

944. Molecular Polarisability. Molar Kerr Constants and Dipole Moments of Five Haloform Molecules as Solutes in Benzene.

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Molar Kerr constants and apparent dipole moments are recorded for 1,1,1-trichloroethane, bromoform, and iodoform in benzene at 25°, and therefrom estimates are made of the principal semi-axes of the C-Cl, C-Br, and C-I bonds. For C-Cl and C-Br the values lie between those previously drawn from methyl and t-butyl halides; with C-I they are close to those from methyl iodide. The C-Cl data from Me·CCl₃ are satisfactorily applicable to NO₂·CCl₃. The mK of Me·CHCl₂ can be calculated *a priori* if the resultant moment acts at 23–29° to the major molecular-polarisability axis. Apparatus for the photoelectric measurement of birefringence is outlined.

THE present measurements were initiated to extend, and test, existing information^{1a} concerning the anisotropic polarisabilities of bonds, particularly those between carbon and halogen in simple aliphatic compounds. The substances examined are listed in Tables 1 and 2.

EXPERIMENTAL

Solutes.—Liquids were dried and redistilled (at *ca.* 760 mm., except for bromoform) immediately before use; drying agents and collection temperatures were: for 1,1,1-trichloroethane, calcium chloride and 75°; for chloropicrin, magnesium sulphate and 112°; for bromoform, calcium chloride for 24 hr. and 57°/25 mm.; for ethylidene dichloride, calcium chloride for 24 hr. and 57°; and for benzotrifluoride, magnesium sulphate and 102°. Iodoform, recrystallised from ethanol, had *m. p.* 119°.

Apparatus.—Dielectric constants have been determined with apparatus as in ref. 2, associated procedures giving polarisations being standard.^{1b} Kerr effects have been recorded in two ways: (a) visually, by using the Szivessy-Dierkesmann mica half-shade compensator and other arrangements detailed in ref. 3, and (b) photometrically, with a modified version of the equipment for technique (a). In terms of Fig. 1 of ref. 3(a) the alterations involved are: the substitution of a whole-plate compensator for H, the replacement of the telescope T by an RCA 931-A photomultiplier-amplifier combination, and the insertion of a light-chopper between the lens L and the polarising prism P. In one rotation of the compensator the four settings corresponding to minima in the amplifier output meter can be read to 0.01°. A general expression for the light intensity in a beam which has passed successively through a polariser, two doubly refracting plates, and an analyser crossed with the polariser, has been written by Jerrard (equation 7a in ref. 4). In our apparatus the Kerr cell is equivalent to one of the plates having a principal vibration direction at 45° to the vibration direction of the polariser; the quoted equation therefore becomes:

$$I = \sin^2(\delta/2) + \sin^2 2\theta \sin^2(\Delta/2) + 2 \sin 2\theta \sin(\Delta/2) \sin(\delta/2) [\cos(\delta/2) \cos(\Delta/2) - \sin(\delta/2) \sin(\Delta/2) \sin 2\theta],$$

where δ is the retardation produced by the electric birefringence, θ is the azimuth of the compensator plate, and Δ is its retardation. At the extinction azimuths, I is a minimum, *i.e.*, $dI/d\theta = 0$; accordingly we have, by differentiation, $\tan \delta = -2 \sin 2\theta \tan(\Delta/2)$. If before and after application of voltage to the Kerr cell the settings of the compensator found to cause intensity minima are, respectively, angles a, b, c, d , and a', b', c', d' , then θ is taken as the mean value of $a - a', b - b'$, etc. For the measurements in Table 1, the compensator factor,

¹ Le Fèvre, (a) *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1; (b) "Dipole Moments," Methuen, London, 3rd edn., 1953, Chapter 2.

² Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

³ Le Fèvre and Le Fèvre, (a) *J.*, 1953, 4041; (b) *J.*, 1954, 1577; (c) *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 262; (d) Chap. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ. Inc., New York, 3rd edn., Vol. I, p. 2459.

⁴ Jerrard, *J. Opt. Soc. Amer.*, 1948, **38**, 35.

