91. *Molecular Polarisability. Dipole Moments, Molar Kerr Constants and Apparent Conformations of Certain α-Substituted Carbonyl Compounds.*

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Dipole moments and molar Kerr constants are reported for chloro- and bromo-acetone, acetyl and chloroacetyl chlorides, and ethyl methyl ketone as solutes in carbon tetrachloride and for propionaldehyde as solute in benzene. The observations are interpreted as indicating that in the experimental environment (a) chloro- and bromo-acetone exist mainly as the *gauche* form; the ratio *gauche*:*cis*-halogen-oxygen equals *ca.* 4 for chloroacetone and *ca.* 5 for bromoacetone; (b) the *gauche* conformation of chloroacetone is defined by $\phi = ca.\ 130°$ and for bromoacetone by $\phi = ca.\ 120°$ on the basis that $\phi = 0°$ for the *cis*-isomer; (c) chloroacetyl chloride does not exist exclusively as the more stable *cis*-form; (d) propionaldehyde and ethyl methyl ketone are present predominantly as a *gauche* type conformer in which the C–C–Me plane is approximately perpendicular to that of the trigonal carbon valencies.

This Paper deals with the interpretation of the polarities and electric birefringences of certain α-substituted carbonyl compounds, examined as solutes in non-polar media, in terms of their apparent molecular conformations. Observations and results are summarised in Tables 1 and 2.

Experimental

Materials and Apparatus.—The solutes were prepared and/or purified immediately before use to give: chloroacetone, b. p. 119°; bromoacetone, b. p. 30°/*ca.* 7 mm.; acetyl chloride,

TABLE 1.

Incremental Kerr effects, refractive indexes, dielectric constants, and densities of solutions at 25°.

Chloroacetone in CCl_4

10^5w_2	810	992	1342	2165	2568	2900
$10^7\Delta B$	0·031	0·040	0·050	0·083	0·099	0·117
$-10^4\Delta n$	4	5	7	11	13	14
ε^{25}	2·3157	2·3353	2·3758	2·4727	2·5233	2·5644
d_4^{25}	1·57943	1·57822	1·57621	1·57112	1·56859	1·56646

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 3{\cdot}90$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}050$; $\Delta\varepsilon = 10{\cdot}6w_2 + 35{\cdot}9w_2^2$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}625$

Bromoacetone in CCl_4

10^5w_2	780	1146	1685	2889	4601
$10^7\Delta B$	—	0·013	0·018	0·034	0·053
$-10^4\Delta n$	—	—	—	2	3
ε^{25}	2·2860	2·3138	2·3555	2·4526	2·5991
d_4^{25}	1·58487	1·58510	—	1·58632	1·58765

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 1{\cdot}14$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}007$; $\Delta\varepsilon = 7{\cdot}38w_2 + 15{\cdot}4w_2^2$; $\Delta d = 0{\cdot}046w_2 + 0{\cdot}485w_2^2$

Acetyl chloride in CCl_4

10^5w_2	1165	1767	2971	4554	4674
$10^7\Delta B$	0·012	0·020	0·034	0·051	0·057

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 1{\cdot}15$

10^5w_2	505	840	1767
ε^{25}	2·3008	2·3486	2·4859

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 14{\cdot}6$

10^5w_2	1076	1912	4308
d_4^{25}	1·57681	1·57061	1·55342

whence $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}723$

Chloroacetyl chloride in CCl_4

10^5w_2	3236	4079	4334	5120	5344	7600	10,447
$10^7\Delta B$	0·037	0·051	0·051	—	0·068	0·098	0·132
$-10^4\Delta n$	7	9	9	11	11	—	21

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 1{\cdot}25$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}021$

10^5w_2	700	1205	1698	2185	2926
ε^{25}	2·2848	2·3276	2·3701	2·4150	2·4810
d_4^{25}	1·58272	1·58158	1·58043	1·57893	1·57725

whence $\Delta\varepsilon = 8{\cdot}14w_2 + 19{\cdot}0w_2^2$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}250$

