4. *Molecular Polarisability. The Molar Kerr Constants and Dipole Moments of* spiro- *and Other Derivatives of Pentaerythritol.*

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Pentaerythritol tetrachloride, tetrabromide, and tetra-acetate, and the dimethylene- and dibenzylidene-derivatives of pentaerythritol have been examined as solutes in carbon tetrachloride. In each case the total polarisation exceeds the molecular refraction. Reasons are given for viewing the moments of the first three compounds as " apparent," and ascribable to " vibration polarisation," a phenomenon which the flexible tetra-acetate exhibits in an unusual degree. Structures of the type $C(CH_2X)_4$ with the four X groups at the corners of a square plane containing the central carbon atom are reconcilable with all the results now found. In dimethylene-pentaerythritol the two *spiro*-1 : 3-dioxan rings may have " boat " or " chair " conformations. The molar Kerr constant, in conjunction with other properties, indicates as correct a " chair–chair " structure, rather than one in which the rings are " boat–boat " or " boat–chair."

THE three pentaerythritol derivatives (I; X = Cl, Br, or OAc) were examined to obtain information on tetrahedrally symmetric structures additional to that available to Le Fèvre, Le Fèvre, and Narayana Rao[1] for the simple cases CH_4, CCl_4, and CBr_4. Subsequently,

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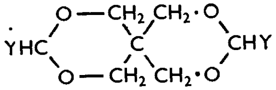
[1] Le Fèvre, Le Fèvre, and Narayana Rao, *J.*, 1956, 708.

the two compounds (II; Y = H or Ph) were added; the first was subjected to conformational analysis through the polarisability ellipsoids[2] recently computed[3] for C–C and C–O bonds. Dielectric polarisations and relaxation times were also determined.

$C(CH_2X)_4$

(I)



(II)

EXPERIMENTAL

Materials.—Pentaerythritol tetrachloride was obtained from pentaerythritol and thionyl chloride in presence of pyridine.[4] (The method involving phosphorus trichloride[5] appeared to be inferior.) It crystallised from aqueous ethanol as white leaflets, m. p. 96·0—97·5° (lit. 97°). Pentaerythritol tetrabromide, prepared as in ref. 5, was twice crystallised from 95% ethanol from 20° to −10°, and had m. p. 157·6—158·2° (lit., 163°,[5] 158°[6]). Pentaerythritol tetra-acetate,[7] from light petroleum, had m. p. 81—82°. *OO'-O''O'''*-Dimethylenepentaerythritol (II; Y = H), made as by Read[8] formed white crystals, m. p. 49—51° (lit., 50°[8,9]), and the dibenzylidene analogue[8] [illegible] white plates, m. p. 156·5—157° (lit., 160°), from chloroform. Tetranitromethane (" p [illegible] nercial sample) was steam-distilled, dried (Na_2SO_4), then partially frozen, and the solid separated; after melting it was redried ($MgSO_4$), filtered, and stored in a well-stoppered flask; m. p. 13°.

Carbon tetrachloride. This was used as solvent throughout all the measurements. It was from the " sulphur-free " bulk supply noted in ref. 10. It was stored over calcium chloride and filtered immediately before use.

Dielectric Polarisations.—These were determined by standard procedures,[11] except that for capacity comparisons the circuit described in ref. 12 was used.

Relaxation Times.—The equipment was that described by Le Fèvre and Sullivan,[13] and Chau, Le Fèvre, and Tardif.[14] The formulæ by which the relaxation time τ of a solute is extracted from the observed Q factors are given in ref. 13.

Electric Double Refractions.—Le Fèvre and Le Fèvre's[2,15] apparatus was used, modified only by the insertion of a " Scalamp " electrostatic voltmeter in parallel with the cell leads to obtain higher accuracy in the voltage readings. Refractive indexes were taken on an Abbé refractometer.

Symbols.—These have significances as follow (suffixes 1, 2, and 12 being applied to indicate respectively solvent, solute, and solution): w, weight fractions; ε, dielectric constants; d, densities; n, refractive indexes; M, molecular weights; R, molecular refractions; p, specific polarisations; ${}_{\infty}P$, total polarisations at infinite dilution; μ, dipole moments; Δf, the widths (in frequency units, mc./sec.) at half-heights of the resonance curves involved in measurements of loss tangents (here called tan ϕ—an inconsistency with refs. 13 and 14 but necessary—since the letter δ is also used in another connection) and relaxation times τ; Δ tan ϕ, the differences between the loss tangents of solutions and solvent; ψ is $(\Delta \tan \phi)/w_2$; B denotes Kerr constants; ΔB, the changes in Kerr constant from solvent to solutions; ${}_{s}K$, specific Kerr constants; ${}_{\infty}({}_{m}K)$, molar Kerr constants at infinite dilution; α, β, γ, δ, are quantities obtained by