TABLE 1.
Incremental Kerr effects, dielectric constants, etc., for solutions in benzene at 25°.

| 1,1,1-Trichloroethane | | | | | | | | | | |
|---|------|------|------|------|--------|--------|------|------|--------|------|
| $10^5 w_2$... | 1746 | 2880 | 3763 | 5711 | 6960 | 9088 | | | | |
| $10^4 \Delta \epsilon$... | 363 | 603 | 800 | 1258 | 1553 | 2081 | | | | |
| $10^4 \Delta d$... | 52 | 86 | 112 | 170 | 210 | 275 | | | | |
| $10^5 w_2$... | 1361 | 1936 | 2523 | 3531 | 4009 | 6257 | 6440 | 7879 | 10,799 | |
| $-10^{11} \Delta B$... | 117 | 171 | 222 | 319 | 331 | 513 | 582 | 696 | 924 | |
| $-10^4 \Delta n$... | 5 | 9 | 10 | 16 | 17 | 28 | 28 | 35 | 48 | |
| whence $\sum \Delta \epsilon / \sum w_2 = 2.21$, $\sum \Delta d / \sum w_2 = 0.300$, $\sum \Delta B / \sum w_2 = -0.866 \times 10^{-7}$, $\sum \Delta n / \sum w_2 = -0.044$. | | | | | | | | | | |
| Nitrochloroform | | | | | | | | | | |
| $10^5 w_2$... | 1421 | 2122 | 2132 | 2533 | 3511 | 4619 | | 6012 | 6290 | |
| $10^4 \Delta \epsilon$... | 326 | — | 462 | — | 767 | 985 | | 1345 | 1384 | |
| $10^4 \Delta d$... | — | 89 | — | 103 | 144 | 192 | | 251 | 263 | |
| $10^5 w_2$... | 1424 | 2109 | 2772 | 3429 | 5225 | 7582 | | | | |
| $-10^{11} \Delta B$... | 71 | 120 | 183 | 191 | 331 | 431 | | | | |
| $-10^4 \Delta n$... | 4 | 6 | 8 | 9 | 12 | 18 | | | | |
| whence $\sum \Delta \epsilon / \sum w_2 = 2.20$, $\sum \Delta d / \sum w_2 = 0.475$, $\sum \Delta B / \sum w_2 = -0.59 \times 10^{-7}$, $\sum \Delta n / \sum w_2 = -0.025$. | | | | | | | | | | |
| Bromoform | | | | | | | | | | |
| $10^5 w_2$... | 3101 | 3616 | 3625 | 3975 | 5095 | 6048 | 6238 | 6261 | 7492 | 9851 |
| $-10^{11} \Delta B$... | 217 | 270 | 264 | 276 | 354 | 452 | 487 | 447 | 560 | 751 |
| $10^4 \Delta n$... | 85 | — | 100 | 115 | 135 | 170 | — | 175 | 220 | 285 |
| whence $\sum \Delta B / \sum w_2 = -0.73 \times 10^{-7}$, $\sum \Delta n / \sum w_2 = 0.029$. | | | | | | | | | | |
| Iodoform | | | | | | | | | | |
| $10^5 w_2$... | 2599 | 2592 | 3494 | 7045 | 7911 | 9279 | | | | |
| $10^4 \Delta \epsilon$... | 103 | 116 | 136 | 280 | 307 | 365 | | | | |
| $10^5 w_2$... | 1277 | 1376 | 2209 | 2226 | 2443 | 2599 | 3014 | 3191 | 4938 | 5506 |
| $10^4 \Delta d$... | 86 | 93 | 149 | 152 | 168 | 178 | 205 | 220 | 344 | 386 |
| $10^5 w_2$... | 3494 | 5370 | 6414 | 7590 | 7832 | 8442 | 9279 | | | |
| $10^4 \Delta n$... | 25 | 35 | 40 | 50 | 51 | 55 | 60 | | | |
| $10^5 w_2$... | 4164 | 6290 | 6890 | 7840 | 10,258 | 12,931 | | | | |
| $-10^{10} \Delta B$... | 7 | 12 | 16 | 15 | 19 | 25 | | | | |
| whence $\sum \Delta \epsilon / \sum w_2 = 0.393$, $\Delta d = 0.669 w_2 + 0.565 w_2^2$, $\sum \Delta n / \sum w_2 = 0.065$, $\sum \Delta B / \sum w_2 = -0.19_4 \times 10^{-7}$. | | | | | | | | | | |
| 1,1-Dichloroethane | | | | | | | | | | |
| $10^5 w_2$... | 857 | 1176 | 1946 | 2367 | 3586 | 3981 | | | | |
| $10^4 \Delta \epsilon$... | 356 | 454 | 789 | 962 | 1442 | 1593 | | | | |
| $10^4 \Delta d$... | 20 | 25 | 42 | 52 | 79 | 87 | | | | |
| $-10^4 \Delta n$... | 5 | 8 | 11 | 15 | 22 | 24 | | | | |
| $10^5 w_2$... | 1541 | 2103 | 3051 | 5044 | 6229 | 6345 | 7597 | 8897 | 12,900 | |
| $10^{11} \Delta B$... | 34 | 60 | 88 | 137 | 134 | 154 | 183 | 251 | 357 | |
| whence $\sum \Delta \epsilon / \sum w_2 = 4.02$, $\sum \Delta d / \sum w_2 = 0.219$, $\sum \Delta n / \sum w_2 = -0.061$, $\sum \Delta B / \sum w_2 = 0.26 \times 10^{-7}$. | | | | | | | | | | |
| Benzotrifluoride | | | | | | | | | | |
| $10^5 w_2$... | 920 | 1296 | 1799 | 1838 | 2172 | 2344 | 2818 | 2997 | 4133 | |
| $10^4 \Delta \epsilon$... | 454 | 615 | 808 | 873 | 1004 | 1119 | 1314 | 1409 | 1962 | |
| $10^4 \Delta d$... | 18 | 28 | 37 | 38 | 45 | 49 | — | 63 | 88 | |
| $-10^4 \Delta n$... | 6 | 10 | — | 13 | — | 17 | — | 22 | 30 | |
| $10^{10} \Delta B$... | 75 | — | 154 | 157 | 183 | — | 242 | 258 | — | |
| whence $\sum \Delta \epsilon / \sum w_2 = 4.70$, $\sum \Delta d / \sum w_2 = 0.209$, $\sum \Delta n / \sum w_2 = -0.073$, $\sum \Delta n^2 / \sum w_2 = -0.217$, $\sum \Delta B / \sum w_2 = 8.52 \times 10^{-7}$. | | | | | | | | | | |

