THE DIPOLE MOMENTS AND MOLAR KERR CONSTANTS OF BENZOTRICHLORIDE AND BENZAL CHLORIDE*

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In the course of a continuing study of environmental variations in the aniso-tropic polarizabilities of carbon–halogen bonds (see refs. listed as 1–7 by Izsák and Le Fèvre[1]) we have measured the dipole moments, μ, and molar Kerr constants, $_\infty(_mK_2)$, of benzotrichloride and benzal chloride as solutes in carbon tetrachloride at 25°. Experimental observations and results are shown in Tables 1 and 2; symbols are as defined elsewhere.[2] The dipole moments (2·03 D and 2·07 D, respectively) are in good agreement with recorded values.[3] The applicability of available carbon–chlorine bond anisotropies has been tested by comparison of observed and calculated molar Kerr constants for these two molecules. Results previously recorded[4] for benzotrifluoride have also been considered.

Benzotrichloride

Molar Kerr constants for benzotrichloride have been computed by standard methods using anisotropic polarizabilities for the C–Cl bond derived from (a) methyl chloride and (b) chloroform.[5] If the C_{ar}–C–Cl bond angle is assumed to be 110°, and with appropriate allowance for an exaltation of molar refraction, ΔR_D, of 0·7 cm³, molar Kerr constants ($\times 10^{12}$) are calculable as (a) +122, and (b) +70. Further calculations, utilizing the C–Cl bond polarizabilities from methyl chloride, have been performed for C_{ar}–C–Cl bond angles of 115° and 120°; results then emerge as +136 and +151, respectively. The calculated molar Kerr constants are all considerably lower than that observed (+172), and this probably can be attributed to exaltation effects operating within the molecule. Support for this contention can be drawn from the fact that the dipole moment of benzotrichloride (2·03 D) is considerably larger than the moment of methyl chloroform (1·70 D).[4] This difference is in accord with the known mesomeric and inductive effects associated with aromatic CX_3 groups.[6,7] Both of these electronic effects probably would lead to an augmented longitudinal polarizability for the C_{ar}–C bond, which could cause the experimental molar Kerr constant to be larger than that calculated.

[1] Izsák, D., and Le Fèvre, R. J. W., *J. chem. Soc.* B, 1966, 102.

[2] Le Fèvre, C. G., and Le Fèvre, R. J. W., *Rev. pure appl. Chem.*, 1955, **5**, 261.

[3] McClellan, A. L., "Tables of Experimental Dipole Moments." (Freeman: San Francisco 1963.)

[4] Le Fèvre, R. J. W., and Ritchie, G. L. D., *J. chem. Soc.*, 1963, 4933.

[5] Le Fèvre, R. J. W., *Adv. phys. org. Chem.*, 1965, **3**, 1.

[6] Sutton, L. E., *Proc. R. Soc.* A, 1931, **133**, 668.

[7] Gould, E. S., "Mechanism and Structure in Organic Chemistry." p. 218. (Holt, Rinehart, & Winston: New York 1959.)

Benzotrifluoride

A similar divergence between observed and calculated molar Kerr constants occurs with benzotrifluoride, for which $_\infty(_\mathrm{m}K_2)$ and R_D are recorded as $+215 \times 10^{-12}$ and $31 \cdot 2$ cm^3, respectively.[4] Semi-axes for the C–F bond[5] as deduced by Le Fèvre

TABLE 1

INCREMENTAL KERR EFFECTS ETC. FOR SOLUTIONS OF BENZOTRICHLORIDE AND
BENZAL CHLORIDE IN CARBON TETRACHLORIDE AT 25°

Benzotrichloride

$10^5 w_2$	1574	2791	4415	6959	7788	9093
$10^4 \Delta\epsilon$	687	1225	1946	3078	3449	4041
$-10^5 \Delta d$	359	662	1023	1601	1794	2106
$10^4 \Delta n$	19	36	56	83	91	109
$10^5 w_2$	388	800	1160	1602	2252	2798
$10^{11} \Delta B$	323	652	964	1327	1855	2359

whence $\Sigma\Delta\epsilon/\Sigma w_2 = 4 \cdot 42$; $\Sigma\Delta d/\Sigma w_2 = -0 \cdot 231$; $\Sigma\Delta n/\Sigma w_2 = 0 \cdot 121$; $\Sigma\Delta n^2/\Sigma w_2 = 0 \cdot 35$;
$$10^7 \Sigma\Delta B/\Sigma w_2 = 8 \cdot 31$$

