688. *Dipole Moments and Molecular Structure. Part IV.* Ether Derivatives of Pentaerythritol.*

By I. T. MILLAR, C. T. MORTIMER, and H. D. SPRINGALL.

The dipole moments of pentaerythritol tetramethyl ether and of 5 : 5'-*spiro*bis-1 : 3-dioxan have been measured, and the results are used in a consideration of possible limitations of rotation about the $C_{(1)}$–$C_{(2)}$ and $C_{(2)}$–O bonds in pentaerythritol derivatives.

IN the work described in Part II,[1] concerned primarily with the structure of pentaerythritol tetranitrate, dipole-moment evidence was presented for (i) the inhibition of free rotation about the $C_{(1)}$–$C_{(2)}$ bond in each " leg " (A) of the pentaerythritol molecule [dipole moments of compounds (I; X = I, Br, or Cl) are zero], and (ii) freedom of rotation about the $C_{(2)}$–O bond [dipole moments of derivatives (II), where Y is such that the O–Y moment acts along the O–Y bond, are finite, ~2 D].

The aim of this work has been to investigate these points further by a study of the dipole moments of pentaerythritol tetramethyl ether (II; Y = Me) and of 5 : 5'-*spiro*bis-1 : 3-dioxan (III).

EXPERIMENTAL

Preparation of Materials.—" AnalaR " benzene was frozen four times and refluxed over phosphoric acid. It was distilled immediately before use.

Pentaerythritol tetramethyl ether was prepared as described by Backer and Dijken.[2] 5 : 5'-*spiro*Bis-1 : 3-dioxan was prepared by Read's method.[3]

Determinations of Dipole Moment.—These were made in benzene solutions at 25° by the refractivity method, the heterodyne technique being used for the measurement of dielectric constant, as in Parts I [4] and II.[1]

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* Part III, preceding paper.

[1] Mortimer, Spedding, and Springall, *J.*, 1957, 188.

[2] Backer and Dijken, *Rec. Trav. chim.*, 1936, **55**, 22.

[3] Read, *J.*, 1912, **101**, 2093.

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

The derived data on the extrapolations of *e*, *v*, and *n* (Table 1) to $w = 0$ and the corresponding slopes α, β, and γ are given in Table 2, together with the molar total (${}_{\mathrm{T}}P_2$) and electronic (${}_{\mathrm{E}}P_2$) polarisation terms. These are evaluated from α, β, and γ by the expressions :[1]

$$ {}_{\mathrm{T}}P_2 = M(0{\cdot}34110 + 0{\cdot}18818\alpha + 0{\cdot}29787\beta) $$
$$ {}_{\mathrm{E}}P_2 = M(0{\cdot}33797 + 0{\cdot}29513\beta + 0{\cdot}56986\gamma) $$

The dipole moments are calculated from the total and electronic polarisation terms (the small undetermined part of the atom polarisation being neglected) by the Debye expression $\mu_{25} = 0{\cdot}2211\sqrt{({}_{\mathrm{T}}P_2 - {}_{\mathrm{E}}P_2)}$ D.

TABLE 1.

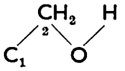
w	*v*	*e*	*n*	*w*	*v*	*e*	*n*
Pentaerythritol tetramethyl ether (*M*, 192·250)				5 : 5′-*spiro*Bis-1 : 3-dioxan (*M*, 160·166)			
0·01804	1·1394	2·3072	1·50260	0·01593	1·1406	2·3466	1·50283
0·03029	1·1348	2·3325	1·50221	0·02664	1·1364	2·3972	1·50260
0·04337	1·1296	2·3557	1·50190	0·03571	1·1331	2·4415	1·50242
0·05334	1·1263	2·3771	1·50151	0·04452	1·1297	2·4778	1·50217

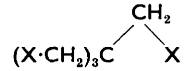
TABLE 2. *Data for* (*A*) *pentaerythritol tetramethyl ether and* (*B*) 5 : 5′-spiro*bis*-1 : 3-*dioxan, extrapolated to* $w = 0$.

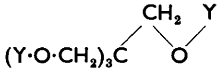
	e_1'	α	v_2'	β	n_1'	γ	${}_{\mathrm{T}}P_2$	${}_{\mathrm{E}}P_2$	μ
A ...	2·2730	1·95	1·1459	−0·372	1·50312	−0·0289	114·7 ± 1·4	40·7 ± 0·5	1·91 ± 0·01
B ...	2·2727	4·73	1·1463	−0·376	1·50316	−0·0224	17·8 ± 1·6	18·3 ± 0·3	0

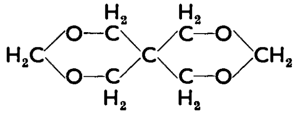
DISCUSSION

Previously only two compounds of type (II) have been subjected to dipole-moment studies, pentaerythritol[5] itself, Y = H ($\mu \sim 2$ D), and the tetranitrate,[1] Y = NO_2 ($\mu = 2{\cdot}48$ D).* Of these, pentaerythritol is insufficiently soluble in suitable solvents to permit its dipole moment to be studied in solution (the accepted value for μ comes from early molecular-beam studies), while the tetranitrate is sufficiently soluble in dioxan, alone, of the range of suitable solvents, for accurate experimental dipole measurement. These solubility restrictions made very desirable the study of a genuine type (II) compound soluble in a non-polar solvent. The tetramethyl ether is such a substance and the observed moment of 1·91 D in benzene solution gives useful support to the earlier findings.


(A)


(I)


(II)


(III)

We interpret this observed moment as solely due to the out-of-phase rotation of the four O–CH_3 systems about the $C_{(2)}$–O bonds. If this interpretation is correct, then the restriction of this rotation to be achieved by replacing the four methyl groups by two methylene bridges to give 5 : 5′-*spiro*bis-1 : 3-dioxan (III) should result in a reduction of the dipole moment. [The individual bond moments are unlikely to differ widely in (II; Y = Me and in (III)).] The observed zero moment for the *spiro*-compound supports this view, indicating that the methylene bridges have inhibited $C_{(2)}$–O rotation to such an extent that the compound is stable in a highly symmetrical configuration in which the four O–CH_2 bond moments have a zero resultant.

UNIVERSITY COLLEGE OF NORTH STAFFORDSHIRE,
KEELE, STAFFORDSHIRE.

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* The moment of the tetra-acetate (II; Y = Ac) has been measured[6] ($\mu = 2{\cdot}2$ D), but in this compound the moment of the O–Y system does *not* act along the O–Y bond, so that the compound would show a resultant moment, due to out-of-phase free rotation about the four O–Y bonds, irrespective of freedom or inhibition of rotation about the $C_{(2)}$–O bonds.

[5] Estermann, *Z. phys. Chem.*, 1929, **2**, *B*, 287; Estermann and Wohlwill, *ibid.*, 1933, **20**, *B*, 195.

[6] Othner and Freyss, *Annalen*, 1930, **484**, 131.