TABLE 2.
Polarisations, refractions, dipole moments, and molar Kerr constants in benzene.

| Solute | $\alpha \epsilon_1$ | β | ∞P_2 (c.c.) | R_D (c.c.) | μ (D) | γ | δ | $10^{12} \kappa$ (mK_2) |
|-----------------------------------|---------------------|---------|---------------------|--------------|-----------|----------|----------|-----------------------------|
| Me·CCl ₃ ... | 2.21 | 0.344 | 85.30 | 26.20 * | 1.70 | -0.029 | -2.11 | -24.7 |
| NO ₂ ·CCl ₃ | 2.20 | 0.475 | 97.45 | 26.53 | 1.86 | -0.017 | -1.44 | -23.9 |
| CHBr ₃ ... | 0.538 † | 0.706 † | — | — | 1.02 † | 0.019 | -1.79 | -33.8 |
| CHI ₃ | 0.393 | 0.766 | 60.52 | 45.52 | 0.86 | 0.043 | -0.473 | -14.0 |
| Me·CHCl ₂ | 4.02 | 0.251 | 100.14 | 21.09 * | 1.96 | -0.041 | 0.634 | -3.4 |
| Ph·CF ₃ ... | 4.70 | 0.239 | 167.1 | 31.2 | 2.56 | -0.049 | 20.78 | +215 |

* From Vogel, *J.*, 1948, 1850. † From Buckingham and Le Fèvre, *J.*, 1953, 3432.

tan $\Delta/2$, has been obtained from observations on pure carbon tetrachloride and benzene in a cell of known dimensions in conjunction with our standard values^{3b} of 0.070×10^{-7} and 0.410×10^{-7} for the Kerr constants for these liquids at 25° with sodium light.