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[2] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.
[3] *Idem, J.*, 1956, 3549.
[4] Mooradian and Cloke, *J. Amer. Chem. Soc.*, 1945, **67**, 942.
[5] Schurink, " Organic Syntheses," Coll. Vol. II, 476.
[6] Ebert, Eisenschitz, and Hartel, *Z. phys. Chem.*, 1928, *B*, **1**, 94.
[7] Orthner and Freyss, *Annalen*, 1930, **484**, 131.
[8] Read, *J.*, 1912, **101**, 2090.
[9] Schulz and Tollens, *Annalen*, 1896, **289**, 28.
[10] Le Fèvre and Le Fèvre, *J.*, 1954, 1577.
[11] Le Fèvre, " Dipole Moments," Methuen, 3rd Edn., 1953, Chap. II.
[12] Buckingham, Chau, Freeman, Le Fèvre, Narayana Rao, and Tardif, *J.*, 1956, 1405.
[13] Le Fèvre and Sullivan, *J.*, 1954, 2873.
[14] Chau, Le Fèvre, and Tardif, *J.*, 1957, 2293.
[15] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.

taking $\varepsilon_{12} = \varepsilon_1(1 + \alpha w_2)$, $d_{12} = d_1(1 + \beta w_2)$, $n_{12} = n_1(1 + \gamma w_2)$, and $B_{12} = B_1(1 + \delta w_2)$. Then:

$$_{\infty}P_2 = [p_1(1 - \beta) + C\alpha\varepsilon_2]M_2$$

and

$$_{\infty}(_{\mathrm{m}}K_2) = {}_{\mathrm{s}}K_1(1 - \beta + \gamma + \delta - H\gamma - J\alpha\varepsilon_2)M_2$$

where C, H, and J are constants for the solvent (see refs. 10 and 11 for further details).

Tables 1—4 record experimental observations, from which the results presented in Tables 5 and 6 are deduced.

TABLE 1. *Dielectric polarisation measurements in carbon tetrachloride at 25°* ($\varepsilon_1 = 2{\cdot}2270$; $d_1 = 1{\cdot}58454$)

Pentaerythritol tetrachloride

10^5w_2	ε_{12}	d_{12}	10^5w_2	ε_{12}	d_{12}
526	2·2293	1·58365	1287	2·2317	1·58260
568	2·2294	1·58354	1298	2·2339	—
767	2·2322	1·58328	2341	—	1·58054

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}484$, $\Sigma\Delta d/\Sigma w_2 = -\,0{\cdot}165$

Pentaerythritol tetra-acetate

10^5w_2	ε_{12}	d_{12}	10^5w_2	ε_{12}	d_{12}
680	2·2501	1·58067	1080	2·2637	1·57821
864	2·2567	1·57946	1333	2·2729	1·57716
942	2·2578	1·57928			

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 3{\cdot}41$, $\Sigma\Delta d/\Sigma w_2 = -\,0{\cdot}564$

Pentaerythritol tetrabromide

10^5w_2	ε_{12}	d_{12}	10^5w_2	ε_{12}	d_{12}
585	2·2302	1·58782	1270	2·2344	1·59137
754	2·2313	1·58894	1521	2·2353	1·59276
1238	2·2341	1·59130	1602	2·2361	1·59348

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}565$, $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}551$

Dimethylenepentaerythritol (II; Y = H)

10^5w_2	ε_{12}	d_{12}	10^5w_2	ε_{12}	d_{12}
336	2·2564	1·58316	878	2·3038	1·58106
750	2·2918	1·58152	1068	2·3196	1·58008
828	2·2978	1·58109	1378	2·3462	1·57848

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 8{\cdot}66$, $\Sigma\Delta d/\Sigma w_2 = -\,0{\cdot}417$

Dibenzylidenepentaerythritol (II; Y = Ph)

10^5w_2	ε_{12}	d_{12}	10^5w_2	ε_{12}	d_{12}
386	2·2416	1·58264	775	2·2570	1·58035
441	2·2447	1·58212	890	2·2637	1·57926
564	2·2488	1·58168			

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 3{\cdot}95_3$, $\Sigma\Delta d/\Sigma w_2 = -\,0{\cdot}545$

Tetranitromethane

10^5w_2	ε_{12}	d_{12}	10^5w_2	ε_{12}	d_{12}
968	2·2285	1·58454	2139	2·2299	1·58454
2005	2·2290	—	2240	2·2296	—

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}122$, $\Sigma\Delta d/\Sigma w_2 = ca.\ 0$

TABLE 2. *Refractions* (Na *light*) *at* 25°.

