Molecular Polarisability. Conformations of the Chlorobenzaldehydes and Chloroacetophenones

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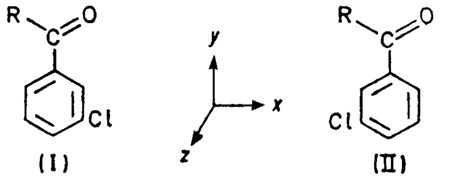
Dipole moments and molar Kerr constants ($\times 10^{12}$) at 25 °C are reported for the following as solutes in carbon tetrachloride: *o*-chlorobenzaldehyde (3·00 D, +437), *m*-chlorobenzaldehyde (2·61 D, +273), *p*-chlorobenzaldehyde (2·00 D, +168), *o*-chloroacetophenone (3·00 D, +138), *m*-chloroacetophenone (2·81 D, +252), and *p*-chloroacetophenone (2·41 D, +53). The results are analysed to provide information concerning the preferred conformations of these molecules.

THIS investigation was prompted by the results of a recent i.r. spectral study of rotational isomerism in *m*-halogenobenzaldehydes by Crowder and Northam.[1] They concluded that in both the vapour and the liquid state two conformers are present, and that the *cis*-form (Ia) of *m*-chloro- and *m*-bromo-benzaldehyde is the more stable. Karabatsos and Vane[2] had, however, deduced from ^{1}H n.m.r. coupling constants that the *trans*-form (IIa) of these two molecules is the energetically favoured structure.



(I) (II)

(Ia,IIa,R = H; Ib,IIb,R = Me)

We have used considerations of molecular polarity and polarisability to resolve this question. Dipole moments and molar Kerr constants are here reported for *o*-, *m*-, and *p*-chloro-benzaldehydes and -acetophenones. Analysis of the data yields information concerning the preferred molecular conformations.

EXPERIMENTAL

Solutes.—*o*-Chloroacetophenone was prepared, by addition of excess of methylmagnesium iodide to *o*-chlorobenzonitrile, followed by hydrolysis (dil. H_2SO_4) of the intermediate ketimine, as a colourless oil (yield 53%), b.p. 70°/*ca.* 1 mm; $\nu_{max.}$ (liquid film) 1698 cm^{-1} (C=O); ^{1}H n.m.r. (in $CDCl_3$): τ 7·32 (s, $COCH_3$) and τ 2·3—2·8 (m, C_6H_4).

m-Chloroacetophenone was obtained (yield 75%) by the method of Leonard and Boyd[3] as a colourless oil, b.p. 80°/*ca.* 1 mm; $\nu_{max.}$ (liquid film) 1686 cm^{-1} (C=O); ^{1}H n.m.r. (in $CDCl_3$): τ 7·40 (s, $COCH_3$) and τ 2·0—2·8 (*m*, C_6H_4). Both these ketones were shown to be pure (>99·5%) by g.l.c.

Other solutes were distilled immediately before use, and had the following b.p.s: *o*-chlorobenzaldehyde, 55—57°/1·5 mm; *m*-chlorobenzaldehyde, 65—67°/2·0 mm; *p*-chlorobenzaldehyde, 108—110°/2·5 mm; *p*-chloroacetophenone, 74—76°/1·5 mm.

Apparatus.—Dielectric constants were determined with apparatus as in ref. 4; associated procedures giving polarisations were standard.[5a] Kerr effects at 589 nm were recorded photometrically.[6]

Results.—These are listed in usual form in Tables 1 and 2. The symbols are those previously explained.[4,5,7]

TABLE 1

Incremental * dielectric constants, densities, refractive indices, and Kerr effects for solutions in carbon tetrachloride at 25°

o-Chlorobenzaldehyde

$10^5 w_2$	135	288	480	671	709	875
$10^4 \Delta\varepsilon$	177	354	639	879	867	1130
$10^4 \Delta n$	2	3	7	11	12	13
$10^5 w_2$	122	284	510	564	770	868
$-10^5 \Delta d$	48	111	200	217	301	—
$10^{11} \Delta B$	350	833	1512	1605	2271	2572

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 12{\cdot}82$, $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}392$, $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}152$, $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}457$, $10^7\Sigma\Delta B/\Sigma w_2 = 29{\cdot}3$

m-Chlorobenzaldehyde

$10^5 w_2$	308	359	455	591	701	834
$10^4 \Delta\varepsilon$	304	352	447	582	688	826
$-10^5 \Delta d$	122	145	184	239	275	345
$10^4 \Delta n$	4	5	7	9	11	13
$10^5 w_2$	196	358	488	568	620	667
$10^{11} \Delta B$	339	653	897	1045	1149	1228

