

129. Molecular Polarisability. The Conformations of Certain Di-ortho-substituted Aromatic Aldehydes and Ketones.

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Dipole moments and molar Kerr constants are reported for 2,4,6-trimethylbenzaldehyde, acetophenone, 2,4,6-trimethylacetophenone, and 2,3,5,6-tetramethylacetophenone as solutes in carbon tetrachloride. The polarisability specifications and thence the molar Kerr constants for various conformations of these molecules have been computed by addition of component bond and group semi-axes. Comparison of the observed and the calculated values shows that ϕ , the interplanar angle between the aromatic ring and the valencies of the extranuclear trigonal carbon atom, is approximately 0 for 2,4,6-trimethylbenzaldehyde and acetophenone and 90° for 2,4,6-trimethylacetophenone and 2,3,5,6-tetramethylacetophenone.

THE effect of *ortho*-substituents on the spectral properties and electric moments of aromatic aldehydes and ketones has been extensively studied.¹⁻⁶ It has been shown that introduction of *ortho*-groups can prevent the assumption of a planar configuration for the group Ph·C=O and this results in a lowering of the mesomeric moment and of the intensity of the *K*-band in the ultraviolet absorption spectrum. This has been utilised by Braude and Sondheimer¹ in estimating the degree of non-planarity between the benzene-ring plane and that of the valencies of the extranuclear trigonal carbon. In the present work we interpret, for five molecules, the magnitude and algebraic sign of the

¹ Braude and Sondheimer, *J.*, 1955, 3754.

² Murray, Cleveland, and Saunders, *J. Amer. Chem. Soc.*, 1942, **64**, 1181.

³ Kadesch and Weller, *J. Amer. Chem. Soc.*, 1941, **63**, 1310.

⁴ Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957.

⁵ Le Fèvre and Le Fèvre, *J.*, 1950, 1829.

⁶ Smith, *J.*, 1957, 4050.

TABLE I.

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

2,4,6-Trimethylbenzaldehyde									
$10^6 w_2$...	1178	4071	4365	5715	$10^6 w_2$...	11,000	14,730	18,310	21,670
$10^7 \Delta B$...	0.039	0.148	0.162	0.208	$10^4 \Delta n$...	15	20	25	29
ϵ^{25}	2.2409	2.2746	2.2787	2.2940	d_4^{25}	1.57468	1.57149	1.56789	1.56515
whence $\sum 10^7 \Delta B / \sum w_2 = 36.3$; $\sum \Delta \epsilon / \sum w_2 = 11.8$. whence $\sum \Delta n / \sum w_2 = 0.135$; $\sum \Delta d / \sum w_2 = -0.897$.									
Acetophenone									
$10^6 w_2$	5753	8433	14,692	25,190					
$10^7 \Delta B$...	0.172	0.253	0.447	0.774					
whence $\sum 10^7 \Delta B / \sum w_2 = 30.5$.									
$10^6 w_2$	6897	8950	17,280	17,680	19,910	23,830	25,310	29,360	34,910
$10^4 \Delta n$	—	—	22	22	25	30	31	37	—
ϵ^{25}	2.3265	2.3567	2.4798	—	2.5177	2.5778	—	2.6607	2.7449
d_4^{25}	—	—	1.57003	1.56974	—	1.56496	1.56348	1.56079	—
whence $\sum \Delta n / \sum w_2 = 0.122$; $\sum \Delta \epsilon / \sum w_2 = 14.6$; $\sum \Delta d / \sum w_2 = -0.834$.									
2,4,6-Trimethylacetophenone									
$10^6 w_2$	17,360	30,122	37,690	39,340					
$10^7 \Delta B$...	-0.123	-0.221	-0.272	-0.284					
whence $\sum 10^7 \Delta B / \sum w_2 = -7.22$.									
$10^6 w_2$	8318	8924	14,510	24,864	26,430	33,270			
$10^4 \Delta n$	8	9	14	25	25	34			
ϵ^{25}	2.3066	2.3134	2.3669	2.4671	2.4825	2.5511			
d_4^{25}	1.57594	1.57525	1.56970	1.55844	1.55785	1.55117			
whence $\sum \Delta n / \sum w_2 = 0.099$; $\sum \Delta \epsilon / \sum w_2 = 9.68$; $\sum \Delta d / \sum w_2 = -1.02$.									
Durene									
$10^6 w_2$	10,060	20,311	28,730	51,550	61,400	72,710	108,600		
$10^7 \Delta B$...	—	—	—	—	0.055	0.068	0.099		
$10^4 \Delta n$	9	19	27	47	56	67	96		
whence $\sum 10^7 \Delta B / \sum w_2 = 0.914$; $\sum \Delta n / \sum w_2 = 0.091$.									
$10^6 w_2$	10,060	20,311	28,730	51,550	69,750				
ϵ^{25}	2.2288	2.2306	2.2322	2.2361	2.2395				
d_4^{25}	1.57160	1.55864	1.54815	1.52066	1.49918				
whence $\sum \Delta \epsilon / \sum w_2 = 0.180$; $\sum \Delta d / \sum w_2 = -1.24$.									
2,3,5,6-Tetramethylacetophenone									
$10^6 w_2$	9849	9887	14,200	14,240	16,930	18,870	20,790	21,300	26,420
$10^7 \Delta B$	-0.103	-0.101	-0.146	-0.150	-0.167	-0.188	-0.204	-0.212	-0.271
whence $\sum 10^7 \Delta B / \sum w_2 = -10.2$.									
$10^6 w_2$	6719	7443	9849	12,640	14,240	14,440	16,930	18,870	19,340
$10^4 \Delta n$	8	—	—	15	—	18	21	—	24
ϵ^{25}	2.2886	2.2934	—	—	2.3529	2.3580	—	2.3928	2.4033
d_4^{25}	1.57777	—	1.57501	—	—	1.57068	1.56696	—	1.56568
whence $\sum \Delta n / \sum w_2 = 0.122$; $\sum \Delta \epsilon / \sum w_2 = 8.97$; $\sum \Delta d / \sum w_2 = -0.981$.									

