

Cotton–Mouton and Kerr Effects of Some Chloro- and Nitro-benzenes

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Experimental molar Cotton–Mouton and Kerr constants obtained at 298 K and 633 nm are reported for 1,3,5-trichloro-, 1,4-dichloro-, and chloro-benzene as solutes in carbon tetrachloride; and for 1,3,5-trinitro-, 1,4-dinitro-, and nitro-benzene as solutes in dioxan. Analysis of the data yielded information concerning the molecular magnetic anisotropies, and the effect of the chloro- and nitro-groups in modifying the magnetisability of benzene.

IN order to ascertain the ability of substituents to modify the magnetic anisotropy of benzene we have extended our studies¹⁻³ of the Cotton–Mouton effect (magnetic birefringence) to the mono-, 1,4-di-, and 1,3,5-tri-substituted chloro- and nitro-benzenes. Although various measurements are on record⁴⁻⁸ for most of these molecules, no systematic study has previously been undertaken. A parallel series of Kerr effect (electric birefringence) measurements was made to obtain information concerning the anisotropy in the molecular polarisability. Infinite-dilution molar Cotton–Mouton and Kerr

carbon disulphide, chloroform, and pyridine dissolved in carbon tetrachloride, cyclohexane, and dioxan established that reliable molecular magnetic anisotropies can be derived from data for solutions in dioxan.

Apparatus, Procedures, and Results.—Improved equipment for measuring magnetic and electric birefringence in liquids and solutions has already been described.¹ The photometric detection system incorporates a He–Ne laser ($\lambda = 632.8$ nm) and Faraday effect polarisation modulator interfaced to a PAR 122 lock-in amplifier. It provides much greater precision and accuracy in measurements of the Cotton–Mouton effect than apparatus previously used in

TABLE I

Molar Cotton–Mouton constants^a and molar Kerr constants^a of solutes at 298 K and 633 nm from observations of incremental relative permittivities, densities, refractive indices, magnetic birefringences, and electric birefringences of solutions in carbon tetrachloride or dioxan

Solute	$\alpha\epsilon_1$	β	γ	δ'	δ	$10^{27}\alpha_{(mC_2)}/m^5A^{-2}mol^{-1}$	$10^{27}\alpha_{(mK_2)}/m^5V^{-2}mol^{-1}$
1,3,5-Trichlorobenzene ^b	0.404 ^d	-0.122 ^d	0.089	-124	17.0	43.0 ± 3.7	31.9 ± 0.6
1,4-Dichlorobenzene ^b	0.295	-0.215	0.080	-148	21.0	41.4 ± 3.2	32.1 ± 0.8
Chlorobenzene ^b	4.84 ^e	-0.431 ^e	0.064	-133	120	28.5 ± 1.3	132.3 ± 2.1
1,3,5-Trinitrobenzene ^c	0.640	0.377	0.094	-64.5	9.36	129 ± 7	28 ± 5
1,4-Dinitrobenzene ^c	0.552	0.382	0.078	-67.9	14.3	107 ± 3	33.5 ± 0.9
Nitrobenzene ^c	15.8	0.220	0.088	-51.6	667	59.1 ± 1.8	1 110 ± 90

^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 Solvent carbon tetrachloride. ^c Solvent dioxan. ^d Ref. 10. ^e Ref. 12.

constants at 633 nm and 298 K are here reported and analysed for the six compounds as solutes in carbon tetrachloride or dioxan.

EXPERIMENTAL

Materials.—The solutes (1,3,5-trichloro-, 1,4-dichloro-, chloro-, 1,3,5-trinitro-, 1,4-dinitro-, and nitro-benzene) were purified before use. Solvents (carbon tetrachloride and dioxan) were prepared as previously described.¹ The low solubility of 1,3,5-trinitro- and 1,4-dinitro-benzene in carbon tetrachloride necessitated the use of dioxan as solvent for the nitrobenzenes. However our measurements¹ of the infinite-dilution Kerr and Cotton–Mouton constants of benzene,

¹ M. R. Battaglia and G. L. D. Ritchie, *J.C.S. Faraday II*, 1977, **73**, 209.

² M. R. Battaglia and G. L. D. Ritchie, *Mol. Phys.*, 1976, **32**, 1481.

³ M. R. Battaglia and G. L. D. Ritchie, *J.C.S. Perkin II*, preceding paper.

⁴ R. J. W. Le Fèvre, P. H. Williams, and J. M. Eckert, *Austral. J. Chem.*, 1965, **18**, 1133.

