Synthesis and *X*-Ray Crystal Structure of *O*,*O*-Bicyclohexyl-1,1′-diyl Thiosulphite[1]

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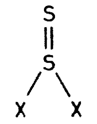
Summary The first *X*-ray crystal structure determination of a thiosulphite *OO′*-diester is reported.

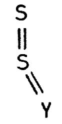
The branch-bonded sulphur species (**1**) were initially considered as structures for the disulphides (**2**) and trisulphides (**3**)[2] and have been suggested as reactive intermediates in various organosulphur transformations.[3] Other branch-bonded species have been reported.[4–9] In the case of the thiosulphite *OO′*-diesters (**1b**) a small number have been synthesized, but are reported[10] to decompose at room temperature or in the light.



(1)
a; X = F
b; X = OR

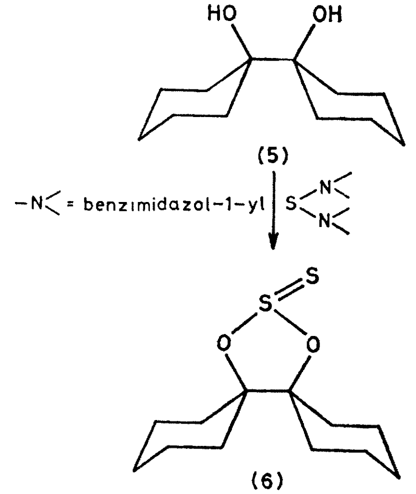
RS·SR
(2)

RS·S·SR
(3)



(4)
a; Y = NR
b; Y = NSNPPh$_3$

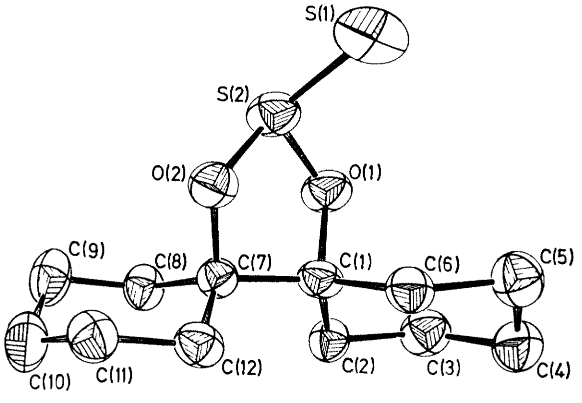
We here report the isolation and first crystal structure of a thiosulphite *OO′*-diester. When the diol (**5**) was treated with the sulphur-transfer reagent bisbenzamidazol-1-yl sulphide in CCl$_4$, a 50% yield of the thiosulphite *OO′*-diester (**6**) was obtained. The compound melts at 100—101 °C with decomposition and subsequent evolution of a gas at 150 °C. Elemental analysis, exact mass measurement, and the ^{13}C spectrum were consistent with structure (**6**).



(5)

(6)

Crystal data: $C_{12}H_{20}O_2S_2$, monoclinic, space group $P2_1/c$, $a = 9{\cdot}482(5)$, $b = 11{\cdot}979(9)$, $c = 11{\cdot}822(8)$ Å, $\beta = 100{\cdot}218(1)°$, $Z = 4$, $D_c = 1{\cdot}308$, $D_o = 1{\cdot}32$ g cm^{-3} (flotation). Data were collected on a Picker FACS-I diffractometer using graphite monochromated Mo-K_α radiation. 1366 Independent reflections with $F > 3\sigma F^2$ were collected with $5° < 2\theta < 50°$ and considered observed. The structure was solved using a combination of direct methods and difference Fourier syntheses Least-squares refinement gave a final *R* value of 0·073 †



FIGURE

The Figure shows the structure of the thiosulphite *OO'*-diester (**6**) The two cyclohexyl-rings are both in the chair conformation, staggered from one another causing the *OO'*-diester ring to be significantly twisted The O(1)C(1)-C(7)O(2) dihedral angle is 37 8° The S(1)–S(2) bond makes an angle of 28 0° with the O(1)S(2)O(1) plane and the O(1)–S(2)–O(2) bond angle is 94·3(2)° The S(1)–S(2) bond distance is 1·901(2) Å and is directed in what may be considered a quasi-axial position from the twisted, five-membered thiosulphite ring

The S–S bond length (1 901 Å) is of considerable interest in this molecule Other information on branch-bonded S–S distances comes from S_2 itself (1 89 Å),[11] S_2O (1·884 Å),[12] a microwave analysis of the S_2F_2 structure (1·86 Å),[4] thiosulphinylamines (**4a**) (1 898 Å),[8] and (**4b**) (1·908 Å)[9] All these values are considerably below that for an ordinary disulphide (2 02—2 06 Å)[13] and imply significant double bond character in the branch-bonded linkage

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† The atomic co ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre University Chemical Laboratory, Lensfield Road Cambridge CB2 1EW Any request should be accompanied by the full literature citation for this communication

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