TABLE 2.

Polarisations, dipole moments, molar Kerr constants, etc., at infinite dilution in carbon tetrachloride at 25°.

Solute	$\alpha \epsilon_1$	β	γ	δ	∞P_2 (c.c.)	R_D (c.c.)	μ (D) *	$10^{13} \infty (mK_2)$
2,4,6-Trimethylbenzaldehyde	11.8	-0.566	0.093	+519	227	46.5	2.95	+572
Acetophenone	14.6	-0.526	0.084	+436	220	36.3	2.96	+387
2,4,6-Trimethylacetophenone	9.68	-0.645	0.068	-103	215	51.1	2.81	-129
Durene	0.180	-0.783	0.062	+13.1	46.4	45.1	0	+14.8
2,3,5,6-Tetramethylacetophenone	8.97	-0.619	0.084	-146	220	56.1	2.81	-19

* Calc. by assuming $n_D = 1.05 R_D$.

molar Kerr constant (a physical property which is sensitively dependent on the disposition of the carbonyl-group moment relative to the plane of the benzene ring) in terms of the preferred molecular conformation.

EXPERIMENTAL

Materials, Apparatus, etc.—The solutes were prepared and/or purified immediately before use to give: 2,4,6-trimethylbenzaldehyde, b. p. 130—135°/ca. 20 mm.; acetophenone, b. p. 92°/ca. 20 mm.; 2,4,6-trimethylacetophenone, b. p. 122°/ca. 20 mm.; durene, m. p. 79.5°; 2,3,5,6-tetramethylacetophenone, m. p. 73°. Carbon tetrachloride, as solvent, was dried (CaCl₂), fractionated through a 1-m. column packed with glass helices, then stored with fresh calcium chloride. Symbols, headings, and methods of calculation used in the following Tables are explained in ref. 7, pp. 280—283. For carbon tetrachloride at 25°, $\epsilon_1 = 2.2270$, $d_1 = 1.58454$, $(n_D)_1 = 1.4575$, and $B_1 = 0.070 \times 10^{-7}$ (Na light).

Previous Measurements.—Determinations of the dipole moment of acetophenone made before 1948 are listed by Wesson⁸ in the M.I.T. Tables which contain no entries for any of the other solutes examined here. Measurements (in D units) recorded in the literature but not included in these Tables are: acetophenone, 2.88 (ref. 3), 2.96 (ref. 4), 2.96 (ref. 9), 2.97 (recalculated from data of ref. 5); 2,4,6-trimethylbenzaldehyde, 2.96 (ref. 3); 2,4,6-trimethylacetophenone, 2.71 (ref. 3), 2.70 (ref. 9), 2.81 (ref. 4), 2.79 (ref. 5); 2,3,5,6-tetramethylacetophenone, 2.68 (ref. 3). The solvent in each case is benzene; the appropriate reference is given in parentheses. Recalculation on the basis of ${}_D P = 1.05 R_D$ results in dipole moments 0.01—0.02 lower than those listed above.

