

680. Molecular Polarisability. Dipole Moments, Molar Kerr Constants, and Apparent Conformations of Certain Tri-*n*-alkyl Orthoformates.

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The apparent dipole moments and molar Kerr constants of four tri-*n*-alkyl orthoformates, examined as solutes in carbon tetrachloride, are: $(\text{CH}_3\text{O})_3\text{CH}$, 1.66 D and -6.8×10^{-12} ; $(\text{C}_2\text{H}_5\text{O})_3\text{CH}$, 1.67 D and -9.1×10^{-12} ; $(n\text{-C}_3\text{H}_7\text{O})_3\text{CH}$, 1.64 D and -6.1×10^{-12} ; $(n\text{-C}_4\text{H}_9\text{O})_3\text{CH}$, 1.66 D and $+1.6 \times 10^{-12}$. Observations on trimethyl orthoformate are explicable if, in solution, this substance exists as a mixture of rotational isomers in which each methyl group is staggered with respect to the hydrogen on the central carbon atom and the oxygen atoms of the neighbouring methoxy-groups. The tri-*n*-alkyl orthoformates tend to become optically isotropic as the alkyl side-chains increase to C_4 .

THIS Paper deals with relations between the anisotropies of polarisability and the apparent conformations of the lower tri-*n*-alkyl orthoformates, examined as solutes at infinite dilution in carbon tetrachloride at 25°. Observations and results are summarised under usual ^{1,2} headings in Tables 1 and 2.

EXPERIMENTAL

Materials, apparatus, etc.—The solutes were prepared and/or purified immediately before use, to give: trimethyl orthoformate, b. p. 101—102°; triethyl orthoformate, b. p. 144—146°; tri-*n*-propyl orthoformate, b. p. 196—198°; tri-*n*-butyl orthoformate, b. p. 245—247°. Carbon tetrachloride, as solvent, was dried (CaCl_2), fractionated through a 1-m. column packed with glass helices, and stored with fresh calcium chloride. Symbols, headings, and methods of calculation used in the Tables are explained in ref. 2*a*, pp. 280—283. For carbon tetrachloride at 25°, $\epsilon = 2.2270$, $d_1 = 1.58454$, $(n_D)_1 = 1.4575$, and $B_1 = 0.070 \times 10^{-7}$ (Na light).

¹ Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953; Buckingham, Chau, Freeman, Le Fèvre, Rao, and Tardif, *J.*, 1956, 1405.

² Le Fèvre and Le Fèvre, (a) *Rev. Pure Appl. Chem. (Australia)*, 1955, 5, 261; (b) *J.*, 1953, 4041; (c) *J.*, 1954, 1577; (d) ch. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York and London, 3rd edn., Vol. 1, p. 2459.

TABLE 1.

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

Solute: Trimethyl orthoformate									
$10^5 w_2$	5195	5897	7354	7540	8635				
$-10^7 \Delta B$...	0.030	0.034	0.040	0.043	0.053				
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -0.573$.									
$10^5 w_2$	1055	1424	2103	2932	4088	5897	7540		
$-10^4 \Delta n$...	14	21	29	40	53	74	94		
ϵ^{25}	2.2738	2.2905	2.3176	2.3533	2.4029	2.4756	2.5449		
d_4^{25}	1.57334	1.56950	1.56263	1.55475	1.54343	1.52836	1.51283		
whence $\Sigma \Delta n / \Sigma w_2 = -0.130$; $\Delta \epsilon = 4.55w_2 - 3.99w_2^2$; $\Delta d = -1.06_3 w_2 + 1.58w_2^2$.									
Solute: Triethyl orthoformate									
$10^5 w_2$	4565	5993	6684	6746	7891				
$-10^7 \Delta B$...	0.028	0.036	0.040	0.040	0.048				
$-10^4 \Delta n$...	52	70	79	—	91				
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -0.060$; $\Sigma \Delta n / \Sigma w_2 = -0.116$.									
$10^5 w_2$	978	1744	3695	4441	5724				
ϵ^{25}	2.2584	2.2822	2.3448	2.3669	2.4067				
d_4^{25}	1.57221	1.56287	1.53965	1.53084	1.51618				
whence $\Delta \epsilon = 3.22w_2 - 1.41w_2^2$; $\Delta d = -1.26_1 w_2 + 1.37w_2^2$.									
Solute: Tri-n-propyl orthoformate									
$10^5 w_2$	1059	1902	3853	4753	5030	7042	7647	10.091	
$-10^7 \Delta B$...	—	—	0.010	—	0.016	0.016	0.025	0.028	0.037
$-10^4 \Delta n$...	9	—	32	40	42	60	66	86	—
ϵ^{25}	2.2523	—	2.2966	2.3174	2.3384	—	—	2.4029	—
d_4^{25}	1.57106	1.56021	1.54752	1.53595	1.52584	—	—	1.49211	—
whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -0.354$; $\Sigma \Delta n / \Sigma w_2 = -0.085$; $\Delta \epsilon = 2.41w_2 - 1.38w_2^2$; $\Delta d = -1.31_1 w_2 + 1.32w_2^2$.									
Solute: Tri-n-butyl orthoformate									
$10^5 w_2$	1082	2076	3063	4630	7096	8731			
$-10^4 \Delta n$...	8	16	21	32	50	—			
ϵ^{25}	—	2.2707	—	2.3224	2.3693	2.3995			
d_4^{25}	1.57032	1.55762	1.54572	1.52590	1.49645	—			
whence $\Sigma \Delta n / \Sigma w_2 = -0.070$; $\Sigma \Delta \epsilon / \Sigma w_2 = 2.01$; $\Delta d = -1.30_3 w_2 + 0.934w_2^2$. $\Delta B = ca. 0$ for all concentrations examined up to $w_2 = 8731 \times 10^{-5}$.									

