32. *Dipole Moments and Molecular Structure. Part II.* Pentaerythritol Tetranitrate.*

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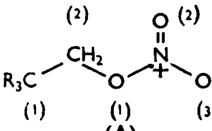
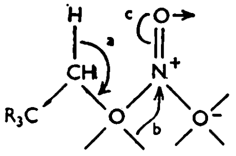
The dipole moments of pentaerythritol tetrabromide and tetraiodide and of pentaerythritol tetranitrate in dilute solution have been determined and the results used in a consideration of the C–O bonding in the tetranitrate.

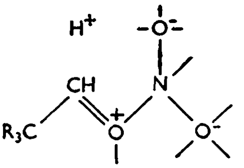
The crystal structure of pentaerythritol tetranitrate $C(CH_2{\cdot}O{\cdot}NO_2)_4$ was studied by Booth and Llewellyn [1] by *X*-ray diffraction. In the crystal the four legs (A) show the expected tetrahedral distribution: each leg has an almost planar zig-zag configuration ($C_{(1)}$ and the four atoms of the nitrate group are co-planar; $C_{(2)}$ is very slightly displaced from this plane; $O_{(2)}$ and $O_{(3)}$ are, as expected, equivalent). The bond angles and most of the bond lengths are not unusual. Particular interest therefore attaches to the remarkably short distance reported for the $C_{(2)}$–$O_{(1)}$ bond, 1·37 Å instead of the value 1·43 Å expected for a normal C–O single bond: [2] the corresponding bonds in crystalline pentaerythritol [3] and its tetra-acetate [4] are 1·46 and 1·43 Å respectively. Booth and Llewellyn were at that time confident that this shortening was real. However, Booth's subsequent work [5] on the accuracy of atomic co-ordinates derived from *X*-ray data and Cruickshank's later work [6] have shown that unless the measured bond lengths are subjected to statistical tests for significance little weight can be placed on particular values.



(A)



(I)



(II)

Were the shortening indeed real, such a considerable contraction of a covalent bond must be accompanied by a marked decrease in the heat function, enthalpy, of the molecule. Molecular stabilisation energies of this magnitude usually occur only in cases where an explanation can be offered in terms of resonance, involving multiply bonded, usually excited, structures. In the case of pentaerythritol tetranitrate, however, reasonable structures involving $C_{(2)}$=$O_{(1)}$ double bonds are not available. Booth and Llewellyn suggest a tentative explanation in terms of resonance involving admittedly "exotic" excited structures such as (II), arising from the ground state structure (I) by the electron shifts, a, b, and c.

Such excited structures are unacceptable on several general grounds; *e.g.*, (i) the hyperconjugation shift (a) seems improbable in such a molecule; (ii) the shift of a complete electron pair (b) from one atom to another is unprecedented; (iii) the nitrogen atom in (II) is tercovalent: in this state the three bonds are normally disposed pyramidally: the observed coplanar arrangement of the nitrogen and the oxygen atoms would, therefore, markedly destabilise structure (II). It was, therefore, decided to seek evidence for or against $C_{(2)}$=$O_{(1)}$ double bonding in the tetranitrate along other lines.

A significant contribution from structure (II) would inhibit free rotation about the $C_{(2)}$–$O_{(1)}$ bond in the molecule, and would constrain the four atoms $C_{(1)}$, $C_{(2)}$, O, and N to a

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* Part I of the series is considered to be *J.*, 1949, 1524.

[1] Booth and Llewellyn, *J.*, 1947, 837.

[2] Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1941, p. 167.

[3] Cox, Llewellyn, and Goodwin, *J.*, 1937, 882.

[4] Goodwin and Hardy, *Proc. Roy. Soc.*, 1938, *A*, **164**, 369.

[5] Booth, *ibid.*, 1946, *A*, **188**, 77; 1947, *A*, **190**, 482.

[6] Cruickshank, *Acta Cryst.*, 1949, **2**, 65; see Jeffrey and Cruickshank, *Quart. Rev.*, 1953, **7**, 335.

planar configuration. This constraint would operate not only in the crystal (where the observed virtual coplanarity of these atoms may be due to intermolecular restraints arising from the regular and relatively close packing in the crystal lattice) but in all phase states of the substance, including dilute solution in inert solvents, and the vapour phase at low pressure where only intramolecular forces affect the configuration of the molecules. A study of the dipole moments of pentaerythritol derivatives was therefore undertaken. (The results have been briefly reported elsewhere [7].)

EXPERIMENTAL

M. p.s were determined on the Kofler stage.

Preparation of Materials.—Benzene (" AnalaR ") and dioxan (purified) were frozen four times and refluxed, respectively over phosphoric oxide and over sodium. They were distilled, in a stream of dry air, immediately before use.

Pentaerythritol tetrabromide was prepared for us by Dr. I. T. Millar (University College of North Staffordshire) from pentaerythritol (L. Light and Company Limited) by Schurink's method.[8] The product, once recrystallised from 95% aqueous ethanol, had m. p. 163°, in agreement with Schurink. Six further recrystallisations from the same solvent, necessary to achieve satisfactory carbon and hydrogen analyses (Found: C, 15·7; H, 1·9. Calc. for $C_5H_8Br_4$: C, 15·5; H, 2·1%), were accompanied by a fall in m. p. to a constant value of 157°.

