1306. *Molecular Polarisability. Apparent Conformations of Dichlorodiphenyltrichloroethane (D.D.T.) and Two Derivatives in Non-polar Solvents*

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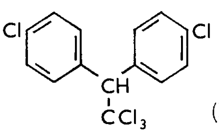
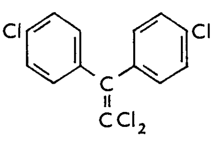
Molar Kerr constants and apparent dipole moments at 25° are recorded for dichlorodiphenyltrichloroethane (D.D.T.) in carbon tetrachloride and benzene, and for its dehydrochlorinated and chlorinated derivatives in carbon tetrachloride. Provided that only equal rotations of the two *p*-chlorophenyl groups be considered, agreement between observed and calculated molar Kerr constants is obtained when ϕ = *ca.* ± 40° (for I), *ca.* ± 50° (for II), and *ca.* ±55° (for III), where ϕ is defined such that $\phi = 0°$ when the *p*-chlorophenyl planes are perpendicular to the C_{Ar}–C(2)–C_{Ar} plane (for I and III) and parallel to the C(2)=C(1)Cl_2 plane (for II).

THE measurements here reported have been made to examine the apparent conformations, in non-polar media, of D.D.T. [1,1,1-trichloro-2,2-di(*p*-chlorophenyl)ethane] (I), its dehydrochlorinated derivative [1,1-dichloro-2,2-di(*p*-chlorophenyl)ethylene] (II), and its chlorinated derivative [1,1,1,2-tetrachloro-2,2-di-(*p*-chlorophenyl)ethane] (III).



(I)



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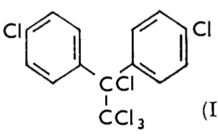

(III)

EXPERIMENTAL

Materials, Apparatus, etc.—Specimens of pure D.D.T. (m. p. 107·5—108·5°) and of its ethylene derivative (m. p. 88—89°) were kindly given by Imperial Industries (Australia and New Zealand Ltd.). A bulk supply of D.D.T. (m. p. 107·5—108·5°) was obtained by several recrystallisations from ethanol of "technical" D.D.T. powder. A sample of 1,1-dichloro-2,2-di-(*p*-chlorophenyl)ethylene (m. p. 88—89°) was prepared [1] by refluxing D.D.T. with ethanolic potassium hydroxide for 3 hr., extracting with ether, drying, and recrystallising several times from ethanol. The chlorination of (I) to 1,1,1,2-tetrachloro-2,2-di-(*p*-chlorophenyl)ethane, m. p. 93—96° (from carbon tetrachloride), was carried out by Mr. K. E. Calderbank to whom we are indebted.

Apparatus, techniques, symbols used, and methods of calculation have been described before.[2,3] The quantities $\Delta\varepsilon$, Δd, Δn, and ΔB are the differences found between the dielectric constants, densities, refractive indices, and Kerr constants, respectively, of carbon tetrachloride or benzene as solvent, and of solutions containing weight fractions w_2 of solute. Observations and results are summarised in Tables 1 and 2. When $w_2 = 0$, the following apply at 25°:

Solvent	ε	d_1	$(n_1)_D$	$10^7(B_1)_D$
Carbon tetrachloride	2·2270	$1{\cdot}5845_4$	1·4575	0·070
Benzene	2·2725	0·8738	1·4973	0·410

Previous Measurements.—Dipole-moment measurements of D.D.T. in benzene, giving estimates ranging from 0·91 to 1·12 D, are in the literature.[4] A moment of 1·12 D has been reported [5] in carbon tetrachloride as solvent. It is to be noted, however, that only one solution (of *ca.* 13% weight fraction) was used in obtaining this value. That the dipole moments reported here are lower than those in ref. 4 is mainly due to different approximations for the

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[1] H. L. Haller *et al.*, *J. Amer. Chem. Soc.*, 1945, **67**, 1599.

[2] R. J. W. Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953.

[3] C. G. Le Fèvre and R. J. W. Le Fèvre, (*a*) *Rev. Pure Appl. Chem.* (*Australia*), 1955, **2**, 261; (*b*) ch. XXXVI in " Physical Methods of Organic Chemistry," ed. A. Weissberger, Interscience, New York and London, 3rd edn., vol. I, p. 2459.

