

ANCHIMERICALLY ASSISTED REDOX REACTIONS

Crystal Structure of an Alkoxysulfonium Salt  
Intermediate: 9-Oxa-1-thionibicyclo[3.3.1]nonane Triiodide

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**Summary:** A bicyclic alkoxysulfonium salt, 9-oxa-1-thionibicyclo[3.3.1]nonane triiodide, formed by transannular-OH participation during the  $I_2$  oxidation of 5-hydroxy-1-thiacyclooctane, has been isolated and its crystal structure determined.

In the course of our investigations of anchimeric assistance of redox reactions at sulfur we noted that the oxidation potential of 5-hydroxy-1-thiacyclooctane was lowered<sup>1</sup> by about 0.6V and the rate of its oxidation by  $I_2$  was accelerated relative to thiacyclooctane.<sup>2</sup> These observations suggested that the hydroxyl group strongly interacts with the thioether group on oxidation. Confirmation of this interaction has now been achieved by the isolation and crystal structure determination of the intermediate bicyclic alkoxysulfonium salt, 9-oxa-1-thionibicyclo[3.3.1]nonane triiodide. Although many alkoxysulfonium salts have been prepared by other methods,<sup>3-6</sup> a search of the literature reveals that no crystals suitable for X-ray analysis were obtained and consequently, no data on the R-O-S<sup>+</sup> functional group has been reported.

Bicyclic alkoxysulfonium intermediates have been proposed in two previous studies on thiacyclohexane derivatives to account for stereochemical control of product formation.<sup>7,8</sup> One study involves the oxidation of 4-hydroxy-1-thiacyclohexane by t-butyl hypochlorite to give the corresponding *trans*-sulfoxide.<sup>7</sup> The other study postulates an alkoxysulfonium intermediate to account for the enhanced rate of solvolysis of *trans*-4-chloro-1-thiacyclohexane 1-oxide compared to the corresponding *cis*-isomer.<sup>8</sup> However the postulated bicyclo[2.2.1] intermediates were never isolated or directly detected.

9-Oxa-1-thionibicyclo[3.3.1]nonane triiodide is formed by a transannular hydroxyl participation with the oxidized sulfur atom during the oxidation of 5-hydroxy-1-thiacyclooctane by  $I_2$  in aqueous phosphate buffer/methanol.<sup>9,10</sup> Under these conditions, typical alkoxysulfonium salts would be expected either to rearrange to the oxosulfonium salt or to hydrolyze to give the corresponding sulfoxide.<sup>4</sup> The unusual stability to hydrolysis may be due to the bicyclic ring structure and to the insolubility of the triiodide salt.

Structure of 9-oxa-1-thionibicyclo[3.3.1]nonane triiodide

The determination of crystal dimensions and intensity measurements were carried out on a Syntex P2<sub>1</sub> diffractometer at 140 K using MoK $_{\alpha}$  radiation. A crystal of dimension 0.19 x 0.16 x

0.17 mm was selected for data collection and mounted along the long axis. Crystal data are: space group,  $C2/c$ ;  $a = 23.569(6)$ ,  $b = 7.453(2)$ ,  $c = 14.881(5)$  Å,  $\beta = 101.02(2)^\circ$ ;  $Z = 8$ ,  $\rho_{\text{exptl}}$  (298 K) =  $2.65 \text{ g cm}^{-3}$ ;  $\mu_{\text{MoK}\alpha} = 73.2 \text{ cm}^{-1}$ . A total of 2010 unique reflections were measured using a variable speed  $\omega$  scan technique. Of these, 1794 with  $I > 3\sigma(I)$  were used in the final refinement of the structure. The structure was solved by Patterson, Fourier and full-matrix least squares methods. The twelve non-hydrogen atoms were refined using anisotropic thermal parameters leading to a conventional R index of 0.053. In the final difference map no hydrogen atoms could be found in the vicinity of the oxygen atom. Some residual electron density was found in the region of the iodine atoms. The thirteen hydrogens bonded to carbon atoms were located very close to their calculated positions. When these hydrogen atoms were included at their calculated positions with  $B_{\text{iso}}$ 's of  $2.0 \text{ \AA}^2$  in the final structure factor calculation, an R of 0.050 was obtained. Tables of positional and thermal parameters, and structure factors are available.<sup>11,12</sup>

The results of the X-ray diffraction crystal structure determination of this compound reveal no unusual contacts in the packing of cations and anions in the unit cell. The closest approach between the triiodide ion and a non-hydrogen atom of the cation is a  $3.38(5)$  Å separation between the central iodine atom and the oxygen atom of the cation. The minimum distance of a hydrogen atom (bonded to C(2)) is  $3.13(5)$  Å to a terminal iodine atom. Bond distances for the triiodide ion are  $2.900(1)$  and  $2.915(1)$  Å with an angle of  $175.8(1)^\circ$ .