⁵ R. J. W. Le Fèvre and D. S. N. Murthy, *Austral. J. Chem.*, 1966, **19**, 179, 1315.

⁶ R. J. W. Le Fèvre, D. S. N. Murthy, and P. J. Stiles, *Austral. J. Chem.*, 1969, **22**, 1421.

⁷ C. L. Cheng, D. S. N. Murthy, and G. L. D. Ritchie, *Austral. J. Chem.*, 1972, **25**, 1301.

these laboratories.^{4,5} Procedures for obtaining infinite-dilution dipole moments, molar Kerr constants, and molar Cotton–Mouton constants were as developed and explained by Le Fèvre and collaborators.^{4,9} Other details (symbols, solvent constants, *etc.*) are given in ref. 1.

The results are summarized in Table I. Factors for conversion of numerical data to the c.g.s. e.s.u., or e.m.u. systems are as follows: 1 C m = 0.299 8 × 10³⁰ D (dipole moment); 1 m⁵ V⁻² mol⁻¹ = 0.898 8 × 10¹⁵ e.s.u. mol⁻¹ (Kerr constant); 1 m⁵ A⁻² mol⁻¹ = 0.633 3 × 10¹⁰ e.m.u. mol⁻¹ (Cotton–Mouton constant); 1 C m² V⁻¹ = 0.898 8 × 10¹⁶ cm³ (polarisability); 1 J T⁻² = 10⁻¹ e.m.u. (magnetisability).

Previous Measurements.—The results shown in Table I apply to 633 nm and 298 K; some variation from previously reported data for 589 nm and 298 or 293 K is to be expected. In addition molar Kerr and Cotton–Mouton constants generally exhibit a solvent-dependence because of the variation with medium of the apparent molecular polarisability anisotropy.

⁸ C. L. Cheng, D. S. N. Murthy, and G. L. D. Ritchie, *Mol. Phys.*, 1971, **22**, 1137.

⁹ C. G. Le Fèvre and R. J. W. Le Fèvre, in 'Techniques of Chemistry,' ed. A. Weissberger, Wiley-Interscience, New York, 1972, vol. 1, part IIIc, ch. 6, p. 399.

The molar Kerr constants now reported for the chlorobenzenes are in reasonable agreement with earlier values;¹⁰⁻¹³ the nitrobenzenes have not previously been examined with dioxan as solvent, but data are on record for other solvents.^{10,14} Le Fèvre and Le Fèvre¹⁰ found a much larger molar Kerr constant for 1,3,5-trinitrobenzene dissolved in benzene; this can be attributed to the occurrence in benzene of a stereospecific solute-solvent interaction. The molar Cotton-Mouton constants in Table 1 for 1,3,5-trichloro- and 1,4-dichloro-benzene are higher than those already on record;^{7,8} that for chlorobenzene is close to earlier results.^{5,8} The magnetic birefringences of the nitrobenzenes as solutes in dioxan have not been measured previously, but solutions of nitrobenzene in carbon tetrachloride, cyclohexane, and benzene have been studied.^{4,5}

DISCUSSION

Method of Data Analysis.—Our primary objective in these studies is to determine by experiment the molecular magnetic anisotropies, $\Delta\chi$, of particular molecules. Procedures for evaluating this quantity from measurements of the Cotton-Mouton and Kerr effects have been described elsewhere;¹⁻³ only essential equations will be summarised here.

For a system of non-interacting diamagnetic molecules the theoretical expression derived by Buckingham and Pople¹⁵ for the molar Cotton-Mouton constant is equation (1), in which α is the high-frequency polaris-

$$mC = (N_A \mu_0^2 / 270 \epsilon_0) \{ \eta_{\alpha\beta:\alpha\beta} - \frac{1}{3} \eta_{\alpha\alpha:\beta\beta} + (kT)^{-1} [\alpha_{\alpha\beta} \chi_{\alpha\beta} - 3\alpha\chi] \} \quad (1)$$

ability; χ is the molecular magnetisability;¹⁶ η is a tensor describing the dependence of the differential polarisability on the magnetic induction; other symbols have their usual meanings. If a three-fold or higher-order rotation axis (labelled with subscript 3) is present, as in 1,3,5-trichloro- and 1,3,5-trinitro-benzene,

$$mC = (N_A \mu_0^2 / 270 \epsilon_0) \{ \eta + (2/3kT) \Delta\alpha \Delta\chi \} \quad (2)$$