Solute	10^5w_2	n_D	γn	Solute	10^5w_2	n_D	γn
—	0	1·4575	—	(II; Y = Ph) ...	543	1·4583	0·1473
$C(CH_2Cl)_4$	3976	1·4602	0·0679	$C(NO_2)_4$	859	1·4572	−0·0348
$C(CH_2Br)_4$	2999	1·4614	0·1302	,, ...	1482	1·4570	
$C(CH_2OAc)_4$	2198	1·4574	−0·0045	,, ...	2287	1·4567	
(II; Y = H) ...	4527	1·4589	0·0309	,, ...	2834	1·4565	

TABLE 3. *Loss tangents for solutions in carbon tetrachloride.*

Pentaerythritol tetra-acetate

At 15°			At 19°		
0	1·79	—	0	1·93	—
1015	2·27	1·91	811	2·15	0·88
1333	2·33	2·15	1063	2·24	1·24
			0	1·83	—
			2248	2·65	3·27

Dimethylenepentaerythritol, at 17°

0	1·70	—	1378	3·91	8·81
829	3·13	5·70			

TABLE 4. *Electric double refractions of solutions in carbon tetrachloride.*

Pentaerythritol tetrachloride

10^5w_2 ...	346	515	1169	1653
$10^7\Delta B$ ...	*ca.* 0	*ca.* 0	*ca.* 0	*ca.* 0

Pentaerythritol tetrabromide

690	820	829	1340	1490
ca. 0	*ca.* 0	*ca.* 0	*ca.* 0	*ca.* 0

Pentaerythritol tetra-acetate

10^5w_2 ...	272	440	892	1108	1544
$10^7\Delta B$ ...	0·001	0·002	0·003	0·004	0·005

whence $\Sigma(w_2\,.\,\Delta B)/\Sigma w_2 = 0{\cdot}342 \times 10^{-7}$

Dimethylenepentaerythritol

527	742	992	1811	1980
−0·006	−0·011	−0·011	−0·028	−0·033

whence $10^7\Delta B = -\,0{\cdot}9450w_2 - 35w_2^2$

Dibenzylidenepentaerythritol

10^5w_2 ...	167	246	248	338
$10^7\Delta B$ ...	−0·004	−0·007	−0·007	−0·009

whence $10^7\Delta B = -\,2{\cdot}656w_2 - 21w_2^2$

Tetranitromethane

859	1758	1860	2084	2834
0·001	0·004	0·004	0·005	0·008

whence $10^7\Delta B = 0{\cdot}074w_2 + 8{\cdot}3w_2^2$

TABLE 5. *Calculations of molar Kerr constants at infinite dilution.*

Solute *	$\alpha\varepsilon_1$	β	γ	δ	M_2	$_\infty(_mK_2) \times 10^{12}$
P.E. tetrachloride	0·484	−0·104	0·047	*ca.* 0	209·9	1·30
P.E. tetrabromide	0·565	0·348	0·089	*ca.* 0	387·8	0·8$_5$
P.E. tetra-acetate	3·41	−0·356	−0·003	4·88	304·3	10·5
Dimethylene-P.E.	8·66	−0·263	0·021	−13·5	160·2	−19·6 †
Dibenzylidene-P.E. ...	3·95	−0·344	0·101	−37·9	312·3	−90·2 †
Tetranitromethane ...	0·122	*ca.* 0	−0·024	1·06	196·0	2·9$_8$

* P.E. = " Pentaerythritol."

† These values amend the (higher) preliminary results included in Table 7 of ref. 2.

TABLE 6. *Calculations of dipole moments and relaxation times.*

Solute	$_\infty P_2$ (c.c.) *	R_D (c.c.)	μ (D) †	ψ	$\tau \times 10^{12}$ (sec.)
$C_5H_8Cl_4$	53·2	44·5	0·65	*ca.* 0	—
$C_5H_8Br_4$	69·5	59·9	0·68	*ca.* 0	—
$C_{13}H_{20}O_8$	185·6	70·5	2·3$_7$	0·146	5
$C_7H_{12}O_4$	184·1	36·4	2·6$_9$	0·658	8·5
$C_{19}H_{20}O_4$	207·7	86·9	2·4$_3$	—	—
$C(NO_2)_4$	38·4$_5$	31·5	0·58	*ca.* 0	—

* Using values of $\alpha\varepsilon_1$, β, and M_2 from Table 5.

† *I.e.*, apparent moment obtained by taking $_DP = R_D$.