TABLE 2.

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

Solute	$\alpha \epsilon_1$	β	γ	δ	${}^\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) *	10^{12} ${}^\infty ({}_m K_2)$
$(CH_3O)_3CH$	4.55	-0.671	-0.089	-8.19	83.6	25.6	1.66	-6.8
$(C_2H_5O)_3CH$	3.22	-0.796	-0.080	-8.59	99.2	40.2	1.67	-9.1
$(n-C_3H_7O)_3CH$	2.41	-0.827	-0.059	-5.06	112.0	54.5	1.64	-6.1
$(n-C_4H_9O)_3CH$	2.01	-0.826	-0.048	ca. 0	127.3	67.7	1.66	+1.6

* Calculated assuming ${}_D P = 1.05 R_D$.

Previous Measurements.—The following dipole moment measurements (in D units) are in the literature: trimethyl orthoformate, 1.88 (in benzene);³ triethyl orthoformate, 1.90 (in benzene),³ 0.76 (in hexane);⁴ tri-n-propyl orthoformate, 1.92 (in benzene).³

DISCUSSION

Bond Polarizabilities and Polarities.—Our approach is to compute the theoretical dipole moments and molar Kerr constants for possible conformations of the molecule under examination and to compare the predicted values with those from experiment. Bond

³ Arbutov and Shavsha-Tolkacheva, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1954, 614.

⁴ Caughlan, Katz, and Hodgson, *J. Amer. Chem. Soc.*, 1951, **73**, 5654.

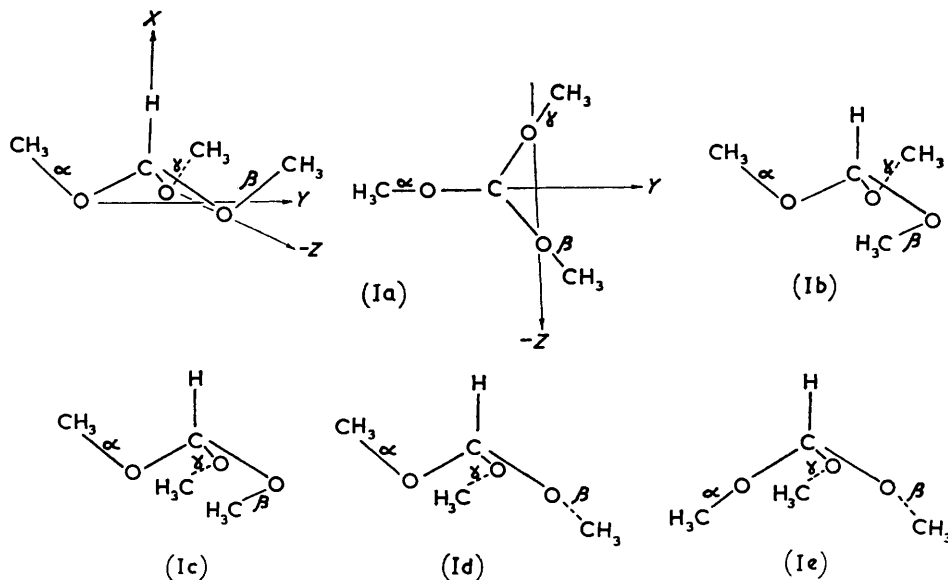
polarisabilities * used in the subsequent calculations are (b_L first, $b_T = b_V$ second): C-H 0.064, 0.064; ^{2a} C-C 0.099, 0.027; ⁵ C-O 0.089, 0.046.⁶ The magnitude of μ ($\text{CH}_3 \rightarrow \text{O}$) is calculable as 1.7 D from $\mu(\text{Me}_2\text{O}) = 1.32 \text{ D}$ ⁷ together with a C-O-C angle of 111° (ref. 8, M138). All bond angles are assumed to be 110° in the molecular models considered; small deviations from this angle do not sensibly affect the calculations. The molecular polarisability semi-axes, b_1 , b_2 , and b_3 , may be specified, for a particular conformational isomer, by the method outlined on p. 2486 of ref. 2*d*. Resolution of the bond-moment vectors along the principal axes yields μ_1 , μ_2 , and μ_3 , the components of the resultant dipole moment along these axes. The molar Kerr constant can then be evaluated by way of the following equations:

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

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

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

Conformations of Trimethyl Orthoformate.—Molecular models indicate that there can only be restricted rotation about the C-O-Me bonds. Initially we consider structures (Ia—e), analogous to those proposed for triethylamine by Brown and Taylor.⁹ Structure (Ia) has C_{3v} symmetry with the methyl groups above the YZ plane (that of the three oxygens). Structure (Ib) is obtained from (Ia) by rotating the OCH₃ group (designated β) about its C-O bond axis, through 120° in the negative Y direction; (Ic) is derived from (Ib) by



rotation of the γ -OCH₃ group about its C-O bond axis through 120° in the $-Y$ direction; (Id) is formed from (Ia) by 120° rotations of β - and γ -OCH₃ in the $+Y$ and $-Y$ directions, respectively; (Ie) is generated from (Ia) by rotations of 120° of all three OCH₃ groups in such a way as to preserve a C_3 symmetry. All other possible conformations involving 120°

* Polarisability semi-axes of bonds, 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.

⁵ Le Fèvre and Le Fèvre, *J.*, 1956, 3549.

⁶ Le Fèvre, Sundaram, and Pierens, *J.*, 1963, 479.

⁷ Aroney, Le Fèvre, and Saxby, *J.*, 1962, 2886.

⁸ Sutton *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.*, No. 11, 1958.

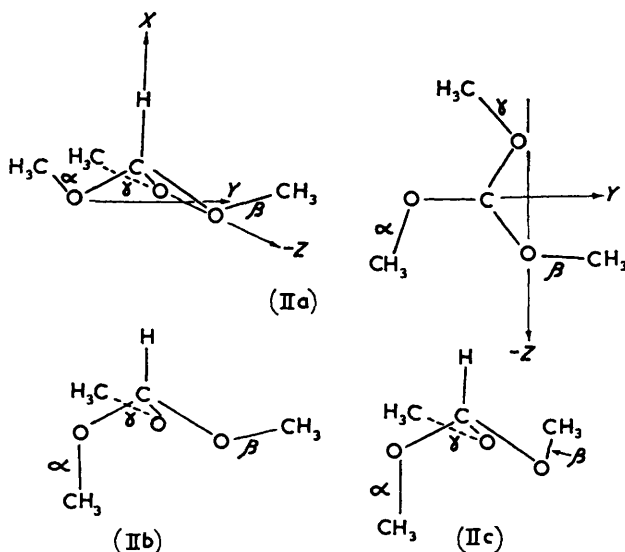
⁹ Brown and Taylor, *J. Amer. Chem. Soc.*, 1947, **69**, 1332.

rotations of one or more OCH_3 groups from (Ia) are either mirror images of the ones considered above (and hence have identical values of the resultant dipole moment and of the molar Kerr constant) or, alternatively, they are sterically not allowable. The polarisability semi-axes and their locations within the co-ordinate system X, Y, Z , the resultant dipole moment, and the molar Kerr constant for each of the conformational isomers (Ia—e) have been calculated (Table 3). Comparison with the observed values [$\mu = 1.66 \text{ D}$ and ${}_{\infty}({}_m K_2) = -6.8 \times 10^{-12}$] shows that no individual conformation or mixture of such conformations

TABLE 3.
Calculated polarisabilities, dipole moments, and molar Kerr constants for conformations (Ia—e) of trimethyl orthoformate.