[4] A. L. McClellan, " Tables of Experimental Dipole Moments," Freeman, San Francisco, 1963.

[5] S. B. Kulkarni, *J. Indian Chem. Soc.*, 1949, **26**, 215.

TABLE 1

Incremental dielectric constants, densities, refractive indices, and Kerr constants of solutions at 25°

Solute: (I). *Solvent*: carbon tetrachloride

(I.C.I. gift sample)

$10^5 w_2$	419	934	1402	2301
$10^4 \Delta\varepsilon$	43	96	138	202
$10^4 \Delta n$	—	18	25	38
$-10^9 \Delta B$	$0{\cdot}0_6$	$0{\cdot}1_7$	$0{\cdot}2_4$	$0{\cdot}2_9$

(Recrystallised technical D.D.T.)

$10^5 w_2$	382	534	547	868	994	1153	1275	1585	1796	1856	1929
$10^4 \Delta\varepsilon$	—	—	—	99	—	—	146	—	—	—	—
$-10^5 \Delta d$	—	—	—	113	131	148	171	—	—	246	—
$10^4 \Delta n$	7	10	10	—	19	21	—	—	—	34	36
$-10^9 \Delta B$	—	—	—	—	—	—	—	$0{\cdot}2_4$	$0{\cdot}2_8$	—	—

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 1{\cdot}04_5$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}132$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}185$; $\Sigma\Delta B/\Sigma w_2 = -0{\cdot}15_7 \times 10^{-7}$

Solute: (I). *Solvent*: benzene

$10^5 w_2$	1198	1697	2042	2940	3525	—
$10^4 \Delta\varepsilon$	69	84	101	150	181	—
$10^5 w_2$	1183	1348	1834	2042	2693	3525
$10^5 \Delta d$	420	485	656	748	954	1284
$10^4 \Delta n$	9	10	15	17	20	28
$-10^9 \Delta B$	$0{\cdot}5_7$	$0{\cdot}6_5$	$0{\cdot}8_0$	$0{\cdot}9_2$	$1{\cdot}2_9$	$1{\cdot}5_3$

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}51_3$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}360$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}078$; $\Sigma\Delta B/\Sigma w_2 = -0{\cdot}45_6 \times 10^{-7}$

Solute: (II). *Solvent*: CCl_4

$10^5 w_2$	616	954	971	1527	2340
$10^4 \Delta\varepsilon$	38	51	—	92	137
$-10^5 \Delta d$	—	200	—	282	432
$10^4 \Delta n$	14	20	—	32	50
$10^9 \Delta B$	$0{\cdot}6_1$	$1{\cdot}1_8$	$1{\cdot}2_1$	$2{\cdot}1_0$	$3{\cdot}4_2$

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}58_5$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}19_0$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}213$; $\Sigma\Delta B/\Sigma w_2 = 1{\cdot}3_3 \times 10^{-7}$

Solute: (III). *Solvent*: CCl_4

$10^5 w_2$	1439	1787	1947	2459
$10^4 \Delta\varepsilon$	—	117	129	166
$10^5 \Delta d$	*ca.* 0 throughout			
$10^4 \Delta n$	29	37	40	49
$10^9 \Delta B$	—	$1{\cdot}4_9$	$1{\cdot}6_8$	$2{\cdot}0_8$

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}66_5$; $\Sigma\Delta d/\Sigma w_2 = 0$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}203$; $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}84_8 \times 10^{-7}$

TABLE 2

Polarisations, refractions, and molar Kerr constants in carbon tetrachloride at 25°

Solute	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) †	$10^{12}{}_\infty({}_mK_2)$
(I)	$1{\cdot}04_5$	−0·083	0·127	$-2{\cdot}2_4$	109·6	87·4	0·93	−4·7
(I) *	$0{\cdot}51_3$	0·412	0·052	$-1{\cdot}11_2$	105·3	85·7	0·86	−22·0
(II)	$0{\cdot}58_5$	−0·120	0·146	19·8	85·0	83·3	0	46·9
(III)	$0{\cdot}66_5$	0	0·139	12·1	98·7	92·6	*ca.* 0	36·8