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 9{\cdot}85$, $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}403$, $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}151$, $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}439$, $10^7\Sigma\Delta B/\Sigma w_2 = 18{\cdot}3$

p-Chlorobenzaldehyde

$10^5 w_2$	182	353	453	456	544	748	852
$10^4 \Delta\varepsilon$	111	211	271	278	317	436	511
$-10^5 \Delta d$	82	152	192	—	233	335	—
$10^{11} \Delta B$	196	405	498	—	633	823	—
$10^5 w_2$	2121	4234	4981	5231	5579	5594	
$10^4 \Delta n$	32	65	73	79	84	84	

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 5{\cdot}95$, $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}436$, $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}150$, $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}438$, $10^7\Sigma\Delta B/\Sigma w_2 = 11{\cdot}2$

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[1] G. A. Crowder and F. Northam, *J. Chem. Phys.*, 1969, **50**, 4865.

[2] G. J. Karabatsos and F. M. Vane, *J. Amer. Chem. Soc.*, 1963, **85**, 3886.

[3] N. J. Leonard and S. N. Boyd, *J. Org. Chem.*, 1946, **11**, 405.

[4] A. D. Buckingham, J. Y. H. Chau, R. J. W. Le Fèvre, D. A. A. S. Narayana Rao, and J. Tardif, *J. Chem. Soc.*, 1956, 1405.

[5] R. J. W. Le Fèvre, (*a*) 'Dipole Moments,' Methuen, London, 3rd edn., 1953, ch. 2; (*b*) *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1; (*c*) *Adv. Phys. Org. Chem.*, 1965, **3**, 1.

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

[7] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, (*a* 1953, 4041; (*b*) 1954, 1577; (*c*) *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 261; (*d*) ch. XXXVI in 'Physical Methods of Organic Chemistry,' ed. Weissberger, Interscience, New York, 3rd edn., 1960, vol. 1, p. 2459.

TABLE 1 (*continued*)

o-Chloroacetophenone

10^5w_2	286	424	473	566	653	889
$10^4\Delta\varepsilon$	330	490	550	658	758	1034
$-10^5\Delta d$	148	211	245	280	327	436
$10^4\Delta n$	3	5	6	7	8	11
$10^{11}\Delta B$	252	366	400	488	559	781

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 11{\cdot}60$, $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}500$, $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}122$, $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}354$, $10^7\Sigma\Delta B/\Sigma w_2 = 8{\cdot}65$

m-Chloroacetophenone

10^5w_2	317	445	655	722	823	924
$10^4\Delta\varepsilon$	322	453	664	736	841	949
$-10^5\Delta d$	163	229	329	369	418	474
$10^4\Delta n$	4	5	7	8	9	11
$10^{11}\Delta B$	494	682	1006	1128	1257	1419

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 10{\cdot}20$, $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}510$, $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}113$, $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}330$, $10^7\Sigma\Delta B/\Sigma w_2 = 15{\cdot}4$

p-Chloroacetophenone

10^5w_2	268	324	447	594	756	828
$10^4\Delta\varepsilon$	205	248	342	453	576	633
$-10^5\Delta d$	142	169	232	307	390	429
$10^{11}\Delta B$	76	106	154	211	253	277
10^5w_2	1350	3319	5240	7882	9215	11,210
$10^4\Delta n$	18	45	71	107	123	151

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 7{\cdot}64$, $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}519$, $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}135$, $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}394$, $10^7\Sigma\Delta B/\Sigma w_2 = 3{\cdot}35$

* When $w_2 = 0$, $\varepsilon_1 = 2{\cdot}2270$, $d_1 = 1{\cdot}58454$, $(n_1)_D = 1{\cdot}4575$, $10^7(B_1)_D = 0{\cdot}083$.

Previous Measurements.—Dipole moments reported in Table 2 are in reasonable agreement with literature data;[8–11] the values given by Ahmad[9] appear to be low.