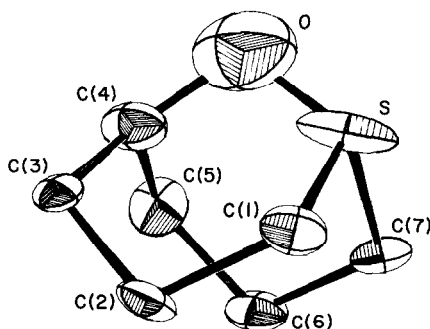


Figure 1. Atom labelling scheme for  $\text{SOC}_7\text{H}_{13}^+$  with the hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

A drawing of the cation is given in Figure 1. The two six-membered rings are fused in a chair-chair conformation, the most common arrangement for the bicyclo[3.3.1]nonane system.<sup>13</sup> Large anisotropic thermal motion is displayed by the sulfur and oxygen atoms. The possibility that the axial hydrogen atoms on C(2) and C(6) interact to introduce some disorder was rejected since their separation of  $1.92$  Å is not unusually short. Our results for the bicyclic alkoxy-sulfonium moiety indicate that the S–O distance is shorter than an S–O single bond. In fact, the calculated value for this distance,  $1.40(2)$  Å, is shorter than the S–O double bond found in sul-

foxides ( $1.49 \pm .02 \text{ \AA}$ ) and sulfones ( $1.44 \pm .02 \text{ \AA}$ ).<sup>14,15</sup> The value computed for the C(4)-O bond is  $1.37(2) \text{ \AA}$ , and the C(4)-O-S angle is  $110(2)^\circ$ .<sup>16</sup> Additional values of bond distances and angles are listed in Table I. Whether the large thermal motion stems from some unexplained disorder in the crystal or from some unusual feature of the alkoxysulfonium  $R_2S^+-OR$  bonding is not clear. Unfortunately, no other structure determinations of these salts have been reported with which we can compare the geometry of this structure. It may be worth noting the similarity of the C-O-S grouping to the C-NH-S grouping in dehydromethionine, which contains a tetrahedral nitrogen atom and an N-S bond that is  $0.06 \text{ \AA}$  shorter than the sum of the covalent radii.<sup>17</sup>

TABLE I. Table of Bond Distances ( $\text{\AA}$ ) and Angles for  $(SOC_7H_{13})(I_3)$ .

I(1)-I(2)	2.900(1)	C(4)-C(5)	1.51(2)	S-C(7)-C(6)	111(1)°
I(2)-I(3)	2.915(1)	C(5)-C(6)	1.54(2)	C(1)-C(2)-C(3)	109(1)°
S-O	1.40(2)	C(6)-C(7)	1.55(2)	C(2)-C(3)-C(4)	114(1)°
C(4)-O	1.38(2)	S...C(4)	2.28(1)	C(3)-C(4)-O	118(1)°
S-C(1)	1.79(1)	I(1)-I(2)-I(3)	175.8(1)°	C(5)-C(4)-O	110(1)°
S-C(7)	1.81(1)	C(4)-O-S	110(1)°	C(4)-C(5)-C(6)	112(1)°
C(1)-C(2)	1.56(2)	O-S-C(1)	112(1)°	C(5)-C(6)-C(7)	109(1)°
C(2)-C(3)	1.55(2)	O-S-C(7)	108(1)°		
C(3)-C(4)	1.48(2)	S-C(1)-C(2)	110(1)°		

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10. No bicyclic [2.2.1] intermediate was obtained when we treated 4-hydroxy-1-thiacyclohexane with iodine under similar conditions.<sup>9</sup>
11. For a crystal of these dimensions the absorption correction factor range is 1.09-1.22. No absorption correction was made.
12. Contact the Directory of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road Cambridge CB2 1EW. Requests should be accompanied by the full literature citation for this communication.
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16. Our attempts to fit the large anisotropic thermal motion to a disordered model of motion in the bridging region were abandoned since this model would necessarily involve a minimum of three atoms and would be quite complex. However, in the absence of such a model, The S-O and C(4)-O bond distances, as well as the C(4)-O-S angle must be viewed with some doubt.
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