232. *Molecular Polarisability. The Anisotropy of the* C=C *Bond.*

By R. Bramley, C. G. Le Fèvre, R. J. W. Le Fèvre, and B. Purnachandra Rao.

Molar Kerr constants and dielectric polarisations in carbon tetrachloride at 25° are recorded for *cis*- and *trans*-dichloro-, 1 : 1-dichloro-, trichloro-, and tetrachloro-ethylenes. Molecular anisotropies are also given for the three (of these five) chloroethylenes which are polar. The longitudinal and transverse polarisabilities of the C–Cl bond are obtained from carbon tetrachloride and chloroform and used to analyse the polarisability ellipsoid of 1 : 1-dichloroethylene. Longitudinal, tranverse, and vertical polarisabilities of the C=C link are deduced therefrom as $0{\cdot}28_0$, $0{\cdot}07_3$, and $0{\cdot}07_7 \times 10^{-23}$ c.c., respectively. These values are tested by application to ethylene and its other chloro-derivatives. Agreement between observed and calculated quantities is satisfactory. Available facts show that *cis*-dichloroethylene is non-planar.

To ascertain the anisotropy of polarisability of the C=C bond, we studied molar Kerr constants and other properties of five chlorinated ethylenes, and analysed them with the help of the known structures of these molecules. Among them, the fundamentally important case is vinylidene dichloride, $CH_2{=}CCl_2$, because in it the resultant dipole moment undoubtedly lies along the C=C bond, and thus along one of the principal axes of the molecular ellipsoid. Accordingly the required longitudinal, transverse, and vertical polarisabilities, $b_L^{C=C}$, $b_T^{C=C}$, and $b_V^{C=C}$ respectively, can be calculated; the values so obtained are of general applicability to ethylene and the other substances examined.

Experimental

Materials.—Carbon tetrachloride, used as solvent throughout, was dried ($CaCl_2$), slowly fractionated (1 m. column packed with glass helices), and stored over calcium chloride. The isomeric dichloroethylenes were obtained from a B.D.H. " technical " grade. This, after being dried (K_2CO_3), was fractionally distilled under oxygen-free nitrogen in absence of light. The following fractions were collected: *trans*-dichloroethylene, b. p. 47·40° ± 0·005°/757·6 ± 0·05 mm., $n_D^{25} = 1{\cdot}44348$; *cis*-dichloroethylene, b. p. 59·85—59·90°/759·2—760·0 mm., $n_D^{25} = 1{\cdot}44615$. These were sealed and kept in the dark. Trichloro- and tetrachloro-ethylenes were specially prepared and fractionated samples (presented by Imperial Chemical Industries, Australia and New Zealand, Limited, whom we thank) with b. p. and n_D^{25} respectively of 86·4—86·6°/760 mm., 1·47503, and 120—122°/760 mm., 1·50328; they also were preserved out of the light. Vinylidene dichloride was obtained by treatment of 1 : 1 : 2-trichloroethane (also presented as above) with lime (cf. Beilstein s " Handbuch," 3rd suppl., Vol. 1, p. 647), b. p. 31·4—32·0°/760 mm.

Apparatus, Techniques, and Methods of Calculation.—These were as described previously.[1-6]

---

[1] Le Fèvre and Le Fèvre, *J.*, 1953, 4041; 1954, 1577.
[2] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.
[3] Le Fèvre and Le Fèvre, *J.*, 1956, 3549.
[4] Le Fèvre, " Dipole Moments," Methuen, London, 3rd Edn., 1953, Chap. II.
[5] Buckingham, Chau, Freeman, Le Fèvre, N. Rao, and Tardif, *J.*, 1956, 1405.
[6] Le Fèvre and P. Rao, *J.*, 1957, 3644; 1958, 1465.