TABLE 7. *Previously recorded polarisations and dipole moments.*

	Temp.	Sol-vent	$_\infty P_2$ (c.c.)	μ (D) quoted	Ref.
$C(CH_2Cl)_4$ ...	—	C_6H_6	52	<0·2	6, 16
	No measurements given			0	17
$C(CH_2OAc)_4$	—	C_6H_6	250	2·6	16
	—	CCl_4	214	—	6
	25°	C_6H_6	140	1·9	17
	22	C_6H_6	175·2	2·18	7
	Molecular beam method			*ca.* 3	18
$C(CH_2Br)_4$ ...	—	C_6H_6	62	*ca.* 0	6
	—	CCl_4	63	*ca.* 0	6
	25°	C_6H_6	56	0	17
	Molecular beam method			0	18
$C(NO_2)_4$	25	C_6H_6	32·5	<0·2	17
	25	CCl_4	36·24	0·19	19
	25	C_6H_6	37·5	0·48	19
	25	CCl_4	41·7	0·71	20
	81·8	gas	38·6	—	21

DISCUSSION

Previous measurements (Table 7) of the polarisations at infinite dilution of pentaerythritol tetrachloride, tetrabromide, and tetra-acetate disagree among themselves. The values now recorded for $C(CH_2Cl)_4$ and $C(CH_2Br)_4$ differ by about the same amount as do the two molecular refractions (*ca.* 16 c.c.), and if R_D were the correct distortion polarisation, would correspond to the apparent moments shown in Table 6. However, the absence of dielectric loss with solutions in carbon tetrachloride, and the smallness of the observed molar Kerr constant (Table 5), are consistent with a near-isotropy and non-polarity of both these molecules, so that the excesses of $_\infty P_2$ over R_D may be attributed to atomic polarisation of the type explained by Coop and Sutton.[21] There seems no case today for considering early suggestions [22] that the central carbon atom has the valency configuration of a quadrilaterally based pyramid. Wagner and Dengel,[23] and de Laszlo,[24] supposed

[16] Ebert and Hartel, *Naturwiss.*, 1927, **15**, 669.

[17] Williams, *Physikal. Z.*, 1928, **29**, 271, 683; *J. Amer. Chem. Soc.*, 1928, **50**, 2350.

[18] Estermann and Wohlwill, *Z. phys. Chem.*, 1933, *B*, **20**, 195.

[19] Weissberger and Sängewald, *Ber.*, 1932, **65**, 701.

[20] Lewis and Smyth, *J. Amer. Chem. Soc.*, 1939, **61**, 3067.

[21] Coop and Sutton, *J.*, 1938, 1269.

[22] Guillemin, *Ann. Physik*, 1926, **81**, 173; Hund, *Leipz. Vortr.*, 1929, 78; Henri, *Chem. Rev.*, 1927, **4**, 189; Cabannes *et al.*, *J. Phys. Radium*, 1925, **6**, 182; *Compt. rend.*, 1926, **182**, 885; Cooley, *Astrophys. J.*, 1925, **62**, 73; Weissenberg, *Ber.*, 1926, **59**, 1526; *Z. Kryst.*, 1925, **62**, 12; Mark and Weissenberg, *Z. Physik*, 1923, **17**, 301; Huggins and Hendricks, *J. Amer. Chem. Soc.*, 1926, **48**, 164; Gerstacker *et al.*, *Z. Kryst.*, 1928, **66**, 355; Mark and Susich, *ibid.*, 1929, **69**, 105; Nitta, *Bull. Chem. Soc. Japan*, 1927, **1**, 62; Schleede, *Z. anorg. Chem.*, 1928, **168**, 313; **172**, 121; Moller and Reis, *Z. Kryst.*, 1928, **68**, 385; Goodwin and Hardy, *Proc. Roy. Soc.*, 1938, *A*, **164**, 369; Booth and Llewellyn, *J.*, 1947, 837.

[23] Wagner and Dengel, *Z. phys. Chem.*, 1932, *B*, **16**, 382.

[24] De Laszlo, *Compt. rend.*, 1934, **198**, 2235.

that the four halogen atoms lay at the corners of a square plane containing the central carbon atom; this conformation was criticised by Hassel and Stromme,[25] who however did not advance any specific alternative. Llewellyn, Cox, and Goodwin [26] have found the four hydroxyl groups in pentaerythritol itself to be similarly situated, while Bientema *et al.*[27] explicitly describe the structure of pentaerythritol tetraphenyl ether as having the central carbon surrounded by four oxygen atoms forming a square horizontal plane with two of the other carbon atoms of the pentaerythritol above it and the other two below it.