* In benzene as solvent. † Assuming $_DP = 1{\cdot}05\, R_D$.

distortion polarisation. For example, a moment of 1·2 D in benzene at 20° has been reported,[6] where the total polarisation observed is 110·5 c.c. (compare 105·3 c.c./25° in Table 2), but $_DP$ is taken as 84·0 c.c. (compare 86·28 c.c. for R_D calculated from Vogel's tables [7]). McClellan [4] has no entry for the ethylene and chlorinated derivatives in carbon tetrachloride. Zero moments have, however, been obtained for (II) in benzene and in heptane, and a moment of 0·50 D has been claimed for (III) in heptane.

DISCUSSION

Molecule (I).—An estimate of the apparent conformation of D.D.T. can be obtained by calculating molar Kerr constants for various angles of rotation of the two *p*-chlorophenyl rings and comparing the calculated values with that observed. The group polarisability semi-axes are chosen as follows: $b_i(C{-}Cl_3)$ from 1,1,1-trichloroethane,[8] $b_i(C_6H_4Cl)$ from chlorobenzene, $b_i(C{-}H)$ from paraffin hydrocarbons, and $b_i(C{-}C)$ from cyclohexane.[9]

[6] H. Wild, *Helv. Chim. Acta*, 1946, **29**, 497.
[7] A. I. Vogel, W. T. Cresswell, G. H. Jeffrey, and J. Leicester, *J.*, 1952, 514.
[8] R. J. W. Le Fèvre and G. L. D. Ritchie, *J.*, 1963, 4933.
[9] R. J. W. Le Fèvre, *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.

If the molar refraction be calculated using Vogel's values [7] corresponding to these groups, the R_D is found to be in good agrement with that observed both in carbon tetrachloride and benzene. The reference àxes (Figure 1) are chosen as the sides of a cube with C(2) at the centre and the four groups at mutually opposite corners (since the preliminary assumption is made that the bond angles are tetrahedral). The angle of rotation ϕ of each of the p-chlorophenyl planes is defined as zero when b_3 for the C_6H_4Cl group is in the C_{Ar}–C(2)–C_{Ar} plane, and as positive for anticlockwise rotations of b_3 [seen from C(2) to C_{Ar}].

Values of the function, $_{\rm m}K(\phi_1, \phi_2)$, are calculated for equal rotations of the two C_6H_4Cl planes, both the symmetric case (where $\phi_1 = \phi_2$) and the antisymmetric one [where $\theta_1 = -\phi_2$, and the H–C(2)–C(1) plane of symmetry is no longer retained]. The results are summarised in Table 3, in which the resultant dipole moment is taken as 0·93 D, acting along the C(2)–H bond direction.

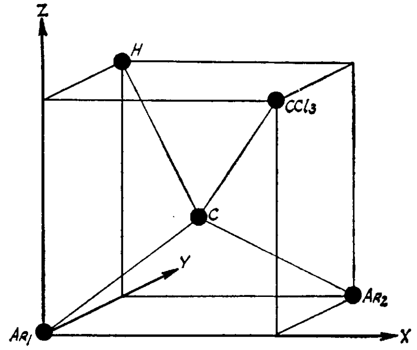

FIGURE 1

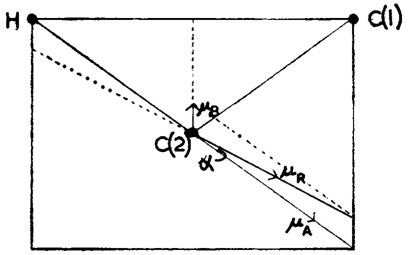

FIGURE 2

The effect of changing the magnitude of the resultant moment can be seen in the following. For $\phi_1 = \phi_2 = \pm 40°$, resultant moments of 0·86, 0·93, 0·96, 1·100, and 1·10 D give $10^{12}{}_{\rm m}K$ values of +2·7, −1·0, −2·6, −4·9, and −11·1, respectively; for $\phi_1 = -5°$, $\phi_2 = +5°$, and the same dipole moments, the calculated values of $_{\rm m}K$ are +0·2, −1·4, −2·2, −3·2, and −6·0, respectively.