equation (1) simplifies to (2), where $\Delta\alpha (= \alpha_{33} - \alpha_{11})$ and $\Delta\chi (= \chi_{33} - \chi_{11})$ are the anisotropies in the polarisability and magnetisability tensors; and $\eta = \eta_{\alpha\beta:\alpha\beta} - \frac{1}{3} \eta_{\alpha\alpha:\beta\beta}$. Evaluation of $\Delta\chi$ for molecules of this symmetry can therefore be achieved provided both $\Delta\chi$ and η are known. For the other molecules studied, however, the magnetisability and polarisability tensors are not axially symmetric (*i.e.*, $\chi_{11} \neq \chi_{22} \neq \chi_{33}$; $\alpha_{11} \neq \alpha_{22} \neq \alpha_{33}$) and the magnetic anisotropy $\Delta\chi = \frac{1}{2}(2\chi_{33} - \chi_{11} - \chi_{22})$ cannot be determined exactly, although the difference between the in-plane components χ_{11} and χ_{22} may be relatively small. With the assumption that $\chi_{11} = \chi_{22}$, equation (1) can be written, for such molecules, as equation (3), in which $\alpha_{33} - \alpha$ is the difference between the out-of-plane and

¹⁰ C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1953, 4041; 1954, 1577.

¹¹ M. L. Kemp and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1965, 3463.

¹² R. J. W. Le Fèvre, D. V. Radford, G. L. D. Ritchie, and P. J. Stiles, *J. Chem. Soc. (B)*, 1968, 148.

¹³ K. E. Calderbank, unpublished data.

¹⁴ K. E. Calderbank, R. J. W. Le Fèvre, and G. L. D. Ritchie, *J. Chem. Soc. (B)*, 1968, 503.

¹⁵ A. D. Buckingham and J. A. Pople, *Proc. Phys. Soc. B*, 1956, 69, 1133.

mean polarisabilities, and $\Delta\chi$ is an estimate of the true magnetic anisotropy, $\frac{1}{2}(2\chi_{33} - \chi_{11} - \chi_{22})$. In the absence of relevant experimental data we have taken the distortion tensor, η , for these molecules as zero. There is indirect evidence¹ that for strongly anisometric molecules this term makes only a small contribution to the molar Cotton-Mouton constant at 298 K.

The polarisability anisotropies required in equations

$$mC = (N_A \mu_0^2 / 270 \epsilon_0) \{ \eta + (kT)^{-1} (\alpha_{33} - \alpha) \Delta\chi \} \quad (3)$$

(2) and (3) were obtained from the Kerr effect measurements. Buckingham and Pople's general expression¹⁷ for the zero-density molar Kerr constant is equation (4), in which β^k and γ^k are the mean first and second Kerr hyperpolarisabilities; $\alpha_{\alpha\beta}$ and $\alpha_{\alpha\beta}^0$ are the high-frequency and static polarisabilities; and the molecular dipole moment p is coincident with the in-plane 1-axis of the polarisability tensor. For the trisubstituted molecules,

$$mK = (N_A / 81 \epsilon_0) \{ \gamma^k + (kT)^{-1} [(2/3) p \beta^k + (3/10) (\alpha_{\alpha\beta} \alpha_{\alpha\beta}^0 - 3\alpha\alpha^0)] + (3/10) (kT)^{-2} p^2 (\alpha_{11} - \alpha) \} \quad (4)$$

which are non-dipolar and have a C_3 rotation axis, equation (4) reduces to (5), where $\Delta\alpha (= \alpha_{33} - \alpha_{11})$ and $\Delta\alpha^0 (= \alpha_{33}^0 - \alpha_{11}^0)$ are the corresponding polarisability anisotropies, so that $\Delta\alpha$ is easily derived. The remaining molecules are of lower symmetry and the three diagonal elements of the polarisability cannot be evaluated rigorously from the two available equations (molar Kerr constant and molar refraction). However as shown by equation (3) an approximate value of the magnetic

$$mK = (N_A / 81 \epsilon_0) \{ \gamma^k + (5kT)^{-1} \Delta\alpha \Delta\alpha^0 \} \quad (5)$$

anisotropy can be obtained if the difference $\alpha_{33} - \alpha$ is estimated, as described below.