DISCUSSION

Bond and Group Polarisabilities.—Our approach is to calculate (by the method outlined on p. 2486 of ref. 10) the polarisability semiaxes and thence the molar Kerr constants expected for possible conformations of each molecule examined and to compare the ${}_m K$'s so obtained with those from experiment. Bond and group polarisability specifications* 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	7	C ₆ H ₅	1.056	1.056	0.672	13
C—C	0.099	0.027	0.027	11	C ₉ H ₁₁	1.624	1.624	1.174	See text
C=O	0.230	0.140	0.046	12	C ₁₀ H ₁₃	1.748	1.872	1.292	„

Le Fèvre and Le Fèvre⁷ record ${}_\infty({}_m K_2)$ for mesitylene as 10.1×10^{-12} and this in conjunction with ${}_E P = 38.8$ c.c. (estimated by addition of the bond parameters listed by Le Fèvre and Steel¹⁴ leads, by equations (1)—(4), to the polarisability semiaxes for mesitylene: $b_1(C_9H_{12}) = b_2(C_9H_{12}) = 1.688$, $b_3(C_9H_{12}) = 1.238$. Subtraction of one C—H bond equivalent from each yields the C₉H₁₁ group polarisability specifications.

$${}_m K = 2\pi N(\theta_1 + \theta_2)/9. \quad (1)$$

$$\theta_1 = {}_D P[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]/45kT{}_E P. \quad (2)$$

$$\theta_2 = [(b_1 - b_2)(\mu_1^2 - \mu_2^2) + (b_2 - b_3)(\mu_2^2 - \mu_3^2) + (b_3 - b_1)(\mu_3^2 - \mu_1^2)]/45k^2 T^2. \quad (3)$$

$${}_E P = 4\pi N(b_1 + b_2 + b_3)/9. \quad (4)$$

The polarisability ellipsoid of durene, unlike that of mesitylene, is not one of revolution and the semiaxes cannot be obtained directly from the experimental values. Summation

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

⁷ Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 261.

⁸ Wesson, "Tables of Electric Dipole Moments," Technology Press, M.I.T., 1948.

⁹ Cherrier, *Compt. rend.*, 1947, **225**, 1306.

¹⁰ Le Fèvre and Le Fèvre, Ch. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ., Inc., New York, London, 3rd edn., Vol. I, p. 2459.

¹¹ Le Fèvre and Le Fèvre, *J.*, 1956, 3549.

¹² Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 2340.

¹³ Aroney and Le Fèvre, *J.*, 1960, 3600.

¹⁴ Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.

of the component bond and group polarisabilities, and assuming undistorted trigonal valency angles for the ring carbons, results in $b_1(\text{C}_{10}\text{H}_{14})$ (calc.) = 1.812, $b_2(\text{C}_{10}\text{H}_{14})$ (calc.) = 1.936, and $b_3(\text{C}_{10}\text{H}_{14})$ (calc.) = 1.356, where these are located as shown in Fig. 1. The calculated molar Kerr constant follows, from equations (1) and (2), as 13.6×10^{-12} (${}_D P = {}_\infty P_2$ from Table 2; ${}_E P$ is calculated from ref. 14 as 43.3 c.c.) in reasonable agreement with that from experiment, so that we accept these semiaxes, less one C-H contribution, as adequately describing the $\text{C}_{10}\text{H}_{13}$ group ellipsoid.

Molecular Conformations.—For each substance examined, the molecular polarisability semiaxes, the components of the permanent dipole moment along the principal axes directions, and the molar Kerr constants, have been computed for conformations defined by $\phi = 0^\circ$ and $\phi = 90^\circ$ where ϕ is the angle between the benzene ring plane and that of

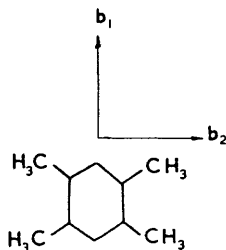


FIG. 1.

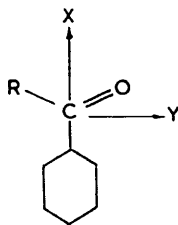


FIG. 2.

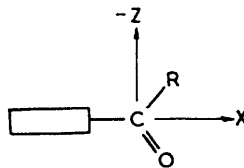


FIG. 3.

