 ± 0.34	35.5 ± 1.0
	CH	6.7—11.2,6	0.25	0.27	0.034	8.14	−51.4	24.0	21.9	0	10.33 ± 0.28	33.9 ± 1.1

[a] Quoted uncertainties are probable errors derived by standard statistical treatment of experimental data (P. D. Lark, B. R. Craven, and R. C. L. Bosworth, 'The Handling of Chemical Data,' Pergamon, Oxford, 1968; L. G. Parratt, 'Probability and Experimental Errors in Science,' Wiley, New York, 1961). [b] Calculated by assuming $_DP = 1.05\,R_D$. [c] D = dioxan; CH = cyclohexane. [d] Data shown indicate the approximate weight-fraction concentration range (expressed here as 10^2w_2) and the number of solutions for which magnetic birefringences were measured. The other experimental quantities ($\alpha\varepsilon_1$, β, γ, and δ) are more easily determined and a smaller number of more dilute solutions generally sufficed. [e] Solubility of pyridazine in cyclohexane insufficient to allow a reliable determination of the Cotton–Mouton constant. [f] W. C. Schneider, *J. Amer. Chem. Soc.*, 1948, **70**, 627. [g] The four solution values of the molar refraction of the diazines, together with pure liquid data for pyridazine (Beilstein: $d_4^{23.5}$ 1.103 5, $n_D^{23.5}$ 1.523 1, R_D 22.2 cm^3) yield a mean R_D value of 21.2 cm^3, from which the two indicated values of β were obtained with sufficient reliability for the present calculations.

TABLE 2

Analysis of the molar Kerr and Cotton–Mouton constants of pyridazine, pyrimidine, and pyrazine

	Solvent [a]	Pyridazine	Pyrimidine	Pyrazine
$10^{27}{}_\infty({}_mK_2)$/m^5 V^{-2} mol^{-1}	D	426 ± 14	154.1 ± 3.8	8.96 ± 0.34
	CH	388 ± 12	156.3 ± 0.7	10.33 ± 0.28
$10^{27}(N_A\gamma^k/81\varepsilon_o)$/m^5 V^{-2} mol^{-1}		0.7 ± 0.3 [b]	0.7 ± 0.3 [b]	0.7 ± 0.3 [b]
$10^{30}p$/C m	D	13.9 ± 0.1	7.77 ± 0.10	0
	CH	13.8 ± 0.1	7.59 ± 0.10	0
$\Delta\alpha^o/\Delta\alpha$		1.0 ± 0.1 [c]	1.0 ± 0.1 [c]	1.0 ± 0.1 [c]
$10^{40}\Delta\alpha$/C m^2 V^{-1}	D	−4.36 ± 0.15	−4.81 ± 0.16	−4.50 ± 0.24
	CH	−4.03 ± 0.14	−5.08 ± 0.12	−4.86 ± 0.25
$10^{27}{}_\infty({}_mC_2)$/m^5 A^{-2} mol^{-1}	D	31.3 ± 0.8	26.2 ± 2.5	35.5 ± 1.0
	CH	—	26.6 ± 1.8	33.9 ± 1.1
$10^{27}(N_A\mu_o^2\eta/270\varepsilon_o)$/m^5 A^{-2} mol^{-1}		0 ± 0.5 [c]	0 ± 0.5 [c]	0 ± 0.5
$10^{29}\Delta\chi$/J T^{-2} molecule^{-1}	D	−111 ± 5	−85 ± 9	−123 ± 7
	CH	—	−81 ± 6	−108 ± 7
$10^{29}\Delta\chi$/J T^{-2} molecule^{-1} (mean value)		−111 ± 5	−83 ± 6	−115 ± 10
$10^5\Delta\chi$/J T^{-2} mol^{-1}		−67 ± 3	−50 ± 4	−70 ± 6

[a] D = dioxan; CH = cyclohexane. [b] Experimental value for benzene (ref. 24). [c] Assumed value.

respectively. However for these very anisometric molecules it is not unreasonable to assume that the in-plane polarisabilities are equal; supporting evidence will be presented below. With this assumption Bucking-

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[22] M. H. Palmer, R. H. Findlay, and A. J. Gaskell, *J.C.S. Perkin II*, 1974, 420.
[23] A. D. Buckingham and J. A. Pople, *Proc. Phys. Soc. A*, 1955, **68**, 905.
[24] M. P. Bogaard, A. D. Buckingham, and G. L. D. Ritchie, *Mol. Phys.*, 1970, **18**, 575.