The effect of changing the direction of the resultant dipole moment was investigated by varying this direction away from the H–C bond, in the H–C(2)–C(1) plane, by an angle α (Figure 2), the variation being such as to increase the direction cosine of μ with respect to the X-axis. For $\phi_1 = \phi_2 = \pm 40°$, and resultant moment 0·93 D, values of α = 0, 5, 10, and 35° gave $10^{12}{}_{\rm m}K$ = −1·0, −4·1, −7·1, and −17·5, respectively.

The third assumption involved in Table 3, *viz.*, that of tetrahedral bond angles, appears valid since a variation in the C_{Ar}–C(2)–C_{Ar} angle from tetrahedral to 115° (the plane of symmetry H–C(2)–C(1) being retained) has negligible effect on the calculated $_{\rm m}K$.

From Table 3, it can be seen that closest agreement between calculated and observed $_{\rm m}K$ values is obtained in the following cases. Assuming $\phi_1 = \phi_2$, ϕ_1 = *ca.* ±40°; assuming

TABLE 3

$_{\rm m}K(\phi_1, \phi_2)$ for D.D.T. (I), $\mu_{\rm res}$ = 0·93 D, along C–H bond

Symmetric rotations

$\phi_1(=\phi_2)$	0	±10	±20	±25	±30	±40	±50	±60	±90
$10^{12}{}_{\rm m}K$	+7·4	+6·2	+3·4	+1·8	+0·4	−1·0	+0·4	+4·4	+15·5

Antisymmetric rotations

$\phi_1(=-\phi_2)$	−90	−60	−50	−45	−40	−30	−20	−10	−5
$10^{12}{}_{\rm m}K$	+15·5	−32·8	−40·8	−42·4	−42·2	−36·8	−25·5	−10·1	−1·4
$\phi_1(=-\phi_2)$	0	+10	+20	+30	+40	+50	+60	+90	
$10^{12}{}_{\rm m}K$	+7·4	+24·7	+39·8	+51·2	+57·9	+59·3	+55·2	+15·5	

$\phi_1 = -\phi_2$, $\phi_1 = ca.\ -5°$ or $-80°$. These latter two estimates of ϕ, involving antisymmetric rotation of the *p*-chlorophenyl groups, would seem to be sterically impossible from scaled atomic models. In the case of symmetric rotation, a plot of ${}_{\mathrm{m}}K$(calc.) against ϕ shows that changes in the resultant moment tend to alter the depth of the minimum rather than its position along the ϕ-axis. Thus, it seems reasonable to conclude that the apparent conformation of D.D.T., as solute in benzene or carbon tetrachloride, is that given by $\phi_1 = \phi_2 = ca.\ \pm 40°$.

Molecule (II).—This compound has been treated in a similar manner to that described above, with the exceptions that: (i) the $C(2){=}C(1)Cl_2$ bond parameters are those from 1,1-dichloroethylene;[10] (ii) the reference axes are chosen such that the X-axis lies along C=C, the $C(2){=}C(1)Cl_2$ group lies in the XY-plane, and the bond angles are assumed to be 120°. The angle of rotation ϕ is defined as zero when the C_6H_4Cl groups are parallel to the XY-plane, and ${}_{\mathrm{m}}K$ is calculated for symmetric ($\phi_1 = \phi_2$) and antisymmetric ($\phi_1 = -\phi_2$) rotations, as shown in Table 4.