TABLE 1. *Depolarisation factors for solutions in carbon tetrachloride.**

Solute: *cis*-Dichloroethylene

10^5f_2 ……………………	3753	7379	11106	14256	16969
$10^2\Delta_{12}$ ……………………	5·873	8·370	10·52	13·00	14·90

Solute: 1 : 1-Dichloroethylene

10^5f_2 ……………………	1559·5	2509	3349·5	3966	5044
$10^2\Delta_{12}$ ……………………	5·391	6·062	6·589	6·968	7·635

Solute: Trichloroethylene

10^5f_2 ……………………	1592	4278	6591	9378·5	11762·5
$10^2\Delta_{12}$ ……………………	5·246	8·175	10·54	13·12	16·39

* $\Delta_1 = 0·0346$ for $f_2 = 0$.

TABLE 2. *Dielectric constants, densities, refractive indexes, and Kerr constants as functions of weight fractions for solutions in carbon tetrachloride * at 25°.*

cis-Dichloroethylene

10^5w_2 ……………	1225	1866	2596	3082	3666	4073
ε_{12} ………………	2·3059	2·3463	2·3936	2·4249	2·4626	2·4890
d_{12} ………………	1·57965	1·57719	1·57432	1·57239	1·57038	1·56853
$10^4\Delta n$ ……………	0	−2	−3	−4	−5	−7
10^5w_2 ……………	5810	6903	7181	9213	14121	16445
$10^7\Delta B$ ……………	0·037	0·041	0·043	0·057	0·087	0·108

whence $\sum\Delta\varepsilon/\sum w_2 = 6·423$; $\sum\Delta d/\sum w_2 = -\ 0·3924$; $\sum\Delta n/\sum w_2 = -\ 0·0127$; $\sum w_2\Delta B/\sum w_2^2 = 0·630_6$.

trans-Dichloroethylene.

10^5w_2 …	546	1576	1603	1824	3010	3655	4411	4735·5	8069
ε_{12} ……	2·2268	2·2262	2·2257	2·2257	2·2247	2·2246	2·2239	2·2239	—
d_{12} ……	1·58201	1·57756	1·57742	1·57652	1·57125	1·56857	1·56544	1·56497	—
$10^4\Delta n$ …	−4	−10	−10	−10	−11	−12	−12	−15	−20
10^5w_2 …	1107	1694·5	3350	3366	4187	8069			
$10^7\Delta B$ …	0·011	0·014	0·029	0·029	0·034	0·071			

whence $\sum\Delta\varepsilon/\sum w_2 = -\ 0·0678$; $\Delta d = -\ 0·4643w_2 + 0·895w_2^2$; $\sum\Delta n/\sum w_2 = 0·0353$; $\sum w_2\Delta B/\sum w_2^2 = 0·865_5$.

1 : 1-Dichloroethylene

10^5w_2 ……………	349	441	567	625	1030	1125·5
ε_{12} ………………	2·2378	2·2401	2·2440	2·2471	2·2572	2·2616
d_{12} ………………	1·58279	1·58228	1·58169	1·58149	1·57941	1·57902
$10^4\Delta n$ ……………	—	—	—	−2	—	−3
10^5w_2 ……………	1341	2211	2533	3227·5	4057	4724
ε_{12} ………………	2·2671	2·2928	2·3019	2·3226	2·3469	2·3665
d_{12} ………………	1·57809	1·57393	1·57240	1·56909	1·56523	1·56207
$10^4\Delta n$ ……………	−3	−6	−7	−10	−13	−14
10^5w_2 ……………	198	413	984	1347	1545	2709
$10^7\Delta B$ ……………	0·008	0·015	0·033	0·043	0·054	0·089

whence $\sum\Delta\varepsilon/\sum w_2 = 2·976$; $\sum\Delta d/\sum w_2 = -\ 0·4767$; $\sum\Delta n/\sum w_2 = -\ 0·0292$; $\sum w_2\Delta B/\sum w_2^2 = 3·32_4$.