Propionaldehyde in C_6H_6

10^5w_2	1693	2135	2277	2792	3128
$10^7\Delta B$	0·130	0·165	0·185	0·230	0·236
d_4^{25}	0·87261	0·87230	0·87221	0·87181	0·87166

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 7{\cdot}87$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}069$

10^5w_2	723	863	1477	1797	2364	2653
$-10^4\Delta n$	10	12	22	26	34	39
ε^{25}	2·3624	2·3758	2·4499	2·4905	2·5582	2·5916

whence $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}145$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 12{\cdot}1$

Ethyl methyl ketone in CCl_4

10^5w_2	665	1005	1476	1943	2292
$10^7\Delta B$	0·077	0·123	0·178	0·236	0·269
$-10^4\Delta n$	10	16	22	30	35
ε^{25}	2·3673	2·4386	2·5365	2·6360	2·7108
d_4^{25}	1·57444	1·56919	1·56205	1·55492	1·54977

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 12{\cdot}0$; $\Sigma\Delta n/\Sigma w_2 = -0{\cdot}153$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 21{\cdot}1$; $\Sigma\Delta d/\Sigma w_2 = -1{\cdot}52$

b. p. 51—52°; chloroacetyl chloride, b. p. 106—108°; propionaldehyde, b. p. 49°; ethyl methyl ketone, b. p. 80°. Carbon tetrachloride and benzene, as solvents, were dried ($CaCl_2$ and Na, respectively) then fractionated. Symbols, headings, and methods of calculation used in

TABLE 2.

Polarisations, dipole moments, and molar Kerr constants from observations on solutions at 25°.

Solute	Solvent	$\alpha\varepsilon_1$	β	γ	δ	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ D*	$10^{12}{}_\infty({}_mK_2)$
Chloroacetone	CCl_4	10·6	−0·394	−0·034	55·7	127·5	20·7	2·27	36·1
Bromoacetone	,,	7·38	0·029	−0·005	16·3	131·4	22·7	2·29	14·1
Acetyl chloride	,,	14·6	−0·456	−0·096 ‡	16·4	142·4	16·2 †	2·48	6·5
Chloroacetyl chloride	,,	8·14	−0·158	−0·014	−17·9	121·4	21·7	2·20	−17·3
Propionaldehyde ...	C_6H_6	12·1	−0·079	−0·097	19·2	153·2	16·2	2·58	64·6
Ethyl methyl ketone	CCl_4	21·1	−0·960	−0·105	171	186·5	20·7	2·84	88·2

* Calculated assuming $_DP = 1{\cdot}05R_D$. † Calculated from the bond refractions of Vogel, Cresswell, Jeffrey, and Leicester, *J.*, 1952, 514. ‡ Calculated from $R_D = 16{\cdot}2$ c.c. and $\beta = -0{\cdot}456$.

Tables 1 and 2 are explained in ref. 1, pp. 280—283. When $w_2 = 0$, the following values apply at 25° (and, where appropriate, for sodium-D light):

	10^7B_D	n_D	ε	d	$10^{14}({}_sK_1)$
CCl_4	0·070	1·4575	2·2270	1·58454	0·749
C_6H_6	0·410	1·4973	2·2725	0·87378	7·56

Previous Measurements.—The following dipole moments (in Debye units) have been recorded (solvent or state, and reference, given in brackets; B = benzene; D = dioxan; Hx = hexane; CT = carbon tetrachloride; CD = carbon disulphide; L = pure liquid; G = gaseous state): chloroacetone, 2·35 (Hx; 2), 2·38 (CT; 3), $2{\cdot}1_7$—$2{\cdot}2_4$ (G; 4); bromoacetone, 2·38 (Hx; 2); acetyl chloride, 2·45 (B; 5), 2·40 (B; 6), 2·68 (G; 4); chloroacetyl chloride, 2·22 (B; 5), 2·06 (CD; 5), 2·2 (G; 4), 2·17 (CT; 7); propionaldehyde, 2·54 (B; 8), 2·73 (G; 9); ethyl methyl ketone, 2·79 (B; 10), 2·78 (B; 11), 3·2 (L; 12), 2·76 (B; 13), 2·82 (D; 13).