Such conformations for the three molecules $C(CH_2X)_4$ are reconcilable with present measurements. First, take the cases where $X = Cl$ or Br. Let b_1 and b_2 act respectively along the two (perpendicular) XX lines, and assume that the angles XCC and CCC have the common value θ; obviously $b_1 = b_2$. Then, by writing b_1 and b_3 in terms of the link polarisabilities [2,3] of the C–C and C–X bonds, and subtracting, we obtain:

$$b_1 - b_3 = 2(\sin^2 \tfrac{1}{2}\theta - 2\cos^2 \tfrac{1}{2}\theta)(b_L{}^{CX} + b_L{}^{CC}) \\ + 2(1 + \cos^2 \tfrac{1}{2}\theta - 2\sin^2 \tfrac{1}{2}\theta)(b_T{}^{CX} + b_T{}^{CC})$$

It is seen that $b_1 - b_3$ is zero when θ is the tetrahedral angle—a situation which cannot be far from the truth. Since ${}_mK$ contains $(b_1 - b_3)^2$, the observation that $C(CH_2Cl)_4$ and $C(CH_2Br)_4$ have very small values of ${}_\infty({}_mK_2)$ is therefore consistent with the molecular structures proposed in refs. 23 and 24.

For pentaerythritol tetra-acetate Goodwin and Hardy [22] have suggested that the acetate units are planar, that each set of C–C–O–C–(C)–C–O–C–C atoms is a flat zig-zag, and that all angles between single bonds in the molecule are tetrahedral within experimental error. Let the polarisability axes be $b_1 = b_2$ along the O–O directions, with b_3 acting at right angles to them through the central carbon atom (C). The difference $b_1 - b_2$ then follows as:

$$+ 4(\sin^2 \tfrac{1}{2}\theta - 2\cos^2 \tfrac{1}{2}\theta)(b_L{}^{CC} + b_L{}^{C-O}) + 4(\cos^2 \tfrac{1}{2}\theta - 2\sin^2 \tfrac{1}{2}\theta + 1)(b_T{}^{CC} + b_T{}^{C-O}) \\ + 2(b_T{}^{C=O} + b_V{}^{C=O} - 2b_L{}^{C=O})$$

so that the molar Kerr constant found should largely depend on the polarisabilities of the ketonic groups. By using values previously reported [3] for C=O, namely, $b_L{}^{C=O} = 0{\cdot}236$, $b_T{}^{C=O} = 0{\cdot}139$, and $b_V{}^{C=O} = 0{\cdot}025$ (all $\times 10^{-23}$ c.c.), $b_1 - b_3$ is found to be $-0{\cdot}616 \times 10^{-23}$, and that part of ${}_\infty({}_mK_2)$ due to the "anisotropy term" emerges as $45{\cdot}2 \times 10^{-12}$ (the ratio ${}_DP/{}_EP$ being 186/71, see Table 6). Since the observed ${}_\infty({}_mK_2)$ is $10{\cdot}5 \times 10^{-12}$, a "dipole term" corresponding to $-34{\cdot}7 \times 10^{-12}$ is also required; a resultant dipole moment of 0·714 D, effective along the b_3 direction, will provide it. The "apparent" moment listed in Table 6 leads to a highly negative value of ${}_\infty({}_mK_2)$, *viz.*, -337×10^{-12}, which is in disagreement with the fact. We conclude therefore that pentaerythritol tetra-acetate exhibits vibration polarisation [28] to a more marked degree than do the related pentaerythritol tetrahalides.

Examination of Catalan models of the three molecules mentioned shows the four CH_2X groups locked in a way that mutually prevents rotations around the C–C bonds. Franklin [29] has noted that "free rotation" should produce apparent moments of 2·6—2·8 D for $C(CH_2Cl)_4$ and $C(CH_2Br)_4$ but that dipole–dipole interactions (equivalent approximately to kT) combined with steric hindrances tend to exclude configurations having large moments. The tetra-acetate, however, compared with, *e.g.*, the tetrabromide, carries its polar C=O groups *ca.* 1 Å farther out from the central carbon than does the tetrabromide its C–Br dipoles (cf. refs. 23, 24), so that not only have the $CO{\cdot}CH_3$ units more room in which to rotate about the C–O axis, but dipole–dipole forces are relatively less

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[25] Hassel and Stromme, *Z. phys. Chem.*, 1938, *B*, **38**, 349.
[26] Llewellyn, Cox, and Goodwin, *J.*, 1937, 883.
[27] Beintema; Terpstra, and van Weerden, *Rec. Trav. chim.*, 1935, **54**, 627.
[28] Sutton, *Ann. Reports*, 1940, **37**, 57.
[29] Franklin, *J. Amer. Chem. Soc.*, 1951, **73**, 3512.