Trichloroethylene

10^5w_2 …	932	1251	1644	1650	2142	2184	2385	2647·5
ε_{12} ……	2·2370	2·2408	2·2451	2·2449	2·2502	2·2512	2·2533	2·2583
d_{12} ……	1·58320	1·58270	1·58218	1·58220	1·58142	1·58141	1·58114	1·58054

10^5w_2	202	604	1209	1726	3369	4317	10^5w_2	12117	12692	12878
$10^7\Delta B$	0·004	0·006	0·012	0·018	0·033	0·045	$10^4\Delta n$	21	21	23

whence $\sum\Delta\varepsilon/\sum w_2 = 1·111$; $\sum\Delta d/\sum w_2 = -\ 0·1451$; $\sum\Delta n/\sum w_2 = 0·0172$; $\sum w_2\Delta B/\sum w_2^2 = 0·97_8$.

Tetrachloroethylene

10^5w_2 …	802	1619	2189	3167	3900	4543	5351	5652
ε_{12} ……	2·2274	2·2278	—	2·2286	2·2290	2·2302	2·2297	2·2301
d_{12} ……	1·58477	1·58505	1·58523	1·58542	1·58558	1·58578	1·58596	1·58606
$10^4\Delta n$ …	0	5	6	11	14	16	20	21
10^5w_2 …	2876	3958	6462	7118	10248	11748		
$10^7\Delta B$ …	0·020	0·028	0·043	0·050	0·070	0·079		

whence $\sum\Delta\varepsilon/\sum w_2 = 0·0551$; $\Delta\sum d/\sum w_2 = 0·0277$; $\sum\Delta n/\sum w_2 = 0·0342$; $\sum w_2\Delta B/\sum w_2^2 = 0·681$.

* Values for $w_2 = 0$, $\varepsilon_1 = 2·2270$, $d_1 = 1·58454$, $n_1 = 1·4574$ (Na-D light), $B_1 = 0·070 \times 10^{-7}$ (Na-D light).

Observations are listed in Tables 1—4, wherein symbols have the following meanings: w_2, weight fraction; f, molar fraction; Δ, depolarisation factor; ε, dielectric constant; d, density; n, refractive index; B, Kerr constant; suffixes 1, 2, and 12 denote respectively solvent, solute, and solution; $\Delta\Delta$, $\Delta\varepsilon$, Δd, etc., represent alterations of the property concerned from solvent to solution; ${}_{\infty}\delta_2{}^2$ is the molecular anisotropy at infinite dilution, and is different from δ in Table 4; α, β, γ, and δ are coefficients in the equations $\varepsilon_{12} = \varepsilon_1(1 + \alpha w_2)$, $d_{12} = d_1(1 + \beta w_2)$, $n_{12} = n_1(1 + \gamma n_1)$, and $B_{12} = B_1(1 + \delta w_2)$; ${}_{\infty}({}_{\mathrm{m}}K_2)$ and ${}_{\infty}P_2$ are molar Kerr constants and total dielectric polarisations at infinite dilution; R_{D}, ${}_{\mathrm{E}}P$, ${}_{\mathrm{D}}P$, and μ indicate molar refractions (sodium light), electronic and distortion polarisations, and dipole moments; b_1, b_2, and b_3 are semi-axes of a molecular polarisability ellipsoid; θ_1 and θ_2 are explained and expanded in ref. 2.

TABLE 3. *Molecular anisotropies of solutes at infinite dilution.*

Solute	R.H.S. of equation giving $\Delta\Delta_{12}$	D *	$10^8{}_{\infty}\delta_2{}^2$
cis-$C_2H_2Cl_2$	$0{\cdot}6261f_2 + 0{\cdot}272f_2{}^2$	$-0{\cdot}2225$	$31{\cdot}5_2$
1 : 1-$C_2H_2Cl_2$	$0{\cdot}7165f_2 - 1{\cdot}18f_2{}^2$	$-0{\cdot}3085$	$35{\cdot}7_1$
C_2HCl_3	$1{\cdot}048f_2 + 0{\cdot}275f_2{}^2$	$-0{\cdot}1200$	$51{\cdot}2_1$

* D is given by $d_{12} = d_1 + Df_2$.