DISCUSSION

Chloroacetone and Bromoacetone.—It has been well established,[3,14-17] mainly from spectroscopic evidence, that the simple α-halogenated ketones $X{\cdot}CH_2{\cdot}CO{\cdot}R$ exist in the liquid state as an equilibrium mixture of *cis*-halogen-oxygen and *gauche* forms—these are shown as (I) and (II), respectively. The more polar isomer (I) has a planar or near-planar arrangement of the atoms X·C·C:O; (II) is generated from (I) by rotation of the CH_2X group through an angle ϕ, *e.g.*, for chloroacetone (R = Me, X = Cl) the azimuthal angle is reported by Mizushima *et al.*[3] to be *ca.* 150°. The relative stabilities of these conformations are determined by the electrostatic repulsion between the halogen and oxygen atoms on the one hand, and by the steric repulsion between the halogen and the alkyl group on the other. In the present work, we derive from the apparent polarities and electric birefringences of chloro- and bromo-acetone, examined as solutes in carbon tetrachloride, the position of the equilibrium (*cis* $\rightleftharpoons$ *gauche*) for each of these molecules in this

[1] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.* (Australia), 1955, **5**, 261.
[2] Mohler, *Helv. Chim. Acta*, 1938, **21**, 67.
[3] Mizushima, Shimanouchi, Miyazawa, Ichishima, Kuratani, Nakagawa, and Shido, *J. Chem. Phys.*, 1953, **21**, 815.
[4] Zahn, *Physikal. Z.*, 1932, **33**, 686.
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[6] Koehl and Wenzke, *J. Amer. Chem. Soc.*, 1937, **59**, 1418.
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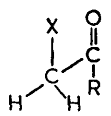
[9] Hurdis and Smyth, *J. Amer. Chem. Soc.*, 1943, **65**, 89.
[10] Wolf and Lederle, *Physikal. Z.*, 1928, **29**, 948; Wolf, *Z. phys. Chem.*, 1929, *B*, **2**, 39.
[11] Wolf and Gross, *Z. phys. Chem.*, 1931, *B*, **14**, 305.
[12] Phadke, Gokhale, Phalnikar, and Bhide, *J. Indian Chem. Soc.*, 1945, **22**, 235.
[13] Estok and Sikes, *J. Amer. Chem. Soc.*, 1953, **75**, 2745.
[14] Bellamy and Williams, *J.*, 1957, 4294.
[15] Bellamy and Williams, *J.*, 1958, 3465.
[16] Josien, Castinel, Chiurdoglu, and Vanlanduyt, *Compt. rend.*, 1957, **244**, 2383.
[17] Mizushima, "Structure of Molecules and Internal Rotation," Academic Press Inc., New York, 1954, pp. 73—74.

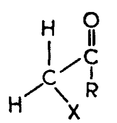
environment. Our procedure is to calculate, by addition of component bond and group parameters, the theoretical dipole moments and polarisability ellipsoid specifications, and thence the molar Kerr constants for various possible conformations, and to compare the values thus predicted with those obtained by experiment. The computational procedures are outlined in ref. 18, pp. 2483—2486. Bond and group polarisability semi-axes * used in the subsequent calculations are:

	b_L	b_T	b_V	Ref.		b_L	b_T	b_V	Ref.
C–H	0·064	0·064	0·064	1	C–Cl ...	0·318	0·220	0·220	1
C–C	0·099	0·027	0·027	19	C–Br	0·465	0·308	0·308	1
C=O	0·230	0·140	0·046	20					

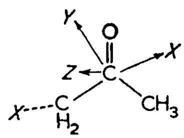
The component bond and group polarities were calculated from the following experimental values: μ (acetone) = 2·74 D,[21] μ (methyl chloride) = 1·72 D,[22] μ (methyl bromide) = 1·70 D,[22] all of which had been measured in carbon tetrachloride solution. The bond angles about the trigonal carbon atom are assumed to be 120°; all other bond angles are taken as tetrahedral. The calculations are summarised in Tables 3 and 4 for chloroacetone and bromoacetone, respectively. The principal axes are located in each case within the co-ordinate system *XYZ* (see III) where *X* and *Y* lie in the plane of the trigonal carbon valencies; *Z* is normal to this plane.