TABLE 2

Polarisations, refractions, dipole moments, and molar Kerr constants

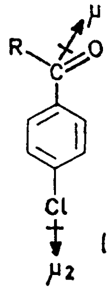
	$\alpha\varepsilon_1$	β	$\gamma' n_1^2$	$_\infty P_2$/cm³	R_D/cm³	μ *	γ	δ	$10^{12}{}_\infty({}_mK_2)$
o-Cl·C$_6$H$_4$·CHO	12·82	−0·247	0·457	222·9	37·3	3·00	0·108	353	+437
m-Cl·C$_6$H$_4$·CHO	9·85	−0·254	0·439	179·0	37·4	2·61	0·104	220	+273
p-Cl·C$_6$H$_4$·CHO	5·95	−0·275	0·438	121·5	37·8	2·00	0·103	135	+168
o-Cl·C$_6$H$_4$·COMe	11·60	−0·316	0·354	227·3	41·1	3·00	0·084	104	+138
m-Cl·C$_6$H$_4$·COMe	10·20	−0·322	0·330	204·5	40·8	2·81	0·078	186	+252
p-Cl·C$_6$H$_4$COMe	7·64	−0·328	0·394	162·7	42·1	2·41	0·093	40·4	+53

* Calculating by assuming $_DP = 1{\cdot}05R_D$.

DISCUSSION

Calculation of Molar Kerr Constants.—Standard methods[5b,5c,12] are used to obtain theoretical molar Kerr constants * by addition of bond and group polarisability tensors. Anisotropic polarisabilities[5c] used in calculations are given in Table 3. We have assumed valence angles of 120° around the carbonyl carbon atom. For each of the compounds studied the experimental molar refraction exceeds the value expected from tabulated bond and group values,[13] and the corresponding exaltation of polarisability (Table 4) must be taken into account when calculating molar Kerr constants. Polarisability-tensor and dipole-moment components (referred to the arbitrary axis system shown), leading to the theoretical molar Kerr constants for specified structures, are summarised in Table 5. For structures (I)—(V) the subscript *a* indicates *R* = H, while *b* refers to *R* = Me.

p-*Chlorobenzaldehyde.*—Although both *o*- and *m*-chlorobenzaldehydes present conformational problems, *p*-chlorobenzaldehyde, by analogy with benzaldehyde, might reasonably be expected to exist as the resonance-stabilised planar form (IIIa). We therefore begin by calculating the expected dipole moment and molar Kerr constant for structure (IIIa). This constitutes a severe test of the applicability of the polarity and polarisability parameters required in the analysis of experimental data for *o*- and *m*-chlorobenzaldehydes.



(III)

The dipole moment of (IIIa) can be considered as the vector resultant of components μ_1 and μ_2, having the same magnitudes and directions as the moments of benzaldehyde and chlorobenzene, respectively. It is known that μ_1 (2·98 D) acts an angle of about 20° to the C=O bond, whereas μ_2 (1·59 D) is directed along the C–Cl axis. The calculated dipole moment of (IIIa) emerges as 2·04 D, which is close to the experimental value (2·00 D).

TABLE 3

Anisotropic polarisabilities of bonds and molecules

	b_L	b_T	b_V
C–H	0·65	0·65	0·65
C–C	0·97	0·26	0·26
C=O	2·30	1·40	0·46
PhCl	14·78	12·55	8·21

With the exaltation of polarisability (Table 4) apportioned equally along the *X* and *Y* axes, the expected

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* Polarisabilities are quoted throughout in 10^{-24} cm³ units (Å³), and molar Kerr constants in 10^{-12} e.s.u.

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

[9] S. I. Ahmad, *Indian J. Pure Appl. Phys.*, 1963, **1**, 434.

[10] V. Baliah and M. Uma, *Tetrahedron*, 1963, **19**, 455.

[11] V. Baliah and K. Aparajithan, *Tetrahedron*, 1963, **19**, 2177.

[12] J. M. Eckert and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1962, 1081.

[13] W. T. Cresswell, G. H. Jeffery, J. Leicester, and A. I. Vogel, *J. Chem. Soc.*, 1952, 514.

molar Kerr constant for the planar conformation (IIIa) is +176, in good agreement with the observed result (+168). We therefore confirm that *p*-chlorobenzaldehyde is planar.