The validity of our assumption that in the diazines the two in-plane polarisabilities are effectively equal can be explored in two ways. First, it seems reasonable to expect the perpendicular component, α_{33}, of the polarisability to show an approximately regular progression in the series benzene, pyridine, diazines, *s*-triazine. Previously reported data for benzene [13] and *s*-triazine,[14] for which α_{11} (= α_{22} by symmetry) and α_{33} are known, can therefore be used to predict α_{33} for the diazines. A simple interpolation suggests that α_{33} should be *ca.* 6.30×10^{-40} C m^2 V^{-1} in the diazines, a prediction which is within the range spanned by the three experimental values. The data are shown in Table 3.

A second approach is to note that in the strongly dipolar molecules pyridazine and pyrimidine the $(\Delta\alpha)^2$ term in equation (1) contributes only a few percent to the Kerr constants of these two molecules. The theoretical expression for the Kerr constant can then be written approximately as equation (2), which can be solved simultaneously with equation (3) for the molar refraction, to yield a unique value of α_{11}, the polarisability

$$ {}_{\mathrm{m}}K = (N_{\mathrm{A}}/810\varepsilon_0)\{10\gamma^{\mathrm{k}} + (k^2T^2)^{-1}\, p^2\,(2\alpha_{11} - \alpha_{22} - \alpha_{33})\} \quad (2) $$

in the direction of the dipole moment. Results emerge as 10.8×10^{-40} C m^2 V^{-1} for pyridazine and 11.0×10^{-40} C m^2 V^{-1} for pyrimidine, in agreement with the values

$$ {}_{\mathrm{m}}R = (N_{\mathrm{A}}/9\varepsilon_0)\,(\alpha_{11} + \alpha_{22} + \alpha_{33}) \quad (3) $$

obtained (Table 3) by assuming equality of the in-plane polarisabilities.

We therefore feel justified in using the values of $\Delta\alpha$ so derived from the Kerr effect in the following analysis of the Cotton–Mouton constants of these molecules.

Magnetic Anisotropies.—With the assumption that the polarisability of the diazines is effectively axially symmetric, the general theoretical expression for the zero-density molar Cotton–Mouton constant [25] reduces to equation (4), where χ_{11}, χ_{22}, and χ_{33} are the corresponding diagonal elements of the magnetisability tensor [26] and $\Delta\chi = \frac{1}{2}(2\chi_{33} - \chi_{11} - \chi_{22})$ is the magnetic anisotropy; η is a tensor describing the dependence of the differential polarisability on the magnetic induction. In the absence of relevant experimental information we have taken η as zero. There is some indirect evidence that for strongly anisotropic molecules this term makes only a small

$$ {}_{\mathrm{m}}C = (N_{\mathrm{A}}\mu_0^2/270\varepsilon_0)\{\eta + (3kT)^{-1}\,\Delta\alpha\,(2\chi_{33} - \chi_{11} - \chi_{22})\} \quad (4) $$

contribution to the molar Cotton–Mouton constant at 298 K.[11,13] The analysis of the Cotton–Mouton constants is also summarised in Table 2, which shows the derived molecular and molar magnetic anisotropies. The values for pyrazine obtained from the two solvents vary by slightly more than the range indicated by the combined probable errors. The discrepancy may be due to a stereospecific interaction between pyrazine and dioxan,[20] such as is known to occur in benzene,[27] although our $\Delta\chi$ values for pyrimidine and pyridine show little evidence of such an effect.