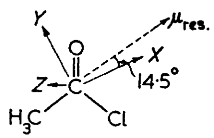
(I) *cis*-form



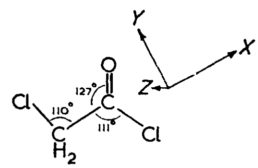
(II) *gauche*-form



(III)



(IV)



(V)

The direction of action of μ (corrected) cannot be ascertained with certainty. It has been assumed in calculating the molar Kerr constants of Tables 3 and 4 that the location of μ (corrected) is in each case the same as that derived (from the vector addition of component bond moments) for the corresponding μ (uncorrected). This introduces no significant error for conformations defined by $90° < \phi < 180°$; there could, however, be an appreciable error in the estimated molar constant for the *cis*-halogen-oxygen form. We calculate that an uncertainty of $\pm 5°$ in the location of μ (corrected) for each isomer ($\phi = 0$) results in a maximum error in the ${}_{m}K$ calc. of $\pm 15 \times 10^{-12}$ for chloroacetone (6%) and $\pm 22 \times 10^{-12}$ for bromoacetone (8%).

If these molecules exist as an equilibrium mixture of planar (apart from the hydrogens)

* Polarisability semi-axes of bonds or groups, b_L, b_T, and b_V, or of molecules, b_1, b_2, and b_3, are quoted throughout in 10^{-23} c.c. units.

[18] Le Fèvre and Le Fèvre, Ch. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ. Inc., New York, 3rd edn., Vol. I, p. 2459.
[19] Le Fèvre and Le Fèvre, *J.*, 1956, 3549.
[20] Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 2340.
[21] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.
[22] Le Fèvre and Le Fèvre, *J.*, 1954, 1577.

TABLE 3.

Polarisabilities, dipole moments, and molar Kerr constants calculated for conformations of chloroacetone.

$\phi°$	b_i	Direction cosines with X	Y	Z	μ	μ (corr.) *	$10^{12}({}_{m}K)$ †
0	$b_1 = 0{\cdot}852$	$+0{\cdot}967$	$+0{\cdot}254$	0			
	$b_2 = 0{\cdot}948$	$-0{\cdot}254$	$+0{\cdot}967$	0	$4{\cdot}0_7$	3·5	$+238 \pm 15$
	$b_3 = 0{\cdot}640$	0	0	+1			
120	$b_1 = 0{\cdot}842$	$+0{\cdot}825$	$-0{\cdot}566$	$-0{\cdot}010$			
	$b_2 = 0{\cdot}904$	$+0{\cdot}549$	$+0{\cdot}804$	$-0{\cdot}227$	$2{\cdot}2_4$	2·0	-24
	$b_3 = 0{\cdot}694$	$+0{\cdot}136$	$+0{\cdot}182$	$+0{\cdot}974$			
130	$b_1 = 0{\cdot}842$	$+0{\cdot}869$	$-0{\cdot}495$	$+0{\cdot}001$			
	$b_2 = 0{\cdot}918$	$+0{\cdot}484$	$+0{\cdot}849$	$-0{\cdot}211$	$1{\cdot}9_8$	1·8	-18
	$b_3 = 0{\cdot}680$	$+0{\cdot}103$	$+0{\cdot}184$	$+0{\cdot}977$			
140	$b_1 = 0{\cdot}842$	$+0{\cdot}897$	$-0{\cdot}443$	$+0{\cdot}004$			
	$b_2 = 0{\cdot}931$	$+0{\cdot}436$	$+0{\cdot}881$	$-0{\cdot}182$	$1{\cdot}7_3$	1·6	-9
	$b_3 = 0{\cdot}667$	$+0{\cdot}077$	$+0{\cdot}165$	$+0{\cdot}983$			
150	$b_1 = 0{\cdot}842$	$+0{\cdot}913$	$-0{\cdot}408$	$+0{\cdot}005$			
	$b_2 = 0{\cdot}942$	$+0{\cdot}404$	$+0{\cdot}903$	$-0{\cdot}143$	$1{\cdot}4_9$	1·4	$+4$
	$b_3 = 0{\cdot}656$	$+0{\cdot}054$	$+0{\cdot}133$	$+0{\cdot}990$			
180	$b_1 = 0{\cdot}843$	$+0{\cdot}930$	$-0{\cdot}367$	0			
	$b_2 = 0{\cdot}958$	$+0{\cdot}367$	$+0{\cdot}930$	0	$1{\cdot}0_9$	1·1	$+28$
	$b_3 = 0{\cdot}640$	0	0	+1			

