Stereochemical Assignments of 3-Substituted Thietan 1-oxides. The Crystal Structures of *cis*- and *trans*-3-*p*-Bromophenylthietan 1-oxides

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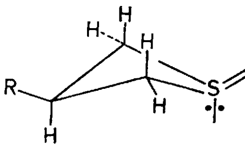
Summary The crystal structures of *cis*- and *trans*-3-*p*-bromophenylthietan 1-oxide show that in the solid state the sulphinyl oxygen is equatorial in both isomers.

There has been much interest in the competing conformational requirements of oxygen and a non-bonding electron pair in cyclic sulphoxides, and the axial preference of sulphinyl oxygen in six-membered rings is well established.[1] In the case of 3-substituted thietan 1-oxides there are two possible conformations for both the *cis*-isomer, (**1**) and (**2**), and the *trans*-isomer, (**3**) and (**4**). Johnson has concluded from dipole moment measurements, chromatography studies and ^{1}H n.m.r. spectroscopy[2] that, in solution, conformers (**1**) and (**3**) predominate for the *cis*- and *trans*-isomers respectively.

We have now investigated a series of both *cis*- and *trans*-3-substituted thietan 1-oxides by ^{1}H, ^{13}C and europium shift n.m.r. spectroscopy and have not been able to interpret satisfactorily the spectra on the basis of these structural assignments, particularly in the case of the *trans*-isomers.[3] We have therefore prepared and determined the crystal structures of the *cis*- and *trans*-isomers of 3-*p*-bromophenylthietan 1-oxide.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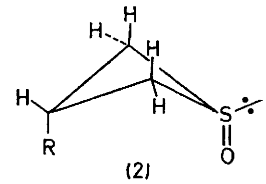
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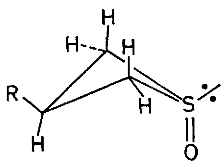
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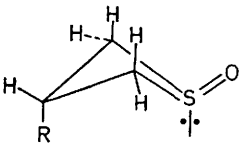
(4)

3-*p*-Bromophenylthietan, prepared from *p*-bromo-α-morpholinostyrene and methanesulphonyl chloride using Johnson's procedure,[4] was oxidised with one equivalent of *m*-chloroperbenzoic acid. Chromatography on silica and elution with ether–methanol (50:1) gave *cis*-3-*p*-bromophenylthietan 1-oxide† m.p. 108—109° (chloroform–light petroleum) τ ($CDCl_3$) 2·63 (2H, d, *J* 8·5 Hz), 3·02 (2H, d, *J* 8·5 Hz), 5·97—6·28 (2H, m), 6·28—6·55 (1H, m), and 6·58—6·88 (2H, m), followed by *trans*-3-*p*-bromophenyl-

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† All new compounds gave satisfactory mass spectra and elemental analyses.

thietan 1-oxide m.p. 112—113° (chloroform–light petroleum) τ ($CDCl_3$) 2·65 (2H, d, *J* 8·5 Hz), 3·02 (2H, d, *J* 8·5 Hz), 5·38—5·93 (1H, m), and 6·45 (4H, d, *J* 6 Hz).

Crystal data: *cis*-C_9H_9BrOS, monoclinic, $M = 245{\cdot}2$, $a = 5{\cdot}35$, $b = 7{\cdot}88$, $c = 11{\cdot}40$ Å, $\beta = 99{\cdot}1°$, $U = 475$ Å^3, $D_c = 1{\cdot}71$ g cm^{-3} for $Z = 2$, space group $P2_1$. *trans*-C_9H_9BrOS, monoclinic, $M = 245{\cdot}2$, $a = 9{\cdot}87$, $b = 8{\cdot}66$, $c = 11{\cdot}00$ Å, $\beta = 97{\cdot}3°$, $U = 933$ Å^3, $D_c = 1{\cdot}75$ g cm^{-3} for $Z = 4$, space group $P2_1/c$.

Standard heavy-atom and block-diagonal least-squares techniques have been applied to Stoe-Weissenberg diffractometer *X*-ray data (monochromatic Mo-K_α), 630 reflections ($> 3\sigma_I$) for the *cis*-isomer converged to $R = 0{\cdot}064$, and 496 reflections for the *trans*-isomer converged to $R = 0{\cdot}078$.

The structure determinations show that in the solid state the *cis*-isomer has conformation (**1**), the thietan ring is folded about the two α-C atoms by 147°, and the equatorial oxygen and *p*-bromophenyl group lie at 118° and 133° to their respective halves of the folded ring. The *trans*-isomer has conformation (**4**) in the solid state, with an angular value of 148° for the thietan ring fold. The equatorial oxygen and axial *p*-bromophenyl group lie at angles of 116° and 233° to the same side of their respective halves of the folded thietan ring. Distances and angles for the two isomers are very similar [S–O 1·482(13) for *cis*, 1·492(19) *trans*; C–S(av) 1·84(1) and 1·83(2); C–C(av) 1·54(2) and 1·52(3) Å]. *trans*-3-Carboxythietan 1-oxide also adopts this conformation in the solid state[5] but extensive intermolecular H-bonding may have made this a special case. There are no exceptional intermolecular contacts in either of the present compounds.

There is remarkable similarity between the ^{1}H n.m.r. spectra of series of both *cis* and *trans* 3-substituted thietan 1-oxides.[2] The four α-protons of *cis*-isomers always exhibit two well separated 2H multiplets, whereas in the *trans*-isomers all four α-protons contribute to a broad doublet with a chemical shift approximately mid-way between the chemical shifts of the two *cis*-multiplets. The observed ^{1}H n.m.r. spectrum of the *cis*-isomer of 3-*p*-bromophenylthietan 1-oxide is consistent with conformer (**1**) predominating in solution.[2] However, in view of the solid state structure of the *trans*-isomer, the assumption[2] that conformer (**3**) is predominant in solutions of the *trans*-isomer needs to be re-examined. We believe that the proton spectrum of the *trans*-isomer is compatible with the coexistence of conformers (**3**) and (**4**) in solution.

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[3] C. R. Hall and D. J. H. Smith, unpublished observations.

[4] W. O. Siegl and C. R. Johnson, *J. Org. Chem.*, 1970, **35**, 3657.

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