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THE MOLECULAR STRUCTURE OF A COMPOUND WITH VERY SHORT S---O CONTACTS IN AN O---S---O GROUP

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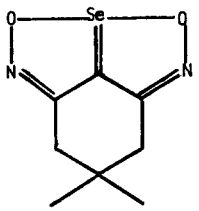
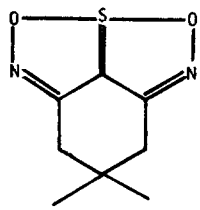
Recently, we reported the structural and geometrical details for the [1,2,5]oxaselenazolo-[2,3-b][1,2,5]oxaselenazole-7-Se^{IV}(I),[1] a molecule first synthesized by King and Felton.[2] The Se---O distances were 2 017(9) and 2 030(9)Å, thus implying a very strong Se---O interaction, the sum of the single bond covalent radii for Se and O is 1 83Å and that of the corresponding van der Waals radii is 3 40Å.[3] While a wide range of short S---O constants has been noted in molecules with the S—S---O group,[4] the shortest distance found in such a structure was 2 034(5)Å in 3,5-epidithio-2-nitroso-1,5-diphenylpenta-2,4-dien-1-one,[5] where the oxygen atom was part of a nitroso group This S---O distance was 0 15Å shorter than any other S---O distance reported in the S—S---O grouping, the next shortest being 2.184(7)Å in a phenolate derivative.[6] We have carried out an X-ray structural analysis on the sulfur analog (II)[7] of (I) to see if the nitroso group has an equally dramatic effect on the S---O distances in the O---S---O system as it had on the S—S---O system S---O distances in the range 1 878-1 916Å have been reported in the symmetrical molecule (III)[8] and in the sulfurane (IV)[9]

The yellow prisms of (II) were kindly supplied by Dr. R J. S. Beer of the University of Liverpool. Crystal data $C_8H_{10}N_2O_2S$, M = 198 2, orthorhombic, a = 19.866(12), b = 9 217(5), c = 10 107(5)Å, U = 1851 x 10^{-24} cm^3, Z = 8, D_c = 1 42 g cm^{-3}, systematic absences, $h0l$, when $l = 2n + 1$, $0kl$, when $k = 2n + 1$, $hk0$, when $h = 2n + 1$, space group $Pbca$ A total of 806 non-zero structure amplitudes was collected on a Picker FACS-1 diffractometer, using CuK_α radiation The structure was solved by the symbolic addition method and has been refined by full-matrix least-squares methods to an R-factor of 0 096. The model included anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The molecular dimensions are shown in Figure 1.

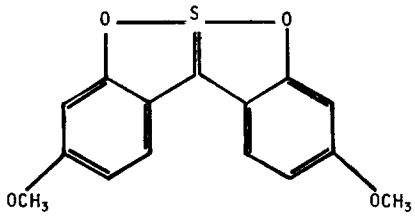
The S---O distances in (II) are 1.875(8) and 1 878(7)Å These are much shorter than the shortest S---O(nitroso) contact[5] reported thus far or than the Se---O distances found in (I) When due allowance is made for the difference (0 13Å) in the covalent radii of sulfur and



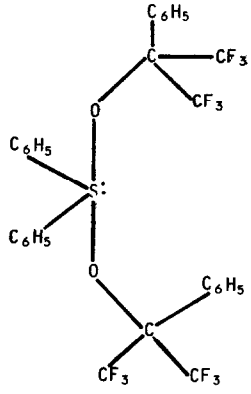
(I)



(II)



(III)



(IV)

selenium,[3] however, the distances in (I) and (II) probably correspond to interactions of comparable strength. However, the S---O distances in (II) are effectively the same as those found in (III) and (IV). When compared to the phenolate group, the nitroso group has much less effect in the O---S---O system than it had in the S-S---O system. The C-S length of 1.643(9)Å in (II) is much shorter than that, 1.720(2)Å, in the phenolate derivative (III) and is one of the shortest C-S bonds thus far reported.[10-12] While the differences in the other molecular dimensions between (I) and (II) are less dramatic, there is some evidence (e.g., in the longer nitroso bond lengths) for increased delocalization in the sulfur analog as compared to the selenium compound

It is noteworthy that while the dimensions and conformation of (I) and (II) are very similar they crystallize in different space groups and with quite different packing Unlike the case of the selenium compound,[1] there appear to be no significant S---O intermolecular interactions in the crystal of (II)