Conformation	b_i	Direction cosines with			$\mu \text{ (D)}$	$10^{12} {}_m K$
		X	Y	Z		
(Ia)	$b_1 = 1.007$	+1	0	0	3.86	+11.5
	$b_2 = 1.000$	0	+1	0		
	$b_3 = 1.000$	0	0	+1		
(Ib)	$b_1 = 0.962$	+0.651	+0.261	-0.713	2.56	-0.8
	$b_2 = 1.002$	-0.576	+0.781	-0.241		
	$b_3 = 1.042$	-0.494	-0.568	-0.659		
(Ic)	$b_1 = 0.981$	+0.980	-0.201	0	2.34	+11.3
	$b_2 = 1.026$	+0.201	+0.980	0		
	$b_3 = 0.999$	0	0	+1		
(Id)	$b_1 = 0.959$	+0.771	+0.298	+0.563	1.34	-2.0
	$b_2 = 1.044$	-0.387	+0.921	+0.042		
	$b_3 = 1.003$	+0.506	+0.250	-0.825		
(Ie)	$b_1 = 0.971$	+1	0	0	0.79	-3.1
	$b_2 = 1.017$	0	+1	0		
	$b_3 = 1.017$	0	0	+1		

will have a sufficiently negative ${}_m K$. Also, it is not possible to find any single "effective" conformation for this molecule which will simultaneously have the required dipole moment and molar Kerr constant.



An examination of Leybold models shows that conformations (Ia—e), though considered likely for triethylamine by Brown and Taylor⁹ (who, in turn, base their assumptions on the conclusions of Stuart¹⁰ for diethyl ether), contain eclipsed arrangements of each methyl

¹⁰ Stuart, "Molekülstruktur," Springer, Berlin, 1934, pp. 236—240.

group with the hydrogen on the central carbon atom or with the oxygen atom of a neighbouring methoxy-group. We now proceed to consider the corresponding staggered forms of which only three types are sterically allowable (IIa—c). Structure (IIa) is generated from (Ia) by rotating each methyl group of (Ia), in the same sense, through 60° ; (IIa) has C_3 symmetry. Rotation of $\alpha\text{-OCH}_3$ of (IIa) through 120° so that it is staggered with respect to the neighbouring group O—C—O, gives form (IIb); (IIc) is derived from (IIb) by a 120° rotation of $\beta\text{-OCH}_3$ in the —Y direction. The calculated quantities for these conformations are summarised in Table 4. The observed dipole moment (1.66 D) is compatible with a mixture of 27% of (IIa) and 73% of (IIb) and/or (IIc). The resultant calculated

TABLE 4.

Calculated polarisabilities, dipole moments, and molar Kerr constants for conformations (IIa—c) of trimethyl orthoformate.

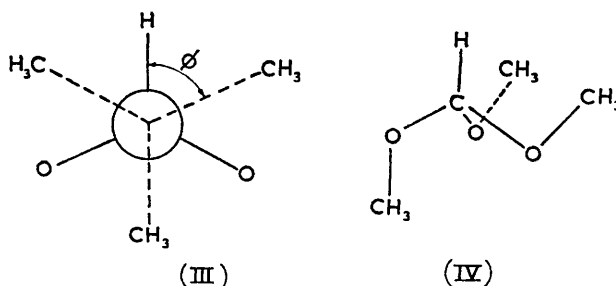
Conformation	b_1	Direction cosines with			μ (D)	$10^{12} mK$
		X	Y	Z		
(IIa)	$\begin{cases} b_1 = 0.945 \\ b_2 = 1.030 \\ b_3 = 1.030 \end{cases}$	$\begin{matrix} +1 \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ +1 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ +1 \end{matrix}$	2.31	-49.7
(IIb)	$\begin{cases} b_1 = 0.974 \\ b_2 = 1.031 \\ b_3 = 1.001 \end{cases}$	$\begin{matrix} +0.813 \\ -0.003 \\ -0.582 \end{matrix}$	$\begin{matrix} -0.299 \\ +0.855 \\ -0.423 \end{matrix}$	$\begin{matrix} -0.499 \\ -0.518 \\ -0.695 \end{matrix}$	1.34	-0.2
(IIc)	$\begin{cases} b_1 = 0.973 \\ b_2 = 1.001 \\ b_3 = 1.032 \end{cases}$	$\begin{matrix} +0.804 \\ -0.594 \\ 0 \end{matrix}$	$\begin{matrix} +0.594 \\ +0.804 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ +1 \end{matrix}$	1.33	-0.2

TABLE 5.