TABLE 4

Exaltations of refraction and polarisability

	R_D (obs.)	R_D (calc.)	Δb
o-Cl·C_6H_4·CHO	37·3	35·5	1·5
m-Cl·C_6H_4·CHO	37·4	35·5	1·5
p-Cl·C_6H_4·CHO	37·8	35·5	2·0
o-Cl·C_6H_4·COMe	41·1	40·2	1·0
m-Cl·C_6H_4·COMe	40·8	40·2	0·8
p-Cl·C_6H_4·COMe	42·1	40·2	2·2

The dipole moments, polarisabilities, and treatment of exaltation found applicable in this unambiguous case are now analogously applied to the *m*- and *o*-isomers.

m-*Chlorobenzaldehyde*.—Previous spectroscopic studies have yielded conflicting results concerning the preferred conformation of this molecule. From ^{1}H n.m.r. spin–spin coupling constants Karabatsos and Vane [2] deduced that, as a solute in CCl_4 or C_6H_6 at room temperature, *m*-chlorobenzaldehyde exists as an equilibrium mixture of *ca.* 35% of the planar *cis*-form (Ia) and 65% of the corresponding *trans*-isomer (IIa). A contrary conclusion regarding relative stabilities was reached by Miller *et al.*[14] from an analysis of the rotational spectrum of the vapour, and by Crowder and Northam [1] from i.r. spectra in vapour, liquid, and solution states.

TABLE 5

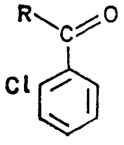
Calculated molar Kerr constants

Structure	b_{xx}	b_{yy}	b_{zz}	b_{xy}	b_{yz}	b_{zx}	μ_x	μ_y	μ_z	$_mK$
(IIIa)	15·90	18·38	8·93	0·387	0	0	1·92	0·69	0	+176
(Ia)	17·33	16·47	8·93	−0·576	0	0	3·29	1·49	0	+576
(IIa)	17·33	16·47	8·93	1·36	0	0	0·54	1·49	0	+168
(IVa)	17·32	16·46	8·93	0·576	0	0	0·54	3·08	0	+364
(Va′)	16·90	16·45	9·33	1·30	0·195	0·700	3·04	3·08	0·98	+1191
(IIIb)	16·98	21·26	10·49	0·082	0	0	2·27	0·31	0	+117
(IIIb′)	16·20	21·26	11·27	0·082	0	1·66	2·27	0·31	0	+48
(Ib)	17·58	18·19	11·56	−0·793	−0·408	2·31	3·52	1·10	0·58	+470
(IIb)	17·58	18·19	11·56	0·957	−0·408	−2·31	1·02	1·10	0·58	+68
(IVb)	15·66	18·49	13·50	−0·766	0·686	−3·01	1·30	2·70	0·97	+141

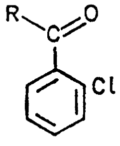
Using the polarity and polarisability components found applicable in the unambiguous case of *p*-chlorobenzaldehyde, we have calculated the expected dipole moments and molar Kerr constants for structures (Ia) and (IIa). The results (which are to be compared with the experimental data in Table 2) are 3·61 D, +576 for (Ia) and 1·59 D, +168 for (IIa). From the observed dipole moment the relative abundances are (Ia), 20% and (IIa), 80%, while the measured Kerr constant yields (Ia), 25% and (IIa), 75%.

These results are in agreement with the conclusion of Karabatsos and Vane that the less-polar *trans*-conformation of *m*-chlorobenzaldehyde is the more stable. It appears that the i.r. spectra [1,14] were erroneously interpreted, probably because peak intensities, rather than integrated band areas, were compared.

o-*Chlorobenzaldehyde*.—A scale model of this molecule suggests that the *trans*-isomer (IVa) should be the preferred conformation. In addition to resonance-stabilisation of this planar structure, there is the possibility of intramolecular hydrogen-bonding. The planar *cis*-form (Va) is sterically hindered, and a rotation of the plane of the -CHO group through about 30° is required for this to be relieved.



(IV)



(V)

The existence of two rotational isomers of *o*-chlorobenzaldehyde in the vapour state was shown by Miller *et al.*,[14] who observed two torsional frequencies in the far-i.r. region. The more stable *trans*-rotamer (IVa) had a relative abundance of *ca.* 70%, but the structure of the other form was not specified. Measurements of ^{1}H n.m.r. coupling constants [2] were interpreted as indicating that in dilute solutions *o*-chlorobenzaldehyde adopts the *trans*-conformation.

The calculated dipole moment for structure (IVa) is 3·17 D, and all other structures have larger moments. Since the experimental result (3·00 D) is slightly smaller than this value, we conclude that *o*-chlorobenzaldehyde as a solute in CCl_4 exists exclusively as (IVa). However the calculated molar Kerr constant for (IVa) is +364, whereas the experimental value is +437. This discrepancy could be due to the presence of a small amount of a second isomer, as is indicated by the rotational spectra. We cannot deduce the conformation of this rotamer, but it seems reasonable to suggest (Va′), a non-planar variant of (Va) having a dihedral angle of *ca.* 30° between the planes of the phenyl and formyl groups. The calculated molar Kerr constant for this structure is +1191, so that the relative abundance of this form would be *ca.* 10%. The calculated dipole moment of 3·17 D for structure (IVa) could be a slight overestimate, since no allowance was made for possible interaction between the aldehydic proton and the chlorine atom.