1,3,5-Trichloro- and 1,3,5-Trinitro-benzene.—The analysis, by using equations (5) and (2), of the experimental Kerr and Cotton-Mouton constants to yield the molecular magnetic anisotropies of these two molecules is summarised in Table 2. It was assumed that in both molecules γ^k is the same as found for benzene,¹⁸ and any dispersion in the polarisability anisotropy was ignored. The data provide a striking illustration of how substituents modify the magnetic anisotropy of benzene: the value of $|\Delta\chi|$ (expressed here as $10^5 |\Delta\chi| / J \text{ T}^{-2} \text{ mol}^{-1}$) for 1,3,5-trichlorobenzene (46) is significantly smaller than that for benzene (64),¹ and the result for 1,3,5-trinitrobenzene (147) is more than twice as large. These variations clearly reflect electronic interactions between the substituents and the ring but any detailed analysis of such effects is greatly complicated by the fact that the observed magnetic anisotropy is determined by a fine balance between large, oppositely signed diamagnetic and paramagnetic contributions.¹⁹ However, some

¹⁶ A. D. Buckingham and J. E. Cordle, *Mol. Phys.*, 1974, 28, 1037.

¹⁷ A. D. Buckingham and J. A. Pople, *Proc. Phys. Soc. A*, 1955, 68, 905.

¹⁸ M. P. Bogaard, A. D. Buckingham, and G. L. D. Ritchie, *Mol. Phys.*, 1970, 18, 575.

¹⁹ W. H. Flygare, *Chem. Rev.*, 1974, 74, 653.

insight into the magnetic consequences of substitution can be obtained by combining the values of $\Delta\chi$ with known mean magnetisabilities to evaluate the individual components of the magnetisability tensors. The results of such analyses are shown in Table 3, where for completeness previously reported data for 1,3,5-trimethyl-(mesitylene), 1,3,5-trifluoro-, and 1,3,5-tribromo-benzene are included; several points emerge.

Although the mean magnetisability of mesitylene is much larger than that of benzene the two molecules have virtually identical magnetic anisotropies. The C-CH₃ and C-H groups therefore have approximately equal magnetic anisotropies, as was recognized long ago from

TABLE 2

Analysis of the molar Kerr and Cotton-Mouton constants of 1,3,5-trichloro- and 1,3,5-trinitro-benzene

	1,3,5-Trichloro-benzene ^a	1,3,5-Trinitro-benzene ^b
$10^{27}\infty(mK_B)/m^5V^{-2} \text{ mol}^{-1}$	31.9 ± 0.6	28 ± 5
$10^{27}\infty(N_A\mu_0^2/81\epsilon_0)/m^5V^{-2} \text{ mol}^{-1}$	0.7 ± 0.3^c	0.7 ± 0.3^c
$\Delta\alpha^2/\Delta\alpha$	1.00 ± 0.05	1.00 ± 0.05
$10^{40} \Delta\alpha/C \text{ m}^2 \text{ V}^{-1}$	-8.75 ± 0.24	-8.2 ± 0.8
$10^{27}\infty(mC_3)/m^5A^{-2} \text{ mol}^{-1}$	43.0 ± 3.7	129 ± 7
$10^{27}(N_A\mu_0^2\eta/270\epsilon_0)/m^5A^{-2} \text{ mol}^{-1}$	0 ± 0.5^d	0 ± 0.5^d
$10^{29}\Delta\chi/J \text{ T}^{-2} \text{ molecule}^{-1}$	-76 ± 7	-244 ± 27
$10^{25}\Delta\chi/J \text{ T}^{-2} \text{ mol}^{-1}$	-46 ± 4	-147 ± 16

^a Solvent carbon tetrachloride. ^b Solvent dioxan. ^c Experimental value for benzene (ref. 1). ^d Assumed value.

TABLE 3

Mean magnetisabilities,^a magnetic anisotropies,^a and magnetisability components^a for benzene and several 1,3,5-trisubstituted benzenes

Substituent	H	CH ₃	F	Cl	Br	NO ₂
χ	-55 ^b	-92 ^b	-67 ^c	-99 ^d	-138 ^e	-75 ^b
$\Delta\chi$	-64 ^f	-64 ^g	-40 ^g	-46	-48 ^e	-147
χ_{11}	-33	-71	-53	-84	-122 ^e	-26
χ_{33}	-97	-135	-93	-130	-170 ^e	-173

^a All magnetisability data quoted here as $10^{25}\chi/J \text{ T}^{-2} \text{ mol}^{-1}$, etc. ^b G. Foëx, 'Constantes Sélectionnées Diamagnétisme et Paramagnétisme' in 'Tables de Constantes et Données Numérique,' vol. 7, Masson, Paris, 1957. ^c M. P. Bogaard, A. D. Buckingham, M. G. Corfield, D. A. Dunmur, and A. H. White, *Chem. Phys. Letters*, 1972, **12**, 558. ^d Estimated from data for benzene, chlorobenzene, and 1,3-dichlorobenzene in compilation cited above. ^e K. Lonsdale and E. W. Toor, *Acta Cryst.*, 1959, **12**, 1048. ^f Ref. 1. ^g Ref. 8.