TABLE 4. *Calculation of results.*

Solute	$(\alpha\varepsilon_1)_{w_2=0}$	$(\beta)_{w_2=0}$	γ	$(\delta)_{w_2=0}$	$10^{12}{}_{\infty}({}_{\mathrm{m}}K_2)$	${}_{\infty}P_2$ (c.c.)	R_{D} (c.c.)
cis-$C_2H_2Cl_2$ ...	$6{\cdot}42_3$	$-0{\cdot}247_6$	$-0{\cdot}009$	$9{\cdot}0_1$	$5{\cdot}2_5$	$88{\cdot}1_3$	20·25 [a]
trans-$C_2H_2Cl_2$	$-0{\cdot}06_8$	$-0{\cdot}293_0$	$-0{\cdot}024$	$12{\cdot}3_6$	$9{\cdot}9_6$	$22{\cdot}2_6$	20·60 [a]
1 : 1-$C_2H_2Cl_2$ ...	$2{\cdot}97_6$	$-0{\cdot}300_8$	$-0{\cdot}020$	$47{\cdot}4_9$	$34{\cdot}4_2$	$53{\cdot}6_7$	20·43 [e]
C_2HCl_3	$1{\cdot}11_1$	$-0{\cdot}091_6$	$0{\cdot}012$	$13{\cdot}9_7$	$14{\cdot}2_9$	$41{\cdot}7_4$	25·42 [g]
C_2Cl_4	$0{\cdot}05_5$	$0{\cdot}017_5$	$0{\cdot}023_5$	$9{\cdot}7_3$	$13{\cdot}2_4$	$30{\cdot}8_2$	30·33 [h]

Solute	${}_{\mathrm{E}}P$ (c.c.)	${}_{\mathrm{D}}P$ (c.c.)	μ (D)	$10^{35}(\theta_1 + \theta_2)$	$10^{23}(b_1 + b_2 + b_3)$	$10^{48}\sum(b_i - b_j)^2$	$10^{35}\theta_2$
cis-$C_2H_2Cl_2$ ...	19·62 [b]	21·6 [c]	1·80	$1{\cdot}24_8$	$2{\cdot}33_3$	17·16	0·228
trans-$C_2H_2Cl_2$	19·92 [b]	22·3 [d]	0	$2{\cdot}36_8$	$2{\cdot}36_9$	—	—
1 : 1-$C_2H_2Cl_2$ ...	19·78 [f]	21·8 [c]	1·25	$8{\cdot}18_5$	$2{\cdot}35_2$	19·75	7·011
C_2HCl_3	24·61 [f]	27·1 [c]	0·85	$3{\cdot}39_8$	$2{\cdot}92_6$	43·84	0·793
C_2Cl_4	29·81 [h]	30·8 [d]	0	$3{\cdot}14_9$	$3{\cdot}54_5$	—	—

[a] Calc. from Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier, New York and London, 1950, pp. 277/8. [b] Extrapolated from R_{α} and R_{β} calc. from *a*. [c] Taken as ${}_{\mathrm{E}}P \times 1{\cdot}1$. [d] *I.e.*, ${}_{\infty}P_2$. [e] From Schildknecht, " Vinyl and Related Polymers," Wiley, New York, 1952, p. 449. [f] *I.e.*, $0{\cdot}968R_{\mathrm{D}}$; cf. ratios ${}_{\mathrm{E}}P/R_{\mathrm{D}}$ for *cis*- and *trans*-isomers. [g] From Beilstein, 3rd Suppl., Vol. 1. [h] Calc. from refractions listed in Landolt and Börnstein's Tables, 1912 Edn.