* Corrected for induction effects, estimates of which have been made for various conformations of chloroacetone by Mizushima *et al.*, ref. 3, p. 817. † Calculated from μ (corrected) in each case.

TABLE 4.

Polarisabilities, dipole moments, and molar Kerr constants calculated for conformations of bromoacetone.

$\phi°$	b_i	Direction cosines with X	Y	Z	μ	μ corr.*	$10^{12}({}_{m}K)$ †
0	$b_1 = 0{\cdot}940$	$+0{\cdot}958$	$+0{\cdot}288$	0			
	$b_2 = 1{\cdot}095$	$-0{\cdot}288$	$+0{\cdot}958$	0	$4{\cdot}0_5$	$3{\cdot}4_5$	$+281 \pm 22$
	$b_3 = 0{\cdot}728$	0	0	+1			
120	$b_1 = 0{\cdot}930$	$+0{\cdot}817$	$-0{\cdot}576$	$-0{\cdot}011$			
	$b_2 = 1{\cdot}029$	$+0{\cdot}536$	$+0{\cdot}767$	$-0{\cdot}353$	$2{\cdot}2_4$	2·0	-36
	$b_3 = 0{\cdot}804$	$+0{\cdot}212$	$+0{\cdot}282$	$+0{\cdot}936$			
130	$b_1 = 0{\cdot}930$	$+0{\cdot}869$	$-0{\cdot}494$	$+0{\cdot}001$			
	$b_2 = 1{\cdot}049$	$+0{\cdot}470$	$+0{\cdot}826$	$-0{\cdot}310$	$1{\cdot}9_8$	1·8	-27
	$b_3 = 0{\cdot}784$	$+0{\cdot}153$	$+0{\cdot}270$	$+0{\cdot}951$			
150	$b_1 = 0{\cdot}942$	$+0{\cdot}920$	$-0{\cdot}315$	$-0{\cdot}235$			
	$b_2 = 1{\cdot}077$	$+0{\cdot}354$	$+0{\cdot}924$	$+0{\cdot}148$	$1{\cdot}5_0$	1·4	$+31$
	$b_3 = 0{\cdot}745$	$+0{\cdot}170$	$-0{\cdot}219$	$+0{\cdot}961$			
180	$b_1 = 0{\cdot}931$	$+0{\cdot}933$	$-0{\cdot}359$	0			
	$b_2 = 1{\cdot}105$	$+0{\cdot}359$	$+0{\cdot}933$	0	$1{\cdot}1_1$	1·1	$+36$
	$b_3 = 0{\cdot}728$	0	0	+1			

* Estimated by assuming that μ (induced) for bromoacetone $\sim\mu$ (induced) for corresponding conformation of chloroacetone. † Calculated from μ (corrected) in each case.

cis- and non-planar *gauche* forms, then the following proportions yield resultant calculated values in best agreement with experiment.

	% *cis*	% *gauche*	μ (calc.) D	μ (obs.) D	$10^{12}({}_{m}K)$ (calc.)	$10^{12}({}_{m}K)$ (obs.)
Chloroacetone...	21	79 ($\phi = 130°$)	2·27	2·27	+36	+36
Bromoacetone...	16	84 ($\phi = 120$)	2·29	2·29	+15	+14

We thus conclude that both substances are present in carbon tetrachloride solution mainly as the *gauche* form; the ratio *gauche*:*cis* equals *ca.* 4 for chloroacetone and *ca.* 5 for bromoacetone. The *gauche* conformation of chloroacetone is defined by $\phi = ca.\ 130°$ and for bromoacetone by $\phi = ca.\ 120°$; the latter, smaller, value reflects the greater steric repulsion between the bromine atom and the methyl group.

