

The Structure of a [1,2,5]Oxaselenazolo[2,3-*b*][1,2,5]oxaselenazole-7-Se^{IV} by X-Ray Crystallography and Nuclear Magnetic Resonance Spectroscopy

By R. J. S. BEER* and J. R. HATTON

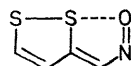
(The Robert Robinson Laboratories, University of Liverpool, Liverpool L69 3BX)

and E. C. LLAGUNO and I. C. PAUL*†

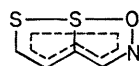
(W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801)

Summary A study of a [1,2,5]oxaselenazolo[2,3-*b*][1,2,5]oxaselenazole-7-Se^{IV} by X-ray methods shows that most of the molecule is planar and that the oxygen atoms are held in close contact (2.017—2.030 Å) with the selenium atom.

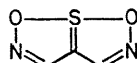
STUDIES¹⁻³ on derivatives of 3-nitrosomethylene-1,2-dithiole (I) have indicated close 'contacts' (2.0—2.1 Å) between oxygen and adjacent sulphur atoms. In cases where there may be competition between the nitroso-group and other groups (CO-Ph, CS-SMe, CS-NMe₂, NO₂) for the position *cis* to the dithiole S-S link, the nitroso-group appears to take precedence. These results suggest that molecules of type (II) should be capable of existence, with a (formally) quadricovalent sulphur atom placed between two 'nitroso'-groups, forming a bicyclic structure stabilised by the presence of a delocalised system of π -electrons, analogous to that discussed⁴ for 6a-thiathiophthen (III).



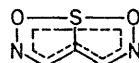
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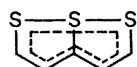
(I)



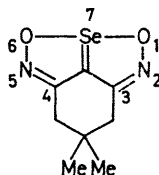
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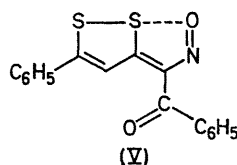
(II)



(III)



(IV)



(V)

We now report structural and other data for the [1,2,5]oxaselenazolo[2,3-*b*][1,2,5]oxaselenazole-7-Se^{IV} (IV), one of a series described by King and Felton.⁵ Various structures were considered⁶ for the products, including those of type (IV), which, however, were thought to be unlikely on steric grounds.

The selenium compound (IV) is thermally stable and is

unreactive towards both bromine in carbon tetrachloride and concentrated sulphuric acid at room temperature. The absence of a normal nitroso-group is shown by lack of reactivity towards aniline in boiling toluene, even in the presence of acidic catalysts. The compound is sensitive, however, to alkaline reagents and to reducing agents; no well defined products have been obtained except dimedone dioxime, in low yield, on reduction with sodium dithionite.

Crystals of (IV) grow as dark red needles, elongated along the *a*-axis. Some weeks after completion of the data collection, it was observed that the crystal had turned yellow. *Crystal data*: C₈H₁₀O₂N₂Se, *M* = 245.0, monoclinic, *a* = 5.837(2), *b* = 20.337(11), *c* = 7.971(2) Å, β = 97°55'(2'), *U* = 956.6 × 10⁻²⁴ cm³, *D_m* = 1.76, *Z* = 4, *D_c* = 1.70, space group P2₁/*n*. Intensity data were collected on a Picker FACS-1 computer-controlled diffractometer (Cu-K α , λ = 1.54178 Å). The structure was solved by the heavy atom method and has been refined by full-matrix least-squares, with anisotropic thermal parameters for the heavy atoms and isotropic thermal parameters for the hydrogen atoms, to an *R*-factor of 0.056 on the 1154 non-zero reflections. A view of the molecular structure is shown in Figure 1.