TABLE 5. *Semi-axes of polarisability ellipsoids.*

	$10^{23}b_1$	$10^{23}b_2$	$10^{23}b_3$
$CH_2{:}CCl_2$	0·896	0·879	0·575
cis-$C_2H_2Cl_2$	$0{\cdot}779_5$	0·946	0·608
C_2HCl_3	1·003	1·231	0·692

Molecular Semi-axes from Experiment.—Semi-axes of the polarisability ellipsoids for the three polar solutes are given in Table 5. They have been calculated on the assumption that $\mu_{\text{resultant}}$ in each case is acting parallel to one of the semi-axes; this may not be valid for trichloroethylene although it obviously is so for the other two molecules. Semi-axes for the non-polar compounds cannot, of course, be obtained directly from experiment (see ref. 2, p. 287).

Previous Measurements.—Dielectric polarisation measurements in carbon tetrachloride have been previously recorded only for trichloroethylene, to which a polarity of 0·8 D is ascribed.[7] Other determinations, either in benzene or " unspecified solvents," are: 1 : 1-dichloroethylene,[8] 1·30 or 1·18 D, *cis*-dichloroethylene,[7] 1·74—1·89 D, *trans*-dichloroethylene,[7] 0—0·7 D, trichloroethylene,[7] 0·94 D, and tetrachloroethylene,[7] 0 D. As a vapour the *cis*-dichloro-compound shows [9] $\mu = 1{\cdot}90 \pm 0{\cdot}02$ D.

Sachsse [10] has stated, without giving observational details, that *cis*- and *trans*-dichloro- and

---

[7] Wesson, " Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

[8] Rogers, *J. Amer. Chem. Soc.*, 1947, **69**, 1243; Errera, *Physikal. Z.*, 1926, **27**, 764.

[9] Maryott and Buckley, " Table of Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State," *Nat. Bur. Stand. Circular* 537, Washington, U.S.A., 1953.

[10] Sachsse, *Physikal. Z.*, 1935, **36**, 357.

tetrachloro-ethylenes in carbon tetrachloride at about 4° had $_mK$'s of 8·2, 8·4, and 12·8 × 10^{-12} respectively. The electric double refractions noted for the *cis*- and *trans*-dihalogeno-substances as gases by Stuart and Volkmann[11] correspond (according to Sachsse) to $_mK$'s of 7·5 and 18·6 × 10^{-12}.

No reference can be found to the depolarisation of light scattered by these five solutes either undiluted or dissolved.

DISCUSSION

Derivation of Bond Polarisability Ellipsoid for C=C.—The desired values of $b_L^{C=C}$, $b_T^{C=C}$, and $b_V^{C=C}$ can be extracted from the molecular ellipsoid found (Table 5) for 1 : 1-dichloroethylene, provided that specifications are known for the structure of $CH_2{=}CCl_2$ and for the polarisability ellipsoids of the C–H and C–Cl bonds.

The C–H link, for reasons given before,[2,12] is taken as isotropic, *i.e.*, $b_L^{C-H} = b_T^{C-H} = b_V^{C-H} = 0{\cdot}064 \times 10^{-23}$ c.c. Information on C–Cl can be obtained from the molecules CCl_4 and $CHCl_3$. For the former,[13] $b_1 = b_2 = b_3 = 1{\cdot}026 \times 10^{-23}$ and for the latter $b_1 = 0{\cdot}673 \times 10^{-23}$ c.c. According to Allen and Sutton's list,[14] the Cl–C–Cl angles in CCl_4 and $CHCl_3$ are tetrahedral and 112° respectively, whence $b_L^{C-Cl} = 0{\cdot}399 \times 10^{-23}$ and $b_T^{C-Cl} = 0{\cdot}185 \times 10^{-23}$ c.c. From ref. 14 the configuration of $CH_2{=}CCl_2$ is set by a Cl–C–C angle of 122° ± 1°. The above facts, together with the appropriate trigonometrical quantities, lead to the equations for $CH_2{:}CCl_2$: $10^{23}b_1 = 0{\cdot}618 + b_L^{C=C}$; $10^{23}b_2 = 0{\cdot}806 + b_T^{C=C}$; and $10^{23}b_3 = 0{\cdot}498 + b_V^{C=C}$, from which, in turn, the bond semi-axes emerge as: $10^{23}b_L^{C=C} = 0{\cdot}280$ c.c.; $10^{23}b_T^{C=C} = 0{\cdot}073$ c.c.; and $10^{23}b_V^{C=C} = 0{\cdot}077$ c.c.