TABLE 3

Molar refractions,[a] mean polarisabilities,[b] polarisability anisotropies,[b] and experimentally determined polarisability components [b] at 633 nm

	Benzene	Pyridine	Pyridazine	Pyrazine	Pyrimidine	*s*-Triazine
${}_{\mathrm{m}}R_{633}$	26.3 [c]	24.1 [c]	21.2 [d]	21.2 [d]	21.2 [d]	18.7 [e]
α	11.6	10.6	9.35	9.35	9.35	8.25
$\Delta\alpha$	−4.18 [f]	−4.2 [f]	−4.36	−4.50	−4.81	−4.8 [g]
α_{33}	8.8	7.8	6.4	6.4	6.1	5.0
α_{11}	13.0	12.0	10.8	10.8	11.0	9.8

[a] From refractive index measurements at 633 nm on a range of pure liquids it was established that $R_{633} = 0.995\ R_{\mathrm{D}}$, so that R_{D} data are sufficiently accurate for present purposes; units cm^3 mol^{-1}. [b] All polarisability data, quoted here as $10^{40}\alpha$/C m^2 V^{-1}, were obtained from observations on solutions in *dioxan*; polarisability anisotropies, $\Delta\alpha$, are values of $\alpha_{33} - \alpha_{11}$ derived by assuming $\alpha_{11} = \alpha_{22}$. [c] R. J. W. Le Fèvre, *Adv. Phys. Org. Chem.*, 1965, **3**, 1. [d] Mean value for diazines; see footnote *g*, Table 1. [e] Estimated by extrapolation of data for benzene, pyridine, and diazines. [f] Ref. 13. [g] Ref. 14.

In discussing these results we note that measurements by Wilson [28] have revealed an unexpectedly large variation in the mean molar magnetisabilities, χ, of the isomeric diazines. The value for pyrimidine was found to be consistent with a regular and stepwise diminution of χ in the series benzene, pyridine, pyrimidine, *s*-triazine, but significantly lower results were found for pyridazine and, even more divergently, pyrazine (see Table 4). To explain these differences Wilson cited theoretical studies [29,30] which showed that the nitrogen lone pair orbitals interact to a varying extent in the three molecules, the effect being small in pyrimidine but considerable in pyridazine and pyrazine. The present work shows that there is also considerable variation in the magnetic anisotropies of the diazines: pyrazine apparently has a larger magnetic anisotropy than benzene,[13] whereas the value for pyrimidine is only slightly greater than that for *s*-triazine.[14]

It is now well recognised that the magnetic anisotropy does not itself provide a direct measure of relative electron delocalisation, and hence of aromaticity. The reason for this is that the values of both the mean molecular magnetisability (χ) and the magnetic anisotropy ($\Delta\chi$) depend on a fine balance between large,

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[28] J. D. Wilson, *J. Chem. Phys.*, 1970, **53**, 467.
[29] E. Clementi, *J. Chem. Phys.*, 1967, **46**, 4737.
[30] R. Hoffmann, A. Imanura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1968, **90**, 1499.

oppositely signed diamagnetic (χ^d, $\Delta\chi^d$) and temperature-independent paramagnetic (χ^p, $\Delta\chi^p$) contributions, and it is the latter which contains the correlation with electron delocalisation.[6,7] From an examination [14] of results for benzene, pyridine, and *s*-triazine it was established that the quantities $|\chi|$, $|\Delta\chi|$, $|\Delta\chi^d|$, $\Delta\chi^p$, $|\chi^d|$, and χ^p all *decrease* on progressive replacement of –CH= by –N=. A similar analysis of the data for pyridazine and pyrimidine, using the results of Palmer and Findlay's *ab initio* calculations of the diamagnetisability tensor,[4] confirms this trend.

Schmalz, Norris, and Flygare[5] have demonstrated that –CH= by –N= leads to a regular and considerable diminution in the electron delocalisation and, on the basis of the magnetic criterion, the aromaticity. Such a trend parallels that already noted in the mean magnetisability, and is entirely consistent with the much studied chemical reactivity and physical properties of these compounds.[1] Aza-substitution of benzene has the effect of localising electronic charge on the nitrogen atoms, leaving the carbon atoms electron-deficient, and so inhibiting electrophilic substitution. Insertion of one nitrogen atom (pyridine) diminishes the stability and aromatic character slightly, but the effect becomes much more evident when two nitrogen atoms occupy ring positions separated by one carbon atom (pyrimidine) so that their mesomeric effects are additive. *s*-Triazine is, of course, extremely reactive, and very susceptible to nucleophilic addition; the present results suggest that electron delocalisation in this molecule is only *ca.* 30% of that in benzene.