Calculated polarisabilities, dipole moments, and molar Kerr constants for conformations (IIIa—c) of trimethyl orthoformate.

Conformation	b_1	Direction cosines with			μ (D)	$10^{12} mK$
		X	Y	Z		
(IIIa) ($\phi = 50^\circ$)	$\begin{cases} b_1 = 0.957 \\ b_2 = 1.025 \\ b_3 = 1.025 \end{cases}$	$\begin{matrix} +1 \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ +1 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ +1 \end{matrix}$	2.75	-57
(IIIb) ($\phi = 180^\circ$)	$\begin{cases} b_1 = 0.973 \\ b_2 = 1.025 \\ b_3 = 1.008 \end{cases}$	$\begin{matrix} +0.692 \\ +0.004 \\ -0.722 \end{matrix}$	$\begin{matrix} -0.427 \\ +0.808 \\ -0.405 \end{matrix}$	$\begin{matrix} -0.582 \\ -0.589 \\ -0.561 \end{matrix}$	1.48	+2.2
(IIIc) ($\phi = 310^\circ$)	$\begin{cases} b_1 = 1.002 \\ b_2 = 0.973 \\ b_3 = 1.030 \end{cases}$	$\begin{matrix} +0.790 \\ +0.613 \\ 0 \end{matrix}$	$\begin{matrix} -0.613 \\ +0.790 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ +1 \end{matrix}$	1.35	+2.3

molar Kerr constant would then be -13.6×10^{-12} , which is more negative than that observed. So far we have not taken into account the inequality in the steric repulsions of oxygen and of hydrogen. In the rotation of each methyl group about its C—O bond axis, the potential minima would be located as shown in (III), with ϕ , in turn, $<60^\circ$, 180° , and



$>300^\circ$. Calculations for structures in which ϕ is 50° (IIIa), 180° (IIIb), and 310° (IIIc) are listed in Table 5. An equilibrium mixture of conformational isomers with *ca.* 13% of

(IIIa) and *ca.* 87% of (IIIb) and (IIIc) would have a calculated dipole moment and molar Kerr constant both in reasonable agreement with the observed quantities. The calculated values are not significantly affected by small changes in the bond moments or the bond polarisabilities; they are, however, sensitively dependent on ϕ . If, for example, ϕ is 0 or 180°, the two types of sterically permissible isomer [(Ia) and (IV)] would have the following calculated parameters [μ (D) and 10^{12} mK]: (Ia), 3.86 and +11.5; (IV), 1.94 and +19.2.

The Higher Tri-n-alkyl Orthoformates.—The four tri-n-alkyl orthoformates examined have similar dipole moments (all lie within the range 1.66 ± 0.02 D), which suggests that the effective dispositions of the C–O bond dipoles with respect to $\mu(\text{O}_3\text{CH})$ must be similar throughout. Because of the large number of possible rotational isomers, calculations for individual conformations are of little significance. If, however, we assume that these molecules can be described by ellipsoids of revolution with $b_1 \neq b_2 = b_3$ and $\mu_1 \neq \mu_2 = \mu_3 = 0$, then the usual equations (1)–(4) can be solved for b_1 and b_2 . The electronic polarisations were estimated by addition of the bond values listed by Le Fèvre and Steel.¹¹ The

$${}_E P = 4\pi N(b_1 + 2b_2)/9 \quad (4)$$

ratios $b_1 : b_2$ approach unity as the alkyl side-chains increase to C_4 , thus indicating a tendency towards optical isotropy.

TABLE 6.

The electronic polarisations and principal polarisability semi-axes of the molecules $(\text{RO})_3\text{CH}$.

Solute	${}_E P$ (c.c.)	b_1	$b_2 = b_3$	b_1/b_2
$(\text{C}_2\text{H}_5\text{O})_3\text{CH}$	39.01	1.527	1.556	0.98 ₁
$(n\text{-C}_3\text{H}_7\text{O})_3\text{CH}$	52.63	2.072	2.093	0.99 ₀
$(n\text{-C}_4\text{H}_9\text{O})_3\text{CH}$	66.26	2.630	2.625	1.00 ₂

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¹¹ Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.