powerful. In the equations written[21, 28, 30, 31] for atomic (or vibration) polarisation, $_{\rm A}P$ is always shown as inversely dependent on the force constants of the various deformations caused by the application of an electric field to a molecule, and especially to the more flexibly held polar bonds thereof. In the present instance the deformation involved is a twisting of $CO{\cdot}CH_3$ about its C–O axis. The appropriate torsional force constant is unknown but is likely to be small compared with the bending force constants usually considered hitherto in this type of problem. Qualitatively, therefore, two consequences seem obvious: (*a*) it is possible for the tetra-acetate to have a large $_{\rm A}P$, and (*b*) the structure is such[32, 33] that " segment orientation " can occur, so that the raising (Table 3) of the loss tangent of carbon tetrachloride by this solute is not unexpected. Incidentally, inspection of models indicates that the C–Br links in $C(CH_2Br)_4$ are more confined sterically than are the corresponding bonds in $C(CH_2Cl)_4$. By the argument used in ref. 1, therefore, that the $_{\rm m}K$ of the chloro-compound exceeds that of the bromo-derivative, is understandable; that both should be less than the $_{\rm m}K$ of tetranitromethane may be due to the greater link polarities associated with the $C(NO_2)_4$ structure than with those of $C(CH_2Cl)_4$ and $C(CH_2Br)_4$.

FIG. 1.

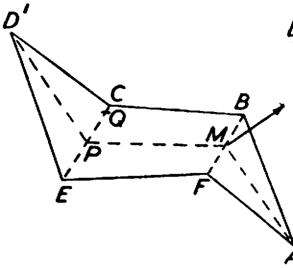
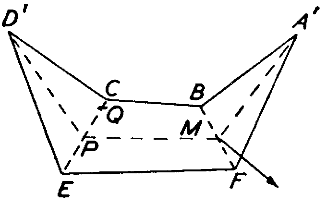


FIG. 2.



The dimethylene- and dibenzylidene-*spiro*-derivatives of pentaerythritol (II) are characterised by having negative molar Kerr constants (Table 5). Their dipole moments are here reported for the first time, although the related condensation product from acetone has been studied by Orthner and Freyss,[7] who found $\mu = 2{\cdot}26$ D. These authors discussed their compound in terms of " boat " and " chair " conformations of the two heterocyclic rings, considering that 36 different arrangements of the whole structure were theoretically possible, so that only those formulæ requiring $\mu = 0$ could be eliminated. The question was left at that stage.

We have attempted an analysis of the moments now obtained (for the *spiro*-compounds) by regarding them as resultants of two components, having mutual orientations depending on the conformations adopted by each of the 1 : 3-dioxan rings, joined by sharing carbon atom 5 in common. It is first necessary to establish the moment (magnitude and direction) appropriate for the " chair " and " boat " versions of 1 : 3-dioxan; the following bond lengths (Å) and valency angles have been assumed:[34] C–C, 1·54; C–O 1·43; $\angle CCC = \angle CCO = \angle OCO = 109°28'$, $\angle COC = 111°$. The moment of the C–O–C bond pair has been taken as that of dimethyl ether,[35] *viz.*, 1·25 D. In Figs. 1 and 2, *D'*, *C*, *A'* and *E* mark the centres of carbon atoms, and *B* and *F* those of the oxygen atoms. The *spiro*-atom is *D'*. In both cases the resultant moment is $1{\cdot}86_5$ D, lying in the planes of the triangles *D'PM* (*P* and *M* being the mid-points of *CE* and *BF*, respectively), and acting in the " chair "

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[30] Le Fèvre and Rao, *Aust. J. Chem.*, 1954, **7**, 155; 1955, **8**, 39.

[31] Freeman, Le Fèvre, Rao, and Ross, *J.*, 1955, 3840.

[32] Smyth, " Dielectric Behaviour and Structure," McGraw-Hill, New York, Toronto, London, 1955, p. 111.

[33] Davies, *Quart. Reviews*, 1954, **8**, 250.

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

[35] Barclay and Le Fevre, *J.*, 1952, 1643.

and " boat " forms at inclinations to $D'P$ of 92° 15′ and 171° 31′. It is noteworthy that Otto[36] has determined the dipole moments of several 1 : 3-dioxans and found values of the order of that just calculated (*e.g.*, 2-methyl-1 : 3-dioxan has $\mu = 1{\cdot}89$ D).