Our results support the previous conclusions that the

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[14] F. A. Miller, W. G. Fately, and R. E. Witkowski, *Spectrochim. Acta*, 1967, **23**, *A*, 891.

trans-conformation of *o*-chlorobenzaldehyde is highly favoured, although a small quantity of a second rotamer may be present.

p-*Chloroacetophenone.*—The experimental molar Kerr constant of acetophenone is consistent with this molecule's having the resonance-stabilised planar conformation.[15] Following Bentley *et al.*,[16] the dipole moment of acetophenone (2·96 D) was taken as acting at an angle of 10° to the C=O bond and the same assumption is now made in analysing the data for the chloroacetophenones.

We begin by considering the coplanar structure (IIIb) which might reasonably be expected for this molecule. With the exaltation of polarisability assigned along the Y-axis, the calculated molar Kerr constant is +125, whereas the experimental value is only +53. In order to lower the magnitude of the theoretical Kerr constant the C–CO–C plane must be rotated from the aromatic plane. Agreement between calculated and observed molar Kerr constants occurs for the structure (IIIb′), a non-planar variant of (IIIb) in which the dihedral angle is 25°.

A possible reason for the effective non-coplanarity of *p*-chloroacetophenone is as follows. The barrier to internal rotation is somewhat smaller in acetophenone than in benzaldehyde,[14] presumably because of greater repulsive interactions between non-bonded atoms in the former molecule. An electron-withdrawing chlorine substituent would be expected to cause a further lowering of this barrier by reducing the conjugative interaction of the acetyl group with the aromatic ring.[17] This explanation is supported by recent results for 1,4-diacetylbenzene.[15] If it is correct, an enhancement of the coplanarity-favouring mesomeric interaction should occur in *p*-methylacetophenone. Further studies of *para*-substituted acetophenones are in progress.

Results for the corresponding *meta*- and *ortho*-isomers are now analysed by use of the same dipole-moment components, polarisabilities, and apportionment of exaltation.

m-*Chloroacetophenone.*—From the results of the previous section it seems likely that the *cis*- (Ib) and *trans*- (IIb) isomers of *m*-chloroacetophenone are not flat, and have a dihedral angle of *ca.* 25° between the C–CO–C and aromatic planes. Calculated dipole moments and molar Kerr constants for structures (Ib) and (IIb) are in Table 5. Comparison with the experimental data (2·81 D, +252) leads to the conclusion that, as a solute in CCl_4, *m*-chloroacetophenone exists as an approximately equimolecular mixture of structures (Ib) and (IIb).

o-*Chloroacetophenone.*—From ^{13}C n.m.r. spectra Dhami and Stothers[18] deduced that this molecule has a non-planar configuration in which the C–CO–C plane is rotated by 26° from the aromatic plane. The occurrence of a doublet at *ca.* 1700 cm^{-1} in the i.r. spectrum has been attributed to the presence of two conformers.[19]

Consideration of steric and electrostatic factors suggests that a *trans*-conformation (IVb) with a dihedral angle of at least 25° should be favoured. Theoretical molar Kerr constants have once again been calculated and comparison with the experimental result (+138) shows that (IVb) would have a dihedral angle of 45°. The dipole moment calculated for this structure is 3·13 D, which is slightly higher than the observed value (3·00 D).

Alternatively the data could be interpreted in terms of mixtures of non-planar *cis*- and *trans*-isomers, as suggested by the i.r. spectrum, but without further information a unique solution cannot be reached.

[0/1959 *Received, November 17th,* 1970]

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[15] P. H. Gore, P. A. Hopkins, R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.*, (*B*), 1971, 120.

[16] J. B. Bentley, K. B. Everard, R. J. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 1949, 2957.

[17] H. G. Silver and J. L. Wood, *Trans. Faraday Soc.*, 1964, **60**, 5.

[18] K. S. Dhami and J. B. Stothers, *Canad. J. Chem.*, 1965, **43**, 479.

[19] R. N. Jones, W. F. Forbes, and W. A. Mueller, *Canad. J. Chem.*, 1957, **35**, 504.