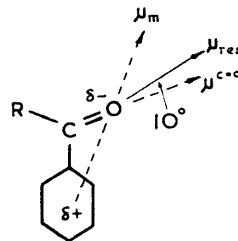


FIG. 4.

the valencies (assumed pure sp^2) of the oxygen-bonded carbon atom. The calculations are summarised in Table 3; the principal axes are located within the co-ordinate system X, Y, Z (see Figs. 2 and 3). Following Bramely and Le Fèvre,¹⁵ we assume that for the planar structures ($\phi = 0$), an exaltation of polarisability [estimated in this work from equation (4) by using $\Delta_E P = 0.95 (R_D \text{ obs.} - R_D \text{ calc. from recorded bond refractions}^{16})]$ acts along the C=O longitudinal axis direction. We assume also that μ_{res} for any molecular model considered equals μ_{obs} (from Table 2) and is directed along the C=O bond axis.

Comparison of the observed molar Kerr constants of benzaldehyde ($+408 \times 10^{-12}$; measured in benzene solution by Bramley and Le Fèvre¹⁵), 2,4,6-trimethylbenzaldehyde ($+572 \times 10^{-12}$), and acetophenone ($+387 \times 10^{-12}$) with the values of Table 3 shows clearly that all three must have planar or nearly planar structures ($\phi \sim 0$). The small apparent differences between ${}_m K_{\text{obs.}}$ and ${}_m K_{\text{calc.}}$ for $\phi = 0$ reflect the uncertainty in the estimates of ΔR_D from which were calculated the exaltations of polarisability (Δb). Our computed values for benzaldehyde differ slightly from those given by Bramley and Le Fèvre¹⁵ whose assumption, that $\Delta b = [9(0.95R_D)/4\pi N] - \Sigma b_i$ (calculated by summing the longitudinal, transverse, and vertical polarisabilities of all component bonds and groups), results in a somewhat smaller exaltation. The calculations are not much affected by the crudity of our assumption that μ_{res} acts along the C=O bond axis. If, for example, in acetophenone, μ_{res} (which can be regarded as the vector sum of $\mu_{\text{C=O}}$ and $\mu_{\text{mesomeric}}$) were disposed 10° away from the C=O axis (as in Fig. 4) then ${}_m K_{\text{calc.}}$ would be $+394 \times 10^{-12}$. The observed molar Kerr constants of 2,4,6-trimethylacetophenone (-129×10^{-12}) and 2,3,5,6-tetramethylacetophenone (-196×10^{-12}) are in excellent agreement with those predicted for $\phi = 90^\circ$.

Smith⁶ had concluded from a comparison of the dipole moments of benzaldehyde (2.92 D) and of 2,4,6-trimethylbenzaldehyde (2.96 D) that there was little or no steric hindrance in the latter. Bentley *et al.*,⁴ in 1949, had shown that μ (2.96 D) for acetophenone, was greater than μ (2.81 D) for 2,4,6-trimethylacetophenone, from which it was inferred that the steric interaction of the 2- and the 6-methyl substituent with the acetyl

¹⁵ Bramley and Le Fèvre, *J.*, 1962, 56.

¹⁶ Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 514.

TABLE 3.
Calculated polarisability semiaxes and molar Kerr constants.