With the exception of the carbon atom bearing the *gem*-dimethyl group and the two methyl carbon atoms, the molecule is almost planar (max. dev. 0.032 Å). The oxygen atoms of the two nitroso-groups are held in close contact with the selenium atom giving Se...O distances of 2.017(9) and 2.030(9) Å. These distances are similar to the SO (nitroso) distance [2.034(5) Å] found in (V).² The C-Se length of 1.802(11) Å is amongst the shortest reported C-Se distances,^{6,7} and presumably involves considerable double bond character. The bond-lengths and angles involving selenium and the near-planar configuration around selenium are quite different from those found in benzeneseleninic acids,⁸ where the selenium has a pyramidal configuration; the Se-C distance is about 1.90 Å, the Se-O distances are in range 1.70—1.77 Å, and the O-Se-O angle is 103.5°. In (IV), the corresponding O-Se-O angle is 199.2(4)°. The N-O lengths in (IV) are 1.337(14) and 1.346(14) Å, significantly longer than those found [1.259(4) and 1.269(4) Å] in the crystal of the *cis*-dimer of nitrosobenzene,⁹ but closer to that [1.312(6) Å] found in (V).² The CNO angles in (IV) and (V) lie in the range 112.5—112.9°, values which are much smaller than those of 120.1—120.8° found in the nitrosobenzene structure.⁹

The molecule has effective C_s symmetry through a plane perpendicular to the plane containing most of the atoms in the molecule, and passing through the selenium atom. The symmetry of the molecule is reflected in the n.m.r. spectrum (measured in CDCl₃) which shows two sharp signals, one at τ 8.92 for the two methyl groups and one at

† Alfred P. Sloan Research Fellow.

6.78 for the two methylene groups. The carbon atom bearing the *gem*-dimethyl group lies 0.617 Å out of the

and of the methylene groups implies rapid oscillation of the Me₂C group about a mean position. Measurement of the

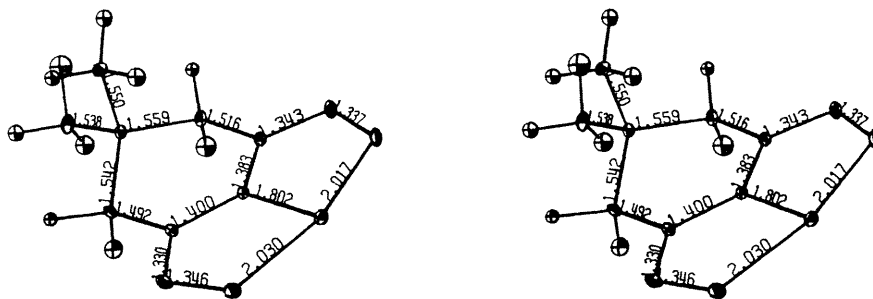


FIGURE. A view of a molecule of (IV) showing bond lengths.

exact (within the accuracy of the analysis) plane through the other five carbon atoms of the six-membered ring. The observed equivalence of the protons of the methyl groups

n.m.r. spectrum at -60° indicated some broadening of the signals, especially of that due to the methyl protons.

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¹ R. J. S. Beer and R. J. Gait, *Chem. Comm.*, 1970, 328; R. J. S. Beer, D. Cartwright, R. J. Gait, and D. Harris, *J. Chem. Soc. (C)*, 1971, 963.

² P. L. Johnson and I. C. Paul, *J. Amer. Chem. Soc.*, 1969, **91**, 781; P. L. Johnson, K. I. G. Reid, and I. C. Paul, *J. Chem. Soc. (B)*, 1971, in the press.

³ K. I. G. Reid and I. C. Paul, *Chem. Comm.*, 1970, 329; *J. Chem. Soc. (B)*, 1971, in the press.

⁴ For recent reviews, see E. Klingsberg, *Quart. Rev.*, 1969, **23**, 537; D. H. Reid, "Organic Compounds of Sulphur, Selenium, and Tellurium," The Chemical Society, London, 1970, Vol. I, p. 321.

⁵ F. E. King and D. G. I. Felton, *J. Chem. Soc.*, 1949, 274.

⁶ E. Shefter, M. N. G. James, and H. G. Mautner, *J. Pharm. Sci.*, 1966, **55**, 643.

⁷ J. H. van den Hende and E. Klingsberg, *J. Amer. Chem. Soc.*, 1966, **88**, 5045.

⁸ J. H. Bryden and J. D. McCullough, *Acta Cryst.*, 1954, **7**, 833; 1956, **9**, 528.

⁹ D. A. Dieterich, I. C. Paul, and D. Y. Curtin, *Chem. Comm.*, 1970, 1710.