X-Ray Crystal and Molecular Structure of a Dispirothiiran: 1,1,3,3,7,7,9,9-Octamethyl-2,8-dioxa-11-thiadispiro[4.0.4.1]undecane-4,10-dione

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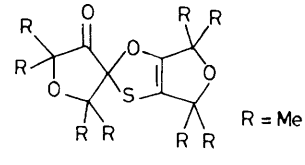
Summary *X*-Ray analysis of the title compound shows the molecule to have two furanone rings spiro-fused to a thiiran ring; during the *X*-ray exposure, small crystal platelets grew on the parent crystal, and these are of a new compound, as yet uncharacterized.

DURING an investigation of heterocyclic spirofuranones, Praefcke and his co-workers[1] found that (I) (the structure of which has recently been confirmed in this laboratory[2]), on heating with copper powder instead of undergoing desulphurization, forms an isomer, for which, on the basis of ^{13}C n.m.r. and i.r. spectra, the thiiran structure (II; chemical numbering) was proposed.[3] This assignment is now shown to be correct by *X*-ray crystal structure analysis.

Irregular, opaque, yellow crystalline fragments of (II) [kindly provided by Prof. Praefcke (Berlin)], like (I), are unstable to air and light and thus an irregular piece *ca.* 0·48 × 0·32 × 0·12 mm was sealed, in subdued light, in a Lindemann glass capillary under nitrogen.

Crystal Data: $C_{16}H_{12}O_4S$, $M = 300{\cdot}34$, monoclinic, space group $P2_1/c$, $a = 9{\cdot}808(9)$, $b = 23{\cdot}394(9)$, $c = 7{\cdot}685(8)$ Å, $\beta = 98{\cdot}31(9)°$, $U = 1744{\cdot}8$ Å^3, $Z = 4$, $D_c = 1{\cdot}14$ g cm^{-1}, μ(Mo-K$_\alpha$) = 1·98 cm^{-1}.



(I) (II)

The instability of the material was shown by the appearance of a small amount of a well formed crystalline deposit on the surface during preliminary photographic work to establish the crystal data. Intensity data were collected (with a new crystal) by a computer-controlled Picker diffractometer with Zr-filtered Mo-K_α radiation using a high scan speed of 4° min^{-1} in the θ—2θ mode and a scan width of 2°. A standard reflection measured after each batch of 30 reflections showed a decay of *ca.* 13% during 3 days.

The structure was solved by direct methods using the computer program TANFOR from the 296 reflections with $E > 1{\cdot}60$. The E-map obtained from the most probable set of phases revealed all 21 non-hydrogen atoms. Fractional co-ordinates of hydrogen atoms were calculated by assuming a C–H bond length of 1·0 Å. Final anisotropic full-matrix least squares refinement based on 1008 observed reflections yielded an R factor of 14·6%. There were no spurious peaks on the final difference map. The high value of R can be attributed to the poor intrinsic quality of the crystal, and to the high speed of data collection necessitated by the solid state reaction.†

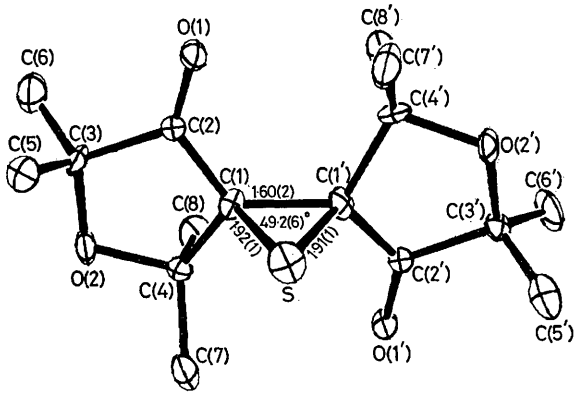


FIGURE. ORTEP plot of the title compound (II) showing 20% probability ellipsoids.

The molecular structure, shown in the Figure, with the furanone rings spiro-fused (*trans*) to the thiiran ring, agrees exactly with that proposed. Consequently the molecule has an almost exact (non-crystallographic) diad axis. The mean (unweighted) square deviation of all non-hydrogen atoms from diad symmetry is only 0·093 Å and only 0·023 Å if methyl carbon atoms are excluded.[4] The crystal is, of course, a racemate containing equal numbers of molecules of opposite chirality.

We have found only two other reported crystal structures of thiirans[5,6] (and one microwave spectral analysis[7]) for comparison with our analysis. Comparisons, therefore, cannot be made with much confidence but these four examples show a general trend of a lengthening of both C–C and S–C bonds with decreasing (average) external R–C–R′ angles. In the present case, the average external angle at 107·3° [compared with 101·8° in compound (I)] is the smallest of the four examples and its bonds the longest, S–C of 1·915(10) Å being probably the longest recorded so far. A similar but less dramatic effect is found in the nitrogen analogue (thiadiaziridine) a derivative of which shows an N–N bond length of 1·67 Å, some 0·2 Å longer than a normal single bond.[8]

Both planes, C(2)–C(1)–C(4) and C(2′)–C(1′)–C(4′) make an angle of 87(2)° with the thiiran ring. However the S–C(1) bond makes much smaller angles with C(1)–C(2) and C(1)–C(4) than does C(1)–C(1′), namely 114(1) and 115(1)° compared with 126(1) and 120(1)°. The angles subtended at C(1′) are similar.

As noted above, the crystal (still sealed in its capillary) was found, after data collection, to be covered in small well formed yellow platelets. (A separate experiment showed that heat was responsible.) A preliminary study gives monoclinic cell dimensions of $a = 6{\cdot}11$, $b = 8{\cdot}57$, $c = 16{\cdot}48$ Å, $\beta = 115°$, $U = 782{\cdot}1$ Å^3, space group $P2_1/c$. The lack of a simple proportionality between the cell volumes indicates that the overgrowths are those of a new material and not of a polymorph. The structure of this compound is currently under investigation.

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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 Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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