crystal measurements on polymethylated benzenes.²⁰ The general effect of halogen substituents is to cause regular increases (H < F < Cl < Br) in $|\chi|$, $|\chi_{11}|$, and $|\chi_{33}|$. Since $|\chi_{11}|$ is, in each case, more affected than $|\chi_{33}|$, the trihalogenobenzenes have smaller values of $|\Delta\chi|$ than does benzene. The particular halogen atom present causes a large variation in the mean magnetisability but has relatively little effect on the magnetic anisotropy. Introduction of three nitro-groups results in a dramatic increase in the magnetic anisotropy, with $|\chi_{33}|$ exhibiting a large increase and $|\chi_{11}|$ a small decrease. It may be possible qualitatively to explain the effects of the various substituents on the magnetic anisotropy in

²⁰ A. A. Bothner-By and J. A. Pople, *Ann. Rev. Phys. Chem.*, 1965, **16**, 43.

²¹ M. P. Bogaard and B. J. Orr, in 'International Review of Science, Physical Chemistry,' Series 2, ed. A. D. Buckingham, vol. 2, Butterworths, London, 1975, p. 149.

terms of their known electronic characteristics, but for the reason mentioned above this will not be pursued here.

Chloro-, 1,4-Dichloro-, Nitro-, and 1,4-Dinitro-benzene.—Le Fèvre and his collaborators^{10,14} have obtained estimates of the three diagonal elements of the polarisability tensors of chloro- and nitro-benzene by combining experimental data from measurements of molar refractions, molar Kerr constants, and depolarisation ratios for Rayleigh scattered light. The procedure makes no allowance for possible contributions to the observed molar Kerr constants of these strongly dipolar molecules from the first Kerr hyperpolarisabilities, β^k , as shown in equation (4). In view of current discussion²¹⁻²³ as to the likely magnitude of these effects, the recorded polarisabilities for such molecules must be treated with some caution. The non-dipolar 1,4-disubstituted benzenes similarly lack a three-fold rotation axis so that their principal polarisabilities cannot be evaluated from available data. Therefore it is possible to derive only rough estimates of the magnetic anisotropies of these four molecules by the following approximate method.

From equation (3) it can be seen that if the out-of-plane polarisability component, α_{33} , and the mean polarisability, α , are known, the magnetic anisotropy $\Delta\chi$ can be evaluated. It seems reasonable to expect α_{33} to show an approximately regular progression from benzene through the mono- and 1,4-di-substituted to the 1,3,5-trisubstituted benzenes. Since the magnitudes of α_{33} for benzene¹ and the two trisubstituted molecules are known, it is possible to predict the corresponding values for the mono- and di-substituted benzenes. These estimates of α_{33} , together with mean polarisabilities derived from molar refractions and the molar Cotton-Mouton constants in Table 1, yield the following magnetic anisotropies (which may be in error by up to $\pm 20\%$): chlorobenzene, -48; 1,4-dichlorobenzene, -53; nitrobenzene, -96; 1,4-dinitrobenzene, -151 (all expressed as $10^{25}\Delta\chi/J \text{ T}^{-2} \text{ mol}^{-1}$).

The results for chlorobenzene and nitrobenzene are close to those previously derived from solution measurements of magnetic birefringence.^{4,5} In the case of 1,4-dichlorobenzene the present value is significantly larger than an earlier determination,^{7,8} but is in good agreement with the magnetic anisotropy obtained from magnetisability measurements on the crystalline solid.²⁴ A value deduced from a similar study²⁵ of crystalline 1,4-dinitrobenzene is not consistent with present findings concerning the effect of introducing nitro-groups into benzene, and may indicate some deviation from a uniplanar molecular conformation in the solid state.

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²² B. F. Levine and C. G. Bethea, *J. Chem. Phys.*, 1975, **63**, 2666.

²³ P. Bordewijk, *Chem. Phys. Letters*, 1976, **39**, 342.

²⁴ M. A. Lasheen, *Phil. Trans. Roy. Soc. A*, 1964, **256**, 357.

²⁵ S. Banerjee, *Z. Krist.*, 1939, **A100**, 316.