Results.—These are listed in usual form in Tables 1 and 2. The symbols used are those previously explained in refs. 1(b), 2, and 3; they have been recently summarised in ref. 5.

DISCUSSION

Visual and Photometric Techniques Compared.—As Table 1 contains many of the first ΔB 's determined photometrically in these laboratories, it is relevant to mention that most of the solutes have also been separately examined in benzene by the older visual technique, and that results by both routes have satisfactorily fitted common $\Delta B-w_2$ curves. Experience shows photometric to be preferable to visual measurement; it is superior in speed and precision, particularly when small ΔB 's are concerned, and, of course, it avoids the eye-fatigue associated with the half-shade matching method hitherto used here.

The last advantage has recently been secured by Cherry *et al.*⁶ with a photomultiplier-containing modification of des Coudres's classical apparatus. Although we think that a second cell must cause more alignment problems than a whole-plate compensator, it is clear that observations by Cherry *et al.* are on a par with ours. Benzotrifluoride has been included to provide a direct comparison; we find $\infty(mK_2)$ to be $+215 \times 10^{-12}$ at 25° ; Cherry *et al.*⁶ reported $+206 \times 10^{-12}$ at 30.4° . These magnitudes have approximately the relationship expected: at 25° , $\theta_1 + \theta_2$ is 51.1×10^{-35} ; if θ_2 is *ca.* 48×10^{-35} (as seems likely), then a temperature rise of 5.4° should diminish the mK by about 7×10^{-12} .

Carbon-Halogen Polarisabilities in Me·CCl₃, CHBr₃, and CHI₃.—These structures should, from their symmetry,⁷ have molecular polarisability ellipsoids of revolution (*i.e.*, specifiable by semi-axes b_1 and $b_2 = b_3$). Since the resultant dipole moments act in directions which correspond to the b_1 's, the differences $b_1 - b_2$ can be computed from the $\infty(mK_2)$'s and μ 's of Table 2. The sums $b_1 + 2b_2$ are drawn from the related electronic polarisations. Refraction-dispersion data needed for the calculation of ${}_E P$ exist⁸ only for 1,1,1-trichloroethane and bromoform; for iodoform we therefore use the "bond ${}_E P$'s" tabulated by Le Fèvre and Steel⁹ (and justify so doing by noting that Vogel's R_λ 's for liquid chloroform and bromoform give, on extrapolation, ${}_E P$'s of 20.83—20.84 and 28.81—28.82 c.c., respectively, whilst the Le Fèvre-Steel bond values add up to 20.73 c.c. for chloroform and 28.84 c.c. for bromoform; by analogy the calculated ${}_E P$ for iodoform, *viz.* 43.40 c.c., seems reasonable). Molecular semi-axes then emerge as in Table 3.

TABLE 3.

Calculation of semi-axes * for Me·CCl₃, CHBr₃, and CHI₃.

| | ${}_E P$ (c.c.) | $b_1 - b_2$ | $b_1 + 2b_2$ | b_1 | $b_2 = b_3$ |
|---------------------------|-----------------|-------------|--------------|-------|-------------|
| Me·CCl ₃ | 25.58 | -0.078 | 3.042 | 0.962 | 1.040 |
| CHBr ₃ | 28.82 | -0.347 | 3.427 | 0.911 | 1.258 |
| CHI ₃ | 43.40 | -0.194 | 5.160 | 1.590 | 1.785 |

* Here, and elsewhere, polarisabilities are quoted in 10^{-23} c.c. units.

The halogen-carbon-halogen angles θ in these three molecules are cited in ref. 7 (M 127, M 105, and M 106); the angles ϕ made by the carbon-halogen bonds with the b_1 directions then follow from $\sin \phi = \sin (\theta/2)/\cos 30^\circ$. The b_1 's of Table 3, with the appropriate polarisabilities^{1a} for C-C and/or C-H, afford estimates of $b_L^{CX} \cos^2 \phi + b_T^{CX} \sin^2 \phi$ (where

⁵ Le Fèvre and Sundaram, *J.*, 1962, 1494.