The moments of different forms of dimethylenepentaerythritol now follow straightforwardly since in (II) the lines $D'P$ for each constituent ring are collinear and the planes of the triangles $D'CE$ are perpendicular about their $PD'D'P$ axis. If the *spiro*-atom D' is at the origin of Cartesian co-ordinates $0z$, $0y$, and $0z$ and the disposition of (II) is defined by the triangles $D'CE$ lying in the planes $y = 0$ and $z = 0$, respectively, then we have for three configurations of (II; Y = H) the following results:

Configuration:	Double " chair "	Double " boat "	" Chair–boat "
Resultant moment (D)	2·66	0·39	$2{\cdot}76_5$
$\mu_{\mathrm{resultant}}$ and $0x$ direction	90°	90°	46° 5′
,, $0y$,, ...	45°	45°	48° 14′
,, $0z$,, ...	45°	45°	47° 37′

Table 6 gives the observed moment of dimethylenepentaerythritol as $2{\cdot}6_9$ D—a value incompatible with a double " boat " configuration, but which does not assist decision between the other two possibilities.

The significance of the $_\infty({}_{\mathrm{m}}K_2)$ observed was next investigated. The polarisabilities of each ring were taken as follows: b_1 along $D'P$, b_2 along EC, and b_3 perpendicular to $D'P$ and EC at P. Certain angles are required, and on the geometrical specifications already given these are: $D'PM$ 131° 53′, PMA' 122° 13′, and CBQ 3° 36′ (the position of Q is such that $PQ = MB$). Then by arguments used before[2, 3] we have for a " chair " ring:

$$\begin{aligned} b_1 &= (2/3)b_{\mathrm{L}}^{\mathrm{CC}} + (4/3)b_{\mathrm{T}}^{\mathrm{CC}} + 1{\cdot}53b_{\mathrm{L}}^{\mathrm{CO}} + 2{\cdot}46_5b_{\mathrm{T}}^{\mathrm{CO}} + 8b^{\mathrm{CH}} \\ b_2 &= (4/3)b_{\mathrm{L}}^{\mathrm{CC}} + (2/3)b_{\mathrm{T}}^{\mathrm{CC}} + 1{\cdot}34b_{\mathrm{L}}^{\mathrm{CO}} + 2{\cdot}66b_{\mathrm{T}}^{\mathrm{CO}} + 8b^{\mathrm{CH}} \\ b_3 &= 2b_{\mathrm{T}}^{\mathrm{CC}} + 1{\cdot}12b_{\mathrm{L}}^{\mathrm{CO}} + 2{\cdot}88b_{\mathrm{T}}^{\mathrm{CO}} + 8b^{\mathrm{CH}} \end{aligned}$$

and for a " boat " ring:

$$\begin{aligned} b_1^{1} &= (2/3)b_{\mathrm{L}}^{\mathrm{CC}} + (4/3)b_{\mathrm{T}}^{\mathrm{CC}} + 0{\cdot}938b_{\mathrm{L}}^{\mathrm{CO}} + 3{\cdot}06b_{\mathrm{T}}^{\mathrm{CO}} + 8b^{\mathrm{CH}} \\ b_2^{1} &\text{ as for } b_2 \text{ `` chair ''} \\ b_3^{1} &= 2b_{\mathrm{T}}^{\mathrm{CC}} + 1{\cdot}72b_{\mathrm{L}}^{\mathrm{CO}} + 2{\cdot}28b_{\mathrm{T}}^{\mathrm{CO}} \end{aligned}$$

From these data the semi-axes for a double " chair " dimethylenepentaerythritol (b_1^{DMP} b_2^{DMP} and b_3^{DMP}, with b_1^{DMP} parallel to $\mu_{\mathrm{resultant}}$, and b_2^{DMP} parallel to $PD'D'P$ in the *spiro*-molecule emerge as:

$$\begin{aligned} b_1^{\mathrm{DMP}} &= b_2 + b_3 - 4b^{\mathrm{CH}} \\ b_2^{\mathrm{DMP}} &= 2b_1 - 4b^{\mathrm{CH}} \\ b_3^{\mathrm{DMP}} &= b_2 + b^3 - 4b^{\mathrm{CH}} \end{aligned}$$

so that:

$$(b_1 - b_2)^{\mathrm{DMP}} = -0{\cdot}6048(b_{\mathrm{L}}^{\mathrm{C-O}} - b_{\mathrm{T}}^{\mathrm{C-O}})$$

Introduction of the value $b_{\mathrm{L}}^{\mathrm{C-O}} = 0{\cdot}081 \times 10^{-23}$ and $b_{\mathrm{T}}^{\mathrm{C-O}} = 0{\cdot}039 \times 10^{-23}$, previously[3] deduced from paraldehyde, gives $(b_1 - b_2)^{\mathrm{DMP}} = -0{\cdot}0254 \times 10^{-23}$, whence $\theta_1 = 0{\cdot}0077 \times 10^{-35}$ and $\theta_2 = -2{\cdot}413 \times 10^{-35}$; the calculated molar Kerr constant is therefore $-10{\cdot}1 \times 10^{-12}$. This value, based on an oxygen angle of 111°, has the correct algebraic sign and order of magnitude but is *ca.* 10 units from the $_\infty({}_{\mathrm{m}}K_2)$ observed.