Acetyl Chloride and Chloroacetyl Chloride.—From the molecular geometry of acetyl chloride (ref. 23, M 126) and the component bond moments, we obtain a calculated resultant moment of 2·34 D [directed as shown in (IV)] in fair accord with that from experiment (2·48 D). In the subsequent calculations we assume that μ (observed) for this molecule is similarly located. Utilisation of the bond and group semi-axes listed earlier to predict the anisotropy of polarisability and thence the molar Kerr constant of acetyl chloride, leads to values considerably in excess of those found from experiment. We note also that analogous calculations for chloroacetyl chloride, which are based on these bond polarisabilities, cannot be reconciled with observation. We conclude, therefore, that our original C–C, C=O, and C–Cl bond parameters (which were derived respectively from cyclohexane, acetone, and methyl chloride) are not applicable within the group C·CO·Cl. Alternatively, if we assume that $b_1 = b_2 > b_3$ [$= b_{zz}$ in (IV)] for acetyl chloride (the polarisability ellipsoid for this molecule must reasonably have a very low degree of anisotropy in view of the large dipole moment yet very small molar Kerr constant) then the usual equations [1] for $_\infty({}_{\mathrm{m}}K_2)$ and $_{\mathrm{E}}P$ (= 15·8 c.c. from addition of the bond and group values of Le Fèvre and Steel [24]) can be solved (taking $_{\mathrm{D}}P$ as 1·1 $_{\mathrm{E}}P$) to give: $b_1 = b_2 = 0{\cdot}63_2$; $b_3 = 0{\cdot}61_3$.

The ellipsoid of polarisability for any conformation of chloroacetyl chloride can now be specified by addition of the polarisabilities of the component groups $H_2C{\cdot}CO{\cdot}Cl$ (obtained by subtracting one C–H bond equivalent from the semi-axes of acetyl chloride) and $\overset{a}{\mathrm{C}}$–Cl (for which $b_{\mathrm{L}} = 0{\cdot}318$; $b_{\mathrm{T}} = b_{\mathrm{V}} = 0{\cdot}220$). Two isomers have been considered: the *cis*-chlorine–oxygen form for which $\phi = 0°$ and the *gauche* form described by $\phi = 120°$. Stable conformations having $\phi > 120°$ are unlikely, because of chlorine/chlorine interactions. The calculated polarisabilities are listed in Table 5; the reference axes XYZ are as shown in (V). The bond angle C–C–$\overset{a}{\mathrm{Cl}}$ was taken as 110°.

TABLE 5.
Calculated molecular polarisabilities and molar Kerr constants for conformations of chloroacetyl chloride.

$\phi°$	b_i	Direction cosines with			$10^{12}({}_{\mathrm{m}}K)$
		X	Y	Z	
0	$b_1 = 0{\cdot}788$	+0·940	+0·342	0	
	$b_2 = 0{\cdot}886$	−0·342	+0·940	0	−9 to +16
	$b_3 = 0{\cdot}769$	0	0	+1	
120	$b_1 = 0{\cdot}788$	+0·809	−0·588	+0·001	
	$b_2 = 0{\cdot}781$	+0·442	+0·611	+0·657	*ca.* −23
	$b_3 = 0{\cdot}874$	−0·387	−0·531	+0·754	

For the *cis*-isomer the C–Cl dipoles are antiparallel (see ref. 23, M 123) so that μ (resultant) must act roughly along the carbon–oxygen bond direction. The predicted molar Kerr constant is given in Table 5 as a range of possible values calculated on the basis that a moment of 2·2 D (= μ observed) is located within an arc ±10° from the C=O bond axis and in the XY plane. Vector addition of the component bond moments leads to a calculated resultant moment of 2·3 D for the *gauche* form, which in turn results in a calculated molar Kerr constant of -23×10^{-12}. Unfortunately, the calculated molar Kerr constants are relatively insensitive to changes in ϕ so that it is not possible (in view of our assumptions underlying the derivation of the polarisability semi-axes of the $H_2C{\cdot}CO{\cdot}Cl$ group) to differentiate between the isomers. It can, however, be reasonably concluded from the negativity of the observed molar Kerr constant ($-17{\cdot}3 \times 10^{-12}$) that the *cis*-form cannot be present alone (cf. ref. 15, p. 3466, where it is shown from spectroscopic evidence that both isomers of chloroacetyl chloride are present in carbon tetrachloride solution with the *cis*-conformation predominating).