⁶ Cherry, Hobbs, and Strobel, *J. Phys. Chem.*, 1957, **61**, 465.

⁷ Sutton *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.*, No. 11, 1958.

⁸ Vogel, *J.*, 1948, 1850.

⁹ Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.

b_L^{CX} and b_T^{CX} are the longitudinal and transverse polarisabilities of the C-X links). Other equations, involving $b_L^{CX} + 2b_T^{CX}$, are also available from the electronic polarisation of carbon tetrachloride (calculated as 25.89 c.c. from Vogel⁸) and, since no dispersion data exist for the refractivities of tetrabromo- or tetraiodo-methane, from the ϵP 's of the C-Br and C-I bonds.⁹ Semi-axes of the C-X bond ellipsoids accordingly appear as in Table 4.

For C-Cl and C-Br the new values are between those previously deduced from methyl and t-butyl halides; for C-I they are close to those from methyl iodide [cf. Table 1 of ref. 1(a) for summary]. The longitudinal polarisabilities of the C-Cl and C-I bonds can be related¹⁰ to C-X stretching frequencies if internuclear separations of 1.79 and 2.09 Å are assumed (Table 5); such r_{CX} 's are within the ranges cited in ref. 7. In bromoform, with a ν_{CBr} of 656 cm.⁻¹, r_{CBr} needs to be 1.96 Å to produce b_L^{CBr} of 0.55; the upper limit for

TABLE 4.
Derivations of b_L and b_T for the C-Cl, C-Br, and C-I bonds.

| θ | ϕ | $b_L^{CX} + 2b_T^{CX}$ | b_L^{CX} | b_T^{CX} |
|-----------------------|---------|------------------------|------------|------------|
| 1,1,1-Trichloroethane | | | | |
| 110.4° | 71° 28' | 0.769 ₈ | 0.352 | 0.209 |
| Bromoform | | | | |
| 113.5° | 74° 56' | 1.077 ₈ | 0.553 | 0.262 |
| 110.8° | 71° 54' | 1.077 ₈ | 0.576 | 0.251 |
| Iodoform | | | | |
| 113.0° | 74° 20' | 1.655 | 0.661 | 0.497 |

r_{CBr} is recorded,⁷ however, as 1.933 Å. Were $b_L^{CBr} + 2b_T^{CBr}$ in Table 4 lowered to 1.044₆, a b_L^{CBr} of 0.51 would follow, but then the electronic polarisation for the C-Br bond becomes 8.785 c.c. or *ca.* 0.935 of the R_D^{CBr} (namely, 9.39 c.c.) given by Vogel, Cresswell, Jeffrey, and Leicester.¹¹ The factor 0.935 is unusually small: the ratios of ϵP (from ref. 9) to R_D (from ref. 8) for C-Cl, C-Br, and C-I are, respectively, 0.977, 0.965, and 0.953; for carbon tetrachloride⁸ the ratio is 25.89/26.45 = 0.9788; the refractivity measurements

TABLE 5.
Predictions of longitudinal polarisabilities from stretching frequencies and internuclear distances.

| Bond | ν (cm. ⁻¹) | r_{CX} (Å) | b_L^{CX} (calc.) | Range of r_{CX} values in ref. 7 |
|-----------|----------------------------|--------------|--------------------|------------------------------------|
| C-Cl..... | 725 * | 1.79 | 0.35 | 1.74—1.795 |
| C-Br..... | 656 † | 1.93 (1.96) | 0.51 (0.55) | 1.89—1.933 |
| C-I..... | 577 ‡ | 2.09 | 0.66 | 2.08—2.16 |

* Pitzer and Hollenberg, *J. Amer. Chem. Soc.*, 1953, **75**, 2220. † Long and Milner, *Trans. Faraday Soc.*, 1958, **54**, 1. ‡ Hexter and Cheung, *J. Chem. Phys.*, 1956, **24**, 1188.