TABLE 4

Mean magnetisabilities,[a] magnetic anisotropies,[a] experimental out-of-plane magnetisabilities,[a] local and non-local out-of-plane magnetisabilities,[a] and relative electron delocalisations

	Benzene	Pyridine [b]	Pyridazine	Pyrazine	Pyrimidine	*s*-Triazine
χ	−54.8 [c]	−48.4	−40.5 [d]	−37.8 [d]	−43.1 [d]	−37.9 [d]
$\Delta\chi$	−64 [e]	−57.4	−67	−70	−50	−49 [f]
χ_{33}	−97	−86.8	−85	−84	−76	−71
$\chi_{33\ \text{local}}$	−58.2	−58.4	−58.6	−58.6	−58.6	−58.8
$\chi_{33\ \text{non-local}}$	−39	−28.4	−27	−26	−18	−12
Relative delocalisation	1.0	0.7	0.7	0.7	0.5	0.3

[a] All magnetisability data quoted here as $10^5\chi/J\ T^{-2}\ mol^{-1}$, *etc.* [b] Ref. 32. [c] G. Foëx, 'Constantes Selectionées, Diamagnétisme et Paramagnétisme,' in 'Tables de Constantes et Donées Numérique,' vol. 7, Masson, Paris, 1957. [d] Ref. 28. [e] Ref. 13. [f] Ref. 14.

a quantitative measure of electron delocalisation in planar, cyclic molecules can be obtained by comparing the measured out-of-plane magnetisability component (χ_{33}) with the value predicted for a hypothetical structure in which the electron distribution is completely localised ($\chi_{33\ \text{local}}$). For a series of isoelectronic molecules, such as benzene and the diazines under consideration here, the difference between the observed and calculated values (*i.e.* $\chi_{33\ \text{non-local}}$) is an estimate of the extent of electron delocalisation and, by inference, of the relative aromaticity. It is of interest to apply this procedure to the diazines and *s*-triazine, using the atom magnetisabilities derived by Flygare and his collaborators [5,31] from a range of non-conjugated molecules, to calculate values of $\chi_{33\ \text{local}}$. The analysis is summarised in Table 4, which includes for completeness our previously reported magnetic anisotropies for benzene and *s*-triazine, together with the data of Wang and Flygare [32] for pyridine. The estimates of $\chi_{33\ \text{non-local}}$ are necessarily rather uncertain because of experimental errors in the magnetic anisotropies (see Table 2), the large uncertainty in the local values for the nitrogen atom,[31] and the general limitations of such an atom-additivity model. Nevertheless some interesting conclusions can be drawn, especially when the values of $\chi_{33\ \text{non-local}}$ are expressed relative to benzene.

Consider first the sequence (relative electron delocalisations in brackets) benzene (1.0), pyridine (0.7), pyrimidine (0.5), *s*-triazine (0.3). Progressive replacement of

It remains to comment on the results for pyridazine and pyrazine, which appear from the magnetisability data in Table 4 to have about the same degree of electron delocalisation as pyridine. Such a conclusion is hardly surprising, since in each of these molecules the π-electron localising effects of the two nitrogen atoms are competitive, rather than additive as in pyrimidine.

From a study of the molecular Zeeman effect in oxazole and isoxazole,[31] as well as in pyridine,[32] Flygare and his collaborators similarly concluded that replacement of one –CH= group by –N= in five- or six-membered rings causes only slight suppression of electron delocalisation. Our results show that in six-membered rings the delocalisation is considerably reduced when two or three nitrogen atoms are present, and that the effect in a particular molecule depends on the relative positions of the nitrogen atoms.

Financial support from the Australian Research Grants Committee is gratefully acknowledged.

[6/1739 *Received*, 13*th September*, 1976]

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