Benzal Chloride

$10^5 w_2$	902	2162	2883	4017	4053	5556	6139	7256
$10^4 \Delta\epsilon$	493	1187	1577	2203	2221	3049	3379	3988
$-10^4 \Delta d$	37	87	111	170	167	215	252	287
$10^5 w_2$	902	1396	2162	3269	4017	4665	6139	6570
$10^4 \Delta n$	11	18	26	40	49	59	75	81
$10^5 w_2$	691	1396	1587	2163	3085	3269	4665	6570
$10^{11} \Delta B$	627	1233	1439	1928	2777	2932	4273	6086

whence $\Sigma\Delta\epsilon/\Sigma w_2 = 5 \cdot 49$; $\Sigma\Delta d/\Sigma w_2 = -0 \cdot 40$; $\Sigma\Delta n/\Sigma w_2 = 0 \cdot 123$; $\Sigma\Delta n^2/\Sigma w_2 = 0 \cdot 360$;
$$10^7 \Sigma\Delta B/\Sigma w_2 = 9 \cdot 09$$

TABLE 2

POLARIZATIONS, REFRACTIONS, DIPOLE MOMENTS, AND MOLAR KERR CONSTANTS OF BENZOTRI-
CHLORIDE AND BENZAL CHLORIDE AT 25°

	$\alpha\epsilon_1$	β	γn_1^2	$_\infty P_2$ (cm^3)	R_D (cm^3)	μ (D)*	γ	δ	$10^{12}{}_\infty(_\mathrm{m}K_2)$
PhCCl$_3$	$4 \cdot 42$	$-0 \cdot 15$	$0 \cdot 35$	$132 \cdot 6$	$46 \cdot 2$	$2 \cdot 03$	$0 \cdot 083$	$+119$	$+172$
PhCHCl$_2$	$5 \cdot 49$	$-0 \cdot 25$	$0 \cdot 36$	$130 \cdot 7$	$41 \cdot 2$	$2 \cdot 07$	$0 \cdot 084$	$+130$	$+155$

* Assuming $_\mathrm{D}P = 1 \cdot 05\ R_\mathrm{D}$.

and Le Fèvre from data for methyl fluoride have been used in calculating molar Kerr constants, and the C_{ar}–C–F bond angle has been assumed to be tetrahedral. If the refraction of the C–F bond in this environment is taken as $1 \cdot 88$ cm^3 (as found

by Macey[8] for n-alkyl esters of trifluoroacetic acid), the calculated molar refraction is $31 \cdot 4$ cm[3], so that there is apparently no exaltation of refraction. The molar Kerr constant then emerges as $+136 \times 10^{-12}$, which is far removed from the experimental value.

The principal molecular polarizabilities for nine halogen-substituted derivatives of benzotrifluoride have been deduced by Cherry, Hobbs, and Strobel[9] from the experimental molar Kerr constants of these compounds. However, these principal polarizabilties must be regarded as approximate values only, because of the assumptions which the authors have made with regard to the magnitude and direction of the molecular dipole moment, and the location of the principal axes. The only member of the series which is without such uncertainties is p-chlorobenzotrifluoride. The dipole moment of this molecule is recorded as $1 \cdot 22$ D,[10] and using the C–F bond semi-axes derived from methyl fluoride together with the usual semi-axes for the p-chlorophenyl group,[5] the calculated molar Kerr constant (without allowance for exaltation) is $+86 \times 10^{-12}$, which is close to that observed ($+93 \times 10^{-12}$).

Benzal Chloride

Two additional uncertainties arise in the case of benzal chloride: both the precise direction of action of the dipole moment and the conformation of the molecule are unknown. The various possible molecular conformations can be defined by the angle, ϕ, between the C_{ar}–C–H plane and that of the benzene ring. In calculating molar Kerr constants it is assumed that the dipole moment acts along the bisector of the Cl–C–Cl angle in the Cl–C–Cl plane. With the C–Cl bond semi-axes from methyl chloride, molar Kerr constants ($\times 10^{12}$) for the conformations defined by $\phi = 0°$ and $\phi = 90°$ emerge as $+98$ and -73, respectively. These values are not greatly changed by the use of alternative C–Cl bond polarizabilities, or by making allowance for exaltation of molar refraction. Neither estimate approaches the experimental value ($+155$), but it is clear that the most probable single effective conformation of the molecule is represented by $\phi = 0°$.

Conclusion

We conclude that because of quantitatively unpredictable exaltation effects within the molecules, the experimental molar Kerr constants of benzotrichloride and benzal chloride are not reconcilable with the values calculated from the appropriate bond and group polarizabilities. Additional information, which would make possible the direct evaluation of the principal polarizabilities of such molecules, could be obtained from measurements of the depolarization factors for light scattered by dilute solutions of these substances.[11]

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[9] Cherry, L. V., Hobbs, M. E., and Strobel, H. A., *J. phys. Chem.*, 1957, **61**, 465.

[10] Myers, A. L., and De Vries, T., *J. Am. chem. Soc.*, 1951, **73**, 1813.

[11] Le Fèvre, R. J. W., and Rao, B. P., *J. chem. Soc.*, 1957, 3644.