on carbon tetrabromide in carbon tetrachloride by Le Fèvre, Le Fèvre, and Rao¹² correspond to an R_D of 37.38 c.c., of which the ϵP calculated from ref. 9 is 97%. The sum 1.077₈ used in Table 4 does not therefore seem excessively large. The difficulty of reconciling Tables 4 and 5 may in considerable part be due to shortcomings in the Le Fèvre equation¹⁰ [we note that in chloroform, having $\nu_{CCl} = 762$ cm.⁻¹, b_L^{CCl} calc. for an r_{CCl} of 1.77 Å (as given in ref. 7) is 0.36 against 0.399 from Kerr effect measurements¹³; a b_L^{CCl} of 0.399 corresponds to an r_{CCl} of 1.79₈ Å, *i.e.*, a 1.7% change in r_{CCl} alters b_L^{CCl} by 11%], but imperfections in the assumptions basic to an additive treatment of polarisability [see p. 299 of ref. 3(c)] probably also affect the situation.

¹⁰ Le Fèvre, *Proc. Chem. Soc.*, 1959, 363.

¹¹ Vogel, Cresswell, Jeffrey, and Leicester, *J.*, 1952, 514.

¹² Le Fèvre, Le Fèvre, and Rao, *J.*, 1956, 708.

¹³ Bramley, Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 1183.

Anisotropic Polarisabilities of Hexachloroethane, Chloropicrin, and Ethylidene Dichloride.—The fact that the anisotropy of a bond varies somewhat with molecular environment has been discussed before [p. 3 of ref. 1(a)] and the viewpoint was taken that b_L 's, b_T 's, and b_V 's, such as those in Table 4 of this paper (or Table 1 of ref. 1a), although empirical, should be safely useable with structures analogous to those from which they have been deduced. However, choice of analogues is not always obvious; for instance, with hexachloroethane and chloropicrin, is it more appropriate to use data drawn from chloroform or 1,1,1-trichloroethane?

Le Fèvre and Le Fèvre^{3b} record ${}_{\infty}(M K_2)$ of hexachloroethane (in carbon tetrachloride) as 4.60×10^{-12} ; ${}_{\infty}P$ from ref. 9 is 39.42 c.c.; with ${}_D P = {}_{\infty}P_2 = 45.1$ c.c., $b_1(C_2Cl_6)$ and $b_2(C_2Cl_6) = b_3(C_2Cl_6)$ become 1.36₃ and 1.66₂, respectively [in ref. 3(b), ${}_{\infty}P$ was taken as 39.6 c.c. from $R(C_2HCl_5)$]. Sutton's compilation⁷ (entry M 119) gives the ClCCl angle in C_2Cl_6 as $108.75^\circ \pm 1.5^\circ$. Use of this or the tetrahedral angle, together with C-Cl semi-axes from (a) chloroform or (b) 1,1,1-trichloroethane yields results as follow:

| | b_L^{Cl} | b_T^{Cl} | $\angle ClCCl = 108.75^\circ$ | | | $\angle ClCCl = 109^\circ 28'$ | | |
|-----|------------|------------|-------------------------------|----------------|--------------|--------------------------------|----------------|--------------|
| | | | $b_1(C_2Cl_6)$ | $b_2(C_2Cl_6)$ | $10^{12} mK$ | $b_1(C_2Cl_6)$ | $b_2(C_2Cl_6)$ | $10^{12} mK$ |
| (a) | 0.399 | 0.185 | 1.45 | 1.66 | 2.3 | 1.36 | 1.71 | 6.4 |
| (b) | 0.352 | 0.209 | 1.52 | 1.63 | 0.63 | 1.45 | 1.66 | 2.3 |

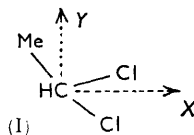
With the smaller ClCCl angle, the (a) set appears slightly the more satisfactory, but as the molar Kerr constant involved is small and probably contains a θ_3 term,¹² a definite conclusion is not justified.