Accordingly, it is of interest to derive $_\infty({}_{\mathrm{m}}K_2)$ by adopting the polarisabilities of the C–O bond obtained from different compounds, and other permissible oxygen valency angles. Table 8 summarises the calculations, and indicates that with a double " chair " conformation for dimethylenepentaerythritol, agreement between calculated and found values $({}_{\mathrm{m}}K_2)$ follows from variation of the oxygen valency angle rather than alteration of C–O bond polarisabilities.

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[36] Otto, *J. Amer. Chem. Soc.*, 1937, **59**, 1590.

TABLE 8. *Dependence of* $_\infty({}_\mathrm{m}K_2)$ *upon* C–O–C *valency angle and* C–O *bond polarisabilities.*

Oxygen angle	$10^{23}b_\mathrm{L}^\mathrm{C-O}$	$10^{23}b_\mathrm{T}^\mathrm{C-O}$	$10^{12}{}_\mathrm{m}K$ (calc.)	Oxygen angle	$10^{23}b_\mathrm{L}^\mathrm{C-O}$	$10^{23}b_\mathrm{T}^\mathrm{C-O}$	$10^{12}{}_\mathrm{m}K$ (calc.)
111°	0·081	0·039	−10·1 [a]	115° 20′	0·081	0·039	−11·1 [a]
,,	0·087	0·042	−10·9 [b]	,,	0·087	0·042	−11·9 [b]
,,	0·091	0·044	−11·4 [c]	,,	0·091	0·044	−12·5 [c]
113°	0·081	0·039	−10·9 [a]	117° 8′	0·081	0·039	−13·5 [a, d]
,,	0·087	0·042	−11·6 [b]	,,	0·087	0·042	−14·4 [b, d]
,,	0·091	0·044	−12·2 [b]	,,	0·091	0·044	−15·1 [c, d]

[a] C–O polarisabilities from paraldehyde.[3] [b] C–O polarisabilities from dioxan (unpublished). C–O polarisabilities from $R_\infty^\mathrm{C-O} = 1{\cdot}500$ c.c. obtained by extrapolating the link refractivity listed by Vogel *et al.*[37] [d] In these three calculations the C–O distance taken was 1·41 Å in place of 1·43 Å.

For the " chair-boat " configuration semi-axes are:

$$b_1^\mathrm{DMP} = b_2 + b_3^1 - 4b^\mathrm{CH}$$
$$b_2^\mathrm{DMP} = b_1 + b_1^1 - 4b^\mathrm{CH}$$
$$b_3^\mathrm{DMP} = b_3 + b_2^1 - 4b^\mathrm{CH}$$

so that:

$$(2b_1 - b_2 - b_3)^\mathrm{DMP} = 1{\cdot}20(b_\mathrm{L}^\mathrm{C-O} - b_\mathrm{T}^\mathrm{C-O})$$

and $\theta_2 = (1/45\boldsymbol{k}^2T^2)[(2\mu_1^2 - \mu_2^2 - \mu_3^2)(b_\mathrm{L}^\mathrm{C-O} - b_\mathrm{T}^\mathrm{C-O})1{\cdot}20]$

where $\mu_1 = \mu_\mathrm{res}\cos 47°\,37'$, $\mu_2 = \mu_\mathrm{res}\cos 34°\,14'$ and $\mu_3 = \mu_\mathrm{res}\cos 46°\,45'$,

whence $\theta_2 = 0{\cdot}302$ and $\theta_1 = 0{\cdot}013$ (both $\times 10^{-35}$), and

$${}_\mathrm{m}K = 1{\cdot}3_2 \times 10^{-12}$$

Summarising, we have for dimethylenepentaerythritol the value of $10^{12}{}_\mathrm{m}K$ calculated for a double " chair " −10 to −15, and for a " chair–boat " + 1·3, the observed value being −19·6, from which the " double-chair " form is obviously to be preferred.

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[37] Vogel, Cresswell, Jeffery, and Leicester, *J.*, 1952, 514.