TABLE 4

${}_{\mathrm{m}}K(\phi_1, \phi_2)$ for (II) *; $\mu_{\mathrm{res}} = 0$

	Symmetric rotations						*Antisymmetric rotations* †			
$\phi_1(= \phi_2)$	0	±30	±40	±50	±60	±90	0	±30	±60	±90
$10^{12}{}_{\mathrm{m}}K$	110·3	76·7	58·9	43·5	32·4	21·7	110·3	86·9	42·6	21·7

* To be compared with $10^{12}{}_{\mathrm{m}}K$ (obs.) = 46·9.
† For these ϕ_1 ($= -\phi_2$)

Small increases in polarity caused only slight changes in the calculated ${}_{\mathrm{m}}K$ values. For this compound, however, the choice of group polarisability semi-axes involves the assumption of negligible conjugation between the carbon–carbon double bond and the π-electrons of the benzene rings. Since this effect would be maximum for $\phi = 0°$, which is sterically impossible, it seems reasonable to assume that any directional properties of exaltation need not be considered. Thus, agreement between calculated and observed values of ${}_{\mathrm{m}}K$ is obtained in the following cases. Assuming $\phi_1 = \phi_2$, $\phi_1 = ca.\ \pm 50°$; assuming $\phi_1 = -\phi_2$, $\phi_1 = ca.\ \pm 60°$. From scaled atomic models, the latter seems sterically unlikely, and thus it is reasonable to conclude that the apparent conformation is that given by $\phi_1 = \phi_2 = ca.\ \pm 50°$.

Molecule (III).—This compound, the chlorinated derivative of D.D.T., has been treated in a similar manner to that described for D.D.T. Both methyl and t-butyl chloride polarisability semi-axes[9] are used for the C(2)–Cl bond, since these represent the probable lower and upper limits of the anisotropy of this bond. The results of calculations, assuming tetrahedral angles and a zero dipole moment, are summarised in Table 5.

TABLE 5

${}_{\mathrm{m}}K(\phi_1, \phi_2)$ * for (III); $\mu_{\mathrm{res}} = 0$

					Symmetric rotations					
$\phi_1(= \phi_2)$ ...	0	±10	±20	±30	±40	±50	±60	±70	±80	±90
$10^{12}{}_{\mathrm{m}}K$ (A)	10·5	10·8	12·1	15·6	22·2	32·1	44·0	55·6	64·1	67·2
$10^{12}{}_{\mathrm{m}}K$ (B)	12·3	12·4	13·1	15·5	20·8	29·4	40·0	50·6	58·4	61·3
					Antisymmetric rotations					
$\phi_1(= -\phi_2)$	−90	−80	−70	−60	−50	−40	−30	−20	−10	
$10^{12}{}_{\mathrm{m}}K$ (A)	67·2	62·2	53·8	43·3	32·3	22·5	14·9	10·3	8·9	
$10^{12}{}_{\mathrm{m}}K$ (B)	61·3	54·2	44·5	33·5	23·0	14·5	9·0	6·9	8·2	
$\phi_1(= -\phi_2)$	0	+10	+20	+30	+40	+50	+60	+70	+80	+90
$10^{12}{}_{\mathrm{m}}K$ (A)	10·5	14·8	21·4	29·9	39·7	49·4	58·3	64·9	68·1	67·2
$10^{12}{}_{\mathrm{m}}K$ (B)	12·3	18·7	26·7	35·6	44·8	53·3	60·1	64·2	64·7	61·3

* To be compared with $10^{12}{}_{\mathrm{m}}K$(obs.) = 36·8.

(A) Using $b_{\mathrm{i}}[C^2{-}Cl]$ from CH_3Cl. (B) Using $b_{\mathrm{i}}[C^2{-}Cl]$ from $(CH_3)_2CCl$.

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[10] R. Bramley, C. G. Le Fèvre, R. J. W. Le Fèvre, and B. P. Rao. *J.*, 1959, 1183.

As in the case of D.D.T., the assumption of tetrahedral angles in (III) is a sufficiently accurate basis for these calculations. Further, the effect on the calculated ${}_{\mathrm{m}}K$ values of a small resultant dipole moment can be shown to be negligible compared with that involved in the choice of polarisability semi-axes for the C(2)–Cl bond. Thus, of the conformations for which agreement occurs between calculated and observed ${}_{\mathrm{m}}K$ values, those involving antisymmetric rotation of the two *p*-chlorophenyl groups would seem to be exlcuded by steric factors. Accordingly, the apparent conformation of this chlorinated derivative of D.D.T. is specified by $\phi_1 = \phi_2 = ca. \pm 55°$.

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