The Stereochemistry of a Cyclic Sulphite of 10β-Pinane-2,3α-diol

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REACTION[1] of (±)-10β-pinane-2,3α-diol (1) with thionyl chloride gave a mixture of two cyclic sulphites, separable by fractional crystallization. Both isomers (A, m.p. 50—52°; B, m.p. 102—103°) gave the diol (1) on mild basic hydrolysis. Two isomers could arise if the 10-Me group were *cis*- or *trans*- to the extracyclic sulphite oxygen atom. A preliminary *X*-ray crystal-structure analysis has established the relative configuration of isomer (A) and the solid state conformation of a *vicinal*-diol cyclic sulphite ring-system shown in the Figure.

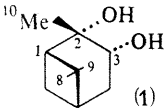
Crystals of the cyclic sulphite (A) grown from pentane are triclinic, space group $P\bar{1}$, $a = 7·42$, $b = 10·94$, $c = 7·18$ Å, $\alpha = 109·1°$, $\beta = 95·2°$ and $\gamma = 90·2°$, $Z = 2$. They are often twinned and sublime readily at 20°. Three-dimensional intensity data were recorded at 4° with a Nonius integrating Weissenberg camera and a crystal sealed in a capillary. The positions of all non-hydrogen atoms were established by conventional Patterson, difference Fourier, and least-squares techniques using 680 reflections, the intensities of which were measured photometrically above background; $R = 18$.

The n.m.r. data for isomer (A) are consistent with the existence of the cyclic sulphite in essentially the same conformation in both the solid and liquid phase. The notable feature of the n.m.r. data for the cyclic sulphites A and B, epimeric at the sulphur atom, is the markedly downfield location of the signals due to the 10-Me and 3-H functions in isomer (A) relative to isomer (B). The deshielding of the 10-Me and 3-H in isomer (A) by the S → O group

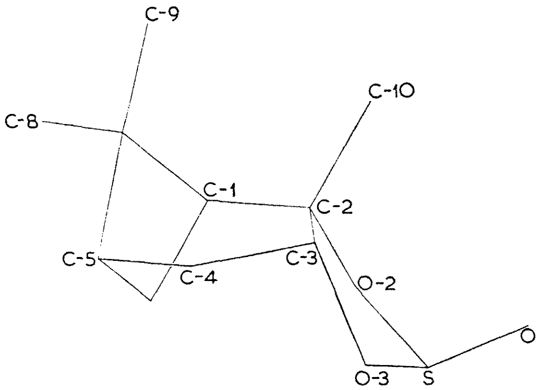
N.m.r. data for cyclic sulphides* (*p.p.m.*)

	8-Me	9-Me	10-Me	3-H		
Isomer A	1·33	0·92	1·82	4·94	$J^{ap}_{3,4\beta}$	7·3 c./sec.
					$J^{ap}_{3,4\alpha}$	1·9
Isomer B	1·39	0·91	1·46	4·72	$J^{ap}_{3,4\beta}$	8·2
					$J^{ap}_{3,4\alpha}$	5·8

* Determined at 60 Mc./sec. for 20% solutions (w/v) in $CDCl_3$ with $CHCl_3$ and Me_4Si as internal standards.



(1)



Figure

is analogous to the "*syn-axial* effect" encountered[2] in the n.m.r. study of six-membered-ring sulphoxides. Clearly, however, reservations about the application of this concept alone to the interpretation[3] of the n.m.r. spectra of sulphoxides must apply also in this study.

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