Pentaerythritol tetraiodide was prepared, by Dr. I. T. Millar, by Schurink's method.[8] Thrice recrystallised from benzene, it had m. p. 233° in accordance with Schurink's value (Found: C, 10·7; H, 1·4. Calc. for $C_5H_8I_4$: C, 10·4; H, 1·4%).

Pentaerythritol tetranitrate (P. E. T. N.), prepared by Stettbacher's method [9] and recrystallised from acetone, had m. p. 139° (Stettbacher gives m. p. 138—140°).

Determinations of Dipole Moment.—These were made in benzene and in dioxan solutions at 25° by the refractivity method, the heterodyne technique being used for the measurement of dielectric constant.

The new circuit used for the measurement of dielectric constant, ε, was based on a design prepared by Dr. L. E. Sutton, F.R.S., and Dr. R. A. W. Hill in Oxford, and the whole arrangement of the Oxford prototype is fully discussed by Hill [10] and briefly by Springall, Hampson, May, and Spedding [11] and Hill and Sutton.[12]

The refractive index, *n*, and the specific volume, *v*, were measured in a Pulfrich refractometer, with the Hg_g line (5461 Å), and by a Sprengel pyknometer respectively. The results of the measurements of *w* (weight fraction), *v*, ε, and *n* are given in Table 1.

TABLE 1.

w	*v*	ε	*n*
Pentaerythritol tetraiodide (*M*, 575·79) *in benzene.*			
0·00750	1·1381	2·2761	1·50280
0·00751	1·1378	2·2759	1·50272
Pentaerythritol tetraiodide (*M*, 575·79) *in* 1 : 4-*dioxan.*			
0·00815	0·9667	2·2223	—
0·00838	0·9661	2·2229	1·42405
0·00850	—	—	1·42394
Pentaerythritol tetrabromide (*M*, 387·77) *in benzene.*			
0·029784	1·1217	2·2788	1·50406
0·040836	1·1137	2·2804	1·50452
0·048789	1·1079	2·2814	1·50489
0·059705	1·1008	2·2830	1·50538
Pentaerythritol tetrabromide (*M*, 387·77) *in* 1 : 4-*dioxan.*			
0·024737	0·9583	2·2380	1·42492
0·039977	0·9511	2·2424	1·42606
0·055827	0·9415	2·2465	1·42736
0·067095	0·9354	2·2502	1·42794
Pentaerythritol tetranitrate (*M*, 316·14) *in* 1 : 4-*dioxan.*			
0·020460	0·9662	2·270	1·4233
0·033042	0·9617	2·304	1·4239
0·037474	0·9600	2·311	1·4241
0·041762	0·9586	2·323	1·4244

The derived data on the extrapolations of ε, *v*, and *n* to $w = 0$ and the corresponding slopes α, β, and γ are given in Table 2. The molar total $({}_{T}P_2)$ and electronic $({}_{E}P_2)$ polarisation terms

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[7] Springall and Spedding, *Research*, 1949, **2**, 295.

[8] Schurink, *Org. Synth.*, Coll. Vol. II, 1943, p. 476.

[9] Stettbacher, *Z. angew Chem.*, 1928, **41**, 716.

[10] Hill, D.Phil. Thesis, Oxford, 1950.

[11] Springall, Hampson, May, and Spedding, *J.*, 1949, 1524.

[12] Hill and Sutton, *J.*, 1953, 1482.

TABLE 2.

Pentaerythritol derivative	Solvent	ε_1'	α	v_1'	β	n_1'	γ	$_TP_2$	$_EP_2$	μ
Tetraiodide	Benzene	(2·2748)	0·165	(1·1444)	−0·86	(1·50235)	0·055	66·7	66·5	0
,,	1 : 4-Dioxan	(2·220)	0·314	(0·9728)	−0·770	(1·42337)	0·079	63·4	53·2	0·7
Tetrabromide	Benzene	2·2748	0·138	1·1444	−0·706	1·50235	0·0426	60·7	59·7	0·22
,,	1 : 4-Dioxan	2·220	0·280	0·9728	−0·560	1·4233	0·0740	64·5	57·3	0·59
Tetranitrate	1 : 4-Dioxan	2·220	2·455	0·9733	−0·351	1·4223	0·0502	184·0	58·2	2·48

(Table 2) are evaluated from α, β, and γ, by Halverstadt and Kumler's method,[13] as discussed by Everard, Hill, and Sutton;[14] the following expressions were used:

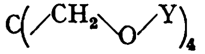
$$_TP_2 = M(0{\cdot}34110 + 0{\cdot}18818\alpha + 0{\cdot}29787\beta) \text{ for benzene solutions}$$
$$_TP_2 = M(0{\cdot}28124 + 0{\cdot}16388\alpha + 0{\cdot}28910\beta) \text{ for dioxan solutions}$$
$$_EP_2 = M(0{\cdot}33797 + 0{\cdot}29513\beta + 0{\cdot}56986\gamma) \text{ for benzene solutions}$$
$$_EP_2 = M(0{\cdot}24782 + 0{\cdot}25475\beta + 0{\cdot}51263\gamma) \text{ for dioxan solutions}$$

These expressions are based on the Halverstadt–Kumler formulæ, and the following data for pure solvents: ε_1, 2·2727 for benzene, 2·220 for dioxan; v_1, 1·14515 for benzene, 0·9728 for dioxan; n_1, 1·50238 for benzene, 1·4232 for dioxan. The dipole moments are calculated from the polarisation terms by the Debye expression $\mu = \tfrac{3}{2}\sqrt{(kT_0P_2/\pi N)}$ e.s.u., whence, the small undetermined part of the atom polarisation being neglected, $\mu_{25^\circ} = 0{\cdot}2211\sqrt{(_TP_2 - {}_EP_2)}$ D.

Owing to the extremely low solubility of pentaerythritol tetraiodide, the polarisation terms for this compound were determined from data on solutions having a very narrow range of very low concentrations, and by use of extrapolated pure-solvent values for ε_1', v_1', and n_1' obtained with the more normal runs on the tetrabromide. This makes for uncertainties in the estimation of the slopes α, β, and γ. The specific volume slope β being large, uncertainties in it dominate the evaluations of $_TP_2$ and $_EP_2$. These uncertainties largely cancel out in $(_TP_2 - {}_EP_2)$ because of the similarity of the coefficients of β in corresponding $_TP_2$ and $_EP_2$ expressions: nevertheless we do not feel that our value of μ for this compound is very accurate.

DISCUSSION

Pentaerythritol derivatives of the type $C(CH_2X)_4$, where X = Cl, Br or I, were investigated by early workers in the dipole-moment field using dilute benzene solution,[15] and vapour-phase molecular-beam methods.[16] The compounds showed no permanent dipole moments (μ = 0). We have re-determined the dipole moments of pentaerythritol tetrabromide and tetraiodide in benzene and in dioxan, using modern technique, and confirm μ = 0 for these compounds in benzene.* The absence of dipole moments in these derivatives indicates that free rotation about the $C_{(1)}$–$C_{(2)}$ bond in pentaerythritol compounds is inhibited, in all phase states, by intramolecular steric forces, due to enforced close atomic packing around the quaternary $C_{(1)}$ atom. Were there free rotation about the $C_{(1)}$–$C_{(2)}$ bond then the four $C_{(2)}$–X moments would be out of phase and the molecule would show a considerable resultant moment.

When pentaerythritol derivatives of the type  $C(CH_2{-}O{-}Y)_4$ in which the dipole moment of the O–Y system acts along the O–Y bond are considered on the assumption that the steric inhibition of free rotation about $C_{(1)}$–$C_{(2)}$, observed with the $C_{(1)}$–$C_{(2)}$–X

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* In dioxan both the tetrabromide and the tetraiodide show small apparent dipole moments of ~0·6 D. These are, however, probably due to small neglected atom polarisation terms. Le Fèvre and Le Fèvre[17] report that pentaerythritol tetrachloride and tetrabromide show similar small moments in carbon tetrachloride solution and state that these "are probably 'apparent' owing to atomic polarisations."

[13] Halverstadt and Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

[14] Everard, Hill, and Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417.

[15] Ebert, Eisenschitz, and von Hartel, *Z. physikal. Chem.*, 1928, *B*, **1**, 94; Williams, *Physikal. Z.*, 1928, **29**, 271, 683.

[16] Estermann and Wohlwill, *Z. physikal. Chem.*, 1933, *B*, **20**, 195.

[17] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

system, persists with the $C_{(1)}$–$C_{(2)}$–O system (a study of scale models indicates that this is likely, despite the fact that the atom of oxygen is smaller than that of chlorine), it follows that these compounds should show *either* a definite permanent dipole moment *or* zero dipole moment according as there is *either* free rotation about the $C_{(2)}$–O bond, when the four O–Y groups will be out of phase, *or* no rotation about the $C_{(2)}$–O bond, when all the component moments in the molecule will be in tetrahedrally distributed sets of four. Pentaerythritol and its tetranitrate are both compounds of this class and both have considerable permanent dipole moments. Pentaerythritol was studied by molecular-beam methods[16] ($\mu \sim 2$ D). Early indications of a moment of ~ 2 D were found for the tetranitrate in work on extremely dilute benzene solutions.[15] We have examined the tetranitrate in dioxan, in which it is reasonably soluble, and find $\mu = 2{\cdot}5$ D.

It thus appears that, once crystal lattice restraints have been overcome, there is free rotation about the $C_{(2)}$–O bond in the nitrate and, therefore, that whatever may be the cause of the shortening of this bond in the crystal observed by Booth and Llewellyn, it cannot be due to possession of any high degree of double-bond character.

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