The case of chloropicrin is clearer. If θ is 110.8° (M 106 in ref. 7), μ is 1.86 D (Table 2), and the polarisabilities of the C-NO₂ unit are as given by Le Fèvre and Rao,¹⁴ we have:

| C-Cl semi-axes | $b_1(CCl_3 \cdot NO_2)$ | $b_2(CCl_3 \cdot NO_2)$ | $b_3(CCl_3 \cdot NO_2)$ | $10^{12} mK$ (calc.) |
|----------------|-------------------------|-------------------------|-------------------------|----------------------|
| Set (a) | 0.96 | 1.12 ₅ | 1.07 ₅ | -52.4 |
| Set (b) | 1.01 | 1.10 | 1.05 | -24.5 |

The observed mK (-23.9×10^{-12}) agrees better with C-Cl semi-axes as (b) than as (a).

Calculations *a priori* for ethylidene chloride are complicated because the direction of action of $\mu_{res.}$ is unknown. Adopting the geometry given in M 130 of ref. 7 (*i.e.*, the angles ClCCl and CClC are 110° and 112.5° , respectively), we have computed the semi-axes to be expected for compound (I) if the polarisabilities of the C-Cl links are as (a) or (b) above. Setting arbitrary reference axes with CX bisecting the ClCCl angle and CZ parallel to the Cl...Cl line, we find:



| C-Cl semi-axes | b_1 | b_2 | b_3 | Angle between b_1 and CX in YCX plane |
|----------------|-------|-------|-------|---|
| Set (a) | 0.835 | 0.684 | 0.940 | $13^\circ 49'$ |
| Set (b) | 0.840 | 0.728 | 0.893 | $19^\circ 55'$ |

With $\mu_{res.}$ taken along CX both these solutions yield positive mK 's (6.7×10^{-12} from the first, 5.3×10^{-12} from the second). Actually, mK as measured is small and negative; it can be achieved if $\mu_{res.}$ acts at $23^\circ 48'$ or $29^\circ 12'$ to b_1 in the two groups, respectively, of semi-axes just quoted. Whether $\mu_{res.}$ should be considered as rotated, in the YCX plane, clockwise or anti-clockwise is problematical; we favour the latter view since $\mu(CH_2Cl_2)$ is less than $\mu(Me \cdot CHCl_2)$, which suggests that $\mu(Me \cdot C)$ exceeds $\mu(H \cdot C)$.

Previous Measurements.—The estimates of dipole moments given in Table 2 are in substantial agreement with recorded values (see Wesson¹⁵ for chloropicrin, bromoform,

¹⁴ Le Fèvre and Rao, *J.*, 1958, 1465.

¹⁵ Wesson, "Tables of Electric Dipole Moments," Technology Press, M.I.T., 1948.

iodoform, and ethylidene chloride, and ref. 16 for benzotrifluoride). For 1,1,1-trichloroethane, the ∞P_2 's of this paper (85.3 c.c.) and those recorded by Sutton¹⁷ (83.2—84.3 c.c.) are very close, the apparent disparities between the moments deduced (1.70 and 1.57 D) being due to the molecular refractions used.

Apart from benzotrifluoride⁶ (mentioned above), the only previously determined $\infty(mK_2)$ is that of ethylidene chloride, for which Sachasse¹⁸ gives -3.9×10^{-12} in carbon tetrachloride at 4°. The International Critical Tables¹⁹ give the Kerr constants B of chloropicrin and bromoform, relative to carbon disulphide, as -0.557 and -0.86 , respectively, at 14.2° and 14.6°. Lippmann²⁰ examined two solutions each of bromoform and iodoform in benzene and observed that these solutes reduced the positive electric birefringence of the solvent.

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¹⁶ Roberts, Webb, and McElhill, *J. Amer. Chem. Soc.*, 1950, **72**, 408; Freiser, Hobbs, and Gross, *ibid.*, 1949, **71**, 111; Brown and De Vries, *ibid.*, 1951, **73**, 1811; Bond and Smith, *J.*, 1956, 4507.

¹⁷ Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668.

¹⁸ Sachasse, *Phys. Z.*, 1935, **36**, 357.

¹⁹ International Critical Tables, McGraw-Hill, New York, 1st edn., 1930, Vol. VII, p. 111.

²⁰ Lippmann, Diss., Leipzig, 1911, *Z. Elektrochem.*, 1911, **17**, 15.