This is actually the second estimate of the anisotropy of polarisability of the C=C bond to be made completely from experiment, Sachsse[10] having reported 0·392, 0·094, and 0·035 × 10^{-23} for the three $b^{C=C}$'s in question. Since Sachsse depended upon the then available intervalency angles for calculation from his $_mK$'s (see above), we consider the present to be the more reliable. Wang[15] and Denbigh[16] quote values of 0·302 and 0·286 × 10^{-23} for $b_L^{C=C}$ but appear to have used the Kerr constant given in the literature for ethylene and assumed, without *a priori* justification, that $b_T^{C=C} = b_V^{C=C}$. Bolton[17] and Mueller,[18] by different theoretical routes, have deduced that $b_L^{C=C} = 0{\cdot}286$ or $0{\cdot}312 \times 10^{-23}$ c.c., respectively. An empirical connection with bond lengths[19] forecasts $b_L^{C=C} = 0{\cdot}275 \times 10^{-23}$.

Derivation of Molecular Ellipsoids of Non-polar Chloroethylenes.—Allen and Sutton[14] give intercentre distances and angles as follows: *trans*-$C_2H_2Cl_2$, C–Cl 1·69 ± 0·03 Å, Cl–Cl 4·7 Å, C–C–Cl angle 122·5° ± 1°; C_2Cl_4, C–C 1·38 or 1·34, both ±0·05 Å, C–Cl 1·71 or 1·73, both ±0·02 Å, C–C–Cl angle 122·2° or 123·7°, both ±1°. Taking for the former molecule a double bond length as in C_2Cl_4, we predict the semi-axes: $10^{23}b_1 = 1{\cdot}082$, $10^{23}b_2 = 0{\cdot}693$, and $10^{23}b_3 = 0{\cdot}575$ (b_1 lying through the Cl . . . Cl centres); $_mK$ (calc.) is therefore 10·7 × 10^{-12} against 10·0 × 10^{-12} found. Improved agreement can be secured by appropriate variations of lengths and angles within the limits stated in ref. 14. If C–Cl is kept at 1·69 Å, but the angle C–C–Cl is put equal to 120°, $_mK$ calc. becomes 9·8 × 10^{-12}.

For tetrachloroethylene it is assumed that the double bond lies along the principal axis b_1. With the Cl–C–C angle at 122·0°, the polarisability semi-axes are $10^{23}b_1 = 1{\cdot}262$, $10^{23}b = 1{\cdot}426$, and $10^{23}b_3 = 0{\cdot}817$, or with the angle at 123·7° they are $10^{23}b_1 = 1{\cdot}284$, $10^{23}b_2 = 1{\cdot}405$, and $10^{23}b_3 = 0{\cdot}817$. The $_mK$'s computed for the two sets are 14·0 × 10^{-12} or 13·6 × 10^{-12} respectively, the " found " value being 13·2 × 10^{-12}.

---

[11] Stuart and Volkmann, *Ann. Phys.*, 1933, **18**, 121.

[12] Le Fèvre and Le Fèvre, *Chem. and Ind.*, 1955, 1121.

[13] Armstrong, Aroney, Le Fèvre, Le Fèvre, and Smith, *J.*, 1958, 1474.

[14] Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

[15] Wang, *J. Chem. Phys.*, 1939, **7**, 1012.

[16] Denbigh, *Trans. Faraday Soc.*, 1940, **36**, 936.

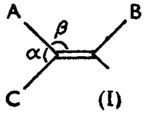
[17] Bolton, *Trans. Faraday Soc.*, 1954, **50**, 1261.

[18] Mueller, *J. Chem. Phys.*, 1954, **22**, 120.

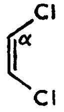
[19] Le Fèvre, *Proc. Chem. Soc.*, 1958, 283.

Prediction of Molar Kerr Constant of Ethylene.—The calculated semi-axes for this molecule are 0·536, 0·329, and 0·333 × 10^{-23}, whence $(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2 = 0{\cdot}084 \times 10^{-46}$; $_mK$ is therefore $1{\cdot}9_1 \times 10^{-12}$, or, if the distortion and electronic polarisations recorded by Watson and Ramaswamy [20] are introduced, $1{\cdot}9_8 \times 10^{-12}$. Two determinations of B_{ethylene} are available: $0{\cdot}19_6 \times 10^{-10}$ at 20°/1 atm., and $\lambda = 5460$ Å, by Kuss,[21] or $0{\cdot}16_3 \times 10^{-10}$ at 0°, 1 atm., and $\lambda = 6500$ Å, by Breazeale; [22] these correspond to $_mK$'s of $1{\cdot}9_1$ or $1{\cdot}8 \times 10^{-12}$. Considering that the quoted B's are both extrapolated from observations taken at pressures considerably above normal, we cannot expect better agreement between $_mK_{\text{obs.}}$ and $_mK_{\text{calc.}}$.

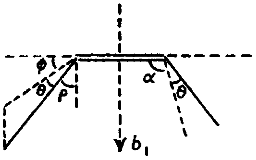
Applicability of Bond Polarisabilities to Trichloroethylene.—Interpretation of data for this case is difficult because the direction of action of the resultant dipole moment is not known exactly. α is 114° and β is 123° in (I).[14] It is highly probable that the axis of



(I)



(II)



(III)

maximum polarisability lies parallel to the bonds holding Cl atoms B and C. On such a basis the semi-axes calculable *a priori* would be: $10^{23}b_1 = 1{\cdot}01_6$, $10^{23}b_2 = 1{\cdot}21_7$, $10^{23}b_3 = 0{\cdot}69_6$. In deducing b_1, b_2, and b_3 from experiment (Table 5), the assumption was made that $\mu_{\text{resultant}}$ acts along one of the principal polarisability axes. Because of the smallness of $\mu_{\text{resultant}}$, *viz.*, 0·85D, the predicted and found b's should be compared to two significant figures only; when this is done, both sets become 1·0, 1·2, and 0·7 × 10^{-23}. Other dispositions of b_{maximum} were tried, but each resulted in a larger value for $b_{1\,\text{calc.}}$. The implication therefore is that $\mu_{\text{resultant}}$ is acting along a line situated some 24° anticlockwise from the bond holding atom A; this seems reasonable.

Conformation of cis-1 : 2-*Dichloroethylene.*—The structure is specified in ref. 14 as (II). If the molecule is planar, the Cl–Cl distance (3·7 Å) and the C–Cl distance (1·67 Å) quoted (from *X*-ray diffraction on the gas) are not reconcilable with a Cl–C=C angle (α) of 123·5°, it necessitates either (*a*) an abnormally [14,23] long C=C bond (*ca.* 1·8 Å), or (*b*) a Cl–C=C angle of 135°. The semi-axes predicted for these two angles are: $b_1 = 0{\cdot}869$, $b_2 = 0{\cdot}908$, $b_3 = 0{\cdot}575 \times 10^{-23}$ (for $\angle$ Cl–C=C = 123·5°), $b_1 = 0{\cdot}785$, $b_2 = 0{\cdot}992$, $b_3 = 0{\cdot}575 \times 10^{-23}$ (for $\angle$ Cl–C=C = 135°) against values from experiment of $0{\cdot}779_5$, 0·946, and 0·608 × 10^{-23}, with which neither set is in good agreement. No variation about 3·7 Å is cited for the Cl–Cl separation but the likelihood of considerable error is diminished by the fact that the corresponding length (given as 4·7 Å) in the *trans*-isomer is close to that calculated (4·6 Å) from the appropriate molecular dimensions.