[23] Sutton *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.*, No. 11, 1958.
[24] Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.

Propionaldehyde and Ethyl Methyl Ketone.—Polarisability semi-axes and molar Kerr constants predicted for various conformations of each of these molecules are listed in Tables 6 and 7. We assume throughout that the molecular dipole moment is directed along the carbonyl group axis; that the bond angles about the sp^2 carbon atom are 120°; and that all other bond angles are tetrahedral. The X, Y, and Z directions are analogous to those described in (III).

TABLE 6.

Polarisabilities and molar Kerr constants calculated for conformations of propionaldehyde.

$\phi°$	b_i	Direction cosines with X	Y	Z	$10^{12}({}_{m}K)$
0	$b_1 = 0.674$	+0.912	−0.410	0	+103
	$b_2 = 0.716$	+0.410	+0.912	0	
	$b_3 = 0.484$	0	0	+1	
90	$b_1 = 0.708$	+0.844	+0.523	−0.121	+70
	$b_2 = 0.622$	−0.504	+0.849	+0.156	
	$b_3 = 0.543$	+0.184	−0.070	+0.980	
120	$b_1 = 0.728$	+0.752	+0.638	−0.167	+96
	$b_2 = 0.620$	−0.656	+0.750	−0.085	
	$b_3 = 0.525$	+0.071	+0.173	+0.982	
150	$b_1 = 0.628$	+0.753	−0.654	+0.073	+131
	$b_2 = 0.750$	+0.658	+0.744	−0.113	
	$b_3 = 0.496$	+0.020	+0.133	+0.991	
180	$b_1 = 0.631$	+0.781	−0.624	0	+148
	$b_2 = 0.759$	+0.624	+0.781	0	
	$b_3 = 0.484$	0	0	+1	

TABLE 7.

Polarisabilities and molar Kerr constants calculated for conformations of ethyl methyl ketone.

$\phi°$	b_i	Direction cosines with X	Y	Z	$10^{12}({}_{m}K)$
0	$b_1 = 0.851$	+0.975	+0.221	0	+126
	$b_2 = 0.922$	−0.221	+0.975	0	
	$b_3 = 0.639$	0	0	+1	
90	$b_1 = 0.848$	+0.632	−0.768	−0.100	+78
	$b_2 = 0.864$	+0.761	+0.640	−0.109	
	$b_3 = 0.699$	+0.148	−0.007	+0.989	
120	$b_1 = 0.841$	+0.831	−0.557	−0.009	+108
	$b_2 = 0.889$	+0.548	+0.820	−0.166	
	$b_3 = 0.681$	+0.100	+0.133	+0.986	
150	$b_1 = 0.841$	+0.910	−0.413	+0.005	+151
	$b_2 = 0.919$	+0.411	+0.904	−0.113	
	$b_3 = 0.652$	+0.043	+0.105	+0.994	
180	$b_1 = 0.842$	+0.927	−0.374	0	+171
	$b_2 = 0.931$	+0.374	+0.927	0	
	$b_3 = 0.639$	0	0	+1	

The observed molar Kerr constants are $+64.4 \times 10^{-12}$ (for propionaldehyde) and $+88.2 \times 10^{-12}$ (for ethyl methyl ketone) in reasonable agreement with the values predicted for conformations having $\phi = ca.$ 90° and $ca.$ 100°, respectively (cf. diethyl ketone [25] for which $\phi = ca.$ 100°). The presence of rotational isomers other than these is not strictly precluded, we infer, however, that these molecules in carbon tetrachloride solution exist mainly as a *gauche* type conformer in which the C–C–Me plane is approximately perpendicular to that of the trigonal carbon valencies.

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[25] Aroney, Izsak, and Le Fèvre, *J.*, 1961, 4148.