Compound	ϕ	b_i (calc.)	Direction cosines with			10^{12} mK (calc.)
			X	Y	Z	
Benzaldehyde	0	$\begin{cases} b_1 = 1.336 \\ b_2 = 1.525 \\ b_3 = 0.809 \end{cases}$	$\begin{cases} +0.770 \\ +0.637 \\ 0 \end{cases}$	$\begin{cases} -0.637 \\ +0.770 \\ 0 \end{cases}$	$\begin{cases} 0 \\ 0 \\ +1 \end{cases}$	+448
„	90	$\begin{cases} b_1 = 1.385 \\ b_2 = 1.193 \\ b_3 = 0.967 \end{cases}$	$\begin{cases} +0.996 \\ 0 \\ -0.094 \end{cases}$	$\begin{cases} 0 \\ +1 \\ 0 \end{cases}$	$\begin{cases} +0.094 \\ 0 \\ +0.996 \end{cases}$	-101
2,4,6-Trimethylbenzaldehyde ...	0	$\begin{cases} b_1 = 1.905 \\ b_2 = 2.148 \\ b_3 = 1.311 \end{cases}$	$\begin{cases} +0.794 \\ +0.608 \\ 0 \end{cases}$	$\begin{cases} -0.608 \\ +0.794 \\ 0 \end{cases}$	$\begin{cases} 0 \\ 0 \\ +1 \end{cases}$	+541
„ „	90	$\begin{cases} b_1 = 1.953 \\ b_2 = 1.761 \\ b_3 = 1.469 \end{cases}$	$\begin{cases} +0.997 \\ 0 \\ -0.081 \end{cases}$	$\begin{cases} 0 \\ +1 \\ 0 \end{cases}$	$\begin{cases} +0.081 \\ 0 \\ +0.997 \end{cases}$	-130
Acetophenone	0	$\begin{cases} b_1 = 1.550 \\ b_2 = 1.647 \\ b_3 = 0.964 \end{cases}$	$\begin{cases} +0.866 \\ +0.500 \\ 0 \end{cases}$	$\begin{cases} -0.500 \\ +0.866 \\ 0 \end{cases}$	$\begin{cases} 0 \\ 0 \\ +1 \end{cases}$	+398
„	90	$\begin{cases} b_1 = 1.555 \\ b_2 = 1.348 \\ b_3 = 1.179 \end{cases}$	$\begin{cases} +0.999_s \\ 0 \\ -0.021 \end{cases}$	$\begin{cases} 0 \\ +1 \\ 0 \end{cases}$	$\begin{cases} +0.021 \\ 0 \\ +0.999_s \end{cases}$	-112
2,4,6-Trimethylacetophenone ...	0	$\begin{cases} b_1 = 2.118 \\ b_2 = 2.305 \\ b_3 = 1.466 \end{cases}$	$\begin{cases} +0.866 \\ +0.500 \\ 0 \end{cases}$	$\begin{cases} -0.500 \\ +0.866 \\ 0 \end{cases}$	$\begin{cases} 0 \\ 0 \\ +1 \end{cases}$	+476
„ „	60	$\begin{cases} b_1 = 2.123 \\ b_2 = 1.994 \\ b_3 = 1.604 \end{cases}$	$\begin{cases} +0.999 \\ -0.042 \\ -0.011 \end{cases}$	$\begin{cases} +0.038 \\ +0.968 \\ -0.247 \end{cases}$	$\begin{cases} +0.021 \\ +0.246 \\ +0.969 \end{cases}$	-20
„ „	90	$\begin{cases} b_1 = 2.123 \\ b_2 = 1.916 \\ b_3 = 1.681 \end{cases}$	$\begin{cases} +0.999_s \\ 0 \\ -0.018 \end{cases}$	$\begin{cases} 0 \\ +1 \\ 0 \end{cases}$	$\begin{cases} +0.018 \\ 0 \\ +0.999_s \end{cases}$	-134
2,3,5,6-Tetramethylacetophenone	0	$\begin{cases} b_1 = 2.263 \\ b_2 = 2.572 \\ b_3 = 1.584 \end{cases}$	$\begin{cases} +0.941 \\ +0.339 \\ 0 \end{cases}$	$\begin{cases} -0.339 \\ +0.941 \\ 0 \end{cases}$	$\begin{cases} 0 \\ 0 \\ +1 \end{cases}$	+591
„ „	60	$\begin{cases} b_1 = 2.249 \\ b_2 = 2.234 \\ b_3 = 1.728 \end{cases}$	$\begin{cases} +0.930 \\ -0.368 \\ -0.011 \end{cases}$	$\begin{cases} +0.360 \\ +0.914 \\ -0.187 \end{cases}$	$\begin{cases} +0.079 \\ +0.170 \\ +0.982 \end{cases}$	-43
„ „	90	$\begin{cases} b_1 = 2.247 \\ b_2 = 2.164 \\ b_3 = 1.799 \end{cases}$	$\begin{cases} +0.999_s \\ 0 \\ -0.017 \end{cases}$	$\begin{cases} 0 \\ +1 \\ 0 \end{cases}$	$\begin{cases} +0.017 \\ 0 \\ +0.999_s \end{cases}$	-191

group would inhibit mesomerism by preventing a planar or near-planar conformation. These results, while only qualitative, are in harmony with our conclusions. Braude and Sondheimer¹ have constructed scale drawings of the uniplanar structures which indicate that “an *o*-methyl group causes no steric overlap with the hydrogen atom of a formyl group, slight overlap with the oxygen atom of a formyl or acetyl group, and considerable overlap with the methyl portion of an acetyl group.” From an examination of the ultraviolet absorption spectra of these substances, they show that introduction of methyl groups in the 2- and the 6-position results in a marked decrease in the *K*-band intensity for acetophenone, but a very small decrease for benzaldehyde. This they relate to the interplanar angle ϕ (for details see ref. 1, p. 3760) which, for 2,4,6-trimethylacetophenone, they estimate as *ca.* 63°. Our calculations for structures, defined by $\phi = 60^\circ$, of 2,4,6-trimethyl- and 2,3,5,6-tetramethyl-acetophenone lead to molar Kerr constants (-20×10^{-12} and -43×10^{-12} , respectively; see Table 3 for polarisability semiaxes, etc.) which differ considerably from our experimental values.

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