Accordingly non-planar models have been considered (III). Taking the C=C distance as 1·34 Å and that for C–Cl as 1·67 Å, we can evaluate an angle θ by geometry as 34° 23′; α is 123·5°; θ is the angle of projection of each C–Cl bond on the plane which contains the long axis of the double bond and is symmetrically between the two planes in which the two Cl–C=C triangles are lying; b_1 also must be situated in this plane, and the C–Cl moments will act at an angle ρ to b_1 (where ρ = 52° 13′). These data being used, b_1 (calc.) becomes $0{\cdot}732 \times 10^{-23}$, while b_1 (expt.) = $0{\cdot}779_5 \times 10^{-23}$. Bearing in mind the fact that b_1 (calc.) is based on two different bond lengths, one atom–atom distance, and one electron-diffraction angle determination, we can accept the agreement reached.

Alternatively, more precise information on the angles θ, ϕ, and ρ can be obtainable from the measured quantity b_1, because there can be no doubt where b_1 lies with reference to the

---

[20] Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144.

[21] Kuss, " Elektro-optischer Kerreffekt bei hohen Drucken im Übergangsgebiet Gasförmig-flüssig," Berlin, 1940.

[22] Breazeale, *Phys. Rev.*, 1936, **49**, 625.

[23] Stuart, " Die Struktur des Freien Moleküls," Springer, Berlin, 1952, pp. 162 and 172.

C=C and the C–Cl links. If we write $b_1 = 2b_L^{C-Cl}\cos^2\rho + 2b_T^{C-Cl}\sin^2\rho + b_T^{C=C} + 2b_L^{C-H}$, where $b_1 = 0{\cdot}779_5 \times 10^{-23}$, we obtain ρ as 45° 44′, θ as 27° 8½′, and ϕ as 51° 40′, while the azimuthal angle between the planes of the C=C–Cl units is 66° 20′. That these angles are more suitable than those deduced by geometry can be seen from the facts that they lead to a Cl–Cl separation of $3{\cdot}5_3$ Å (against 3·7 Å reported[14]) and a $b_{2\,\text{calc.}}$ of $0{\cdot}947 \times 10^{-23}$ (against $0{\cdot}946 \times 10^{-23}$ found); b_2 is assumed to be situated parallel to the Cl–Cl direction. By difference (Table 4), b_3 is $0{\cdot}606_5 \times 10^{-23}$ (against $0{\cdot}608 \times 10^{-23}$ found).

Further Reference to Tri- and Tetra-chloroethylenes.—One might suspect that if *cis*-dichloroethylene is non-planar, the tri- and tetra-chloro-derivatives would be so also, volume factors being presumably responsible. It is therefore relevant to mention that application of the bond lengths and angles listed by Allen and Sutton[14] to planar configurations of these molecules reveals permitted maximum Cl–Cl separations as follow: $3{\cdot}1_8$ Å for *cis*-dichloroethylene, $3{\cdot}2_4$ Å for trichloroethylene, and 3·60 Å for tetrachloroethylene. Since the minimum effective radius of combined chlorine is *ca.* 1·6 Å (Stuart[24] quotes it as 1·58 Å), there can be no objection to the assumption of flatness for the tri- and tetra-chloro-substances. Even so, the degree of non-planarity now inferred for *cis*-dichloroethylene appears excessive if steric causes are alone operative, and no satisfactory alternative explanation suggests itself. The same remarks could be made concerning Bastiansen and Hassel's conclusions[25] that in *o*-dichloro- and hexachloro-benzenes the halogens are bent out of the plane of the ring by 18° and 12° respectively.

The authors acknowledge with gratitude the award of a Research Fellowship (to B. P. R.) by the Nuffield Foundation and of a Research Scholarship (to R. B.) by Messrs. Beetle-Elliott Ltd. of Sydney.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA.

[*Received, September* 19*th*, 1958.]

[24] Stuart, *Z. phys. Chem.*, 1935, *B*, **27**, 350.

[25] Bastiansen and Hassel, *Acta Chem. Scand.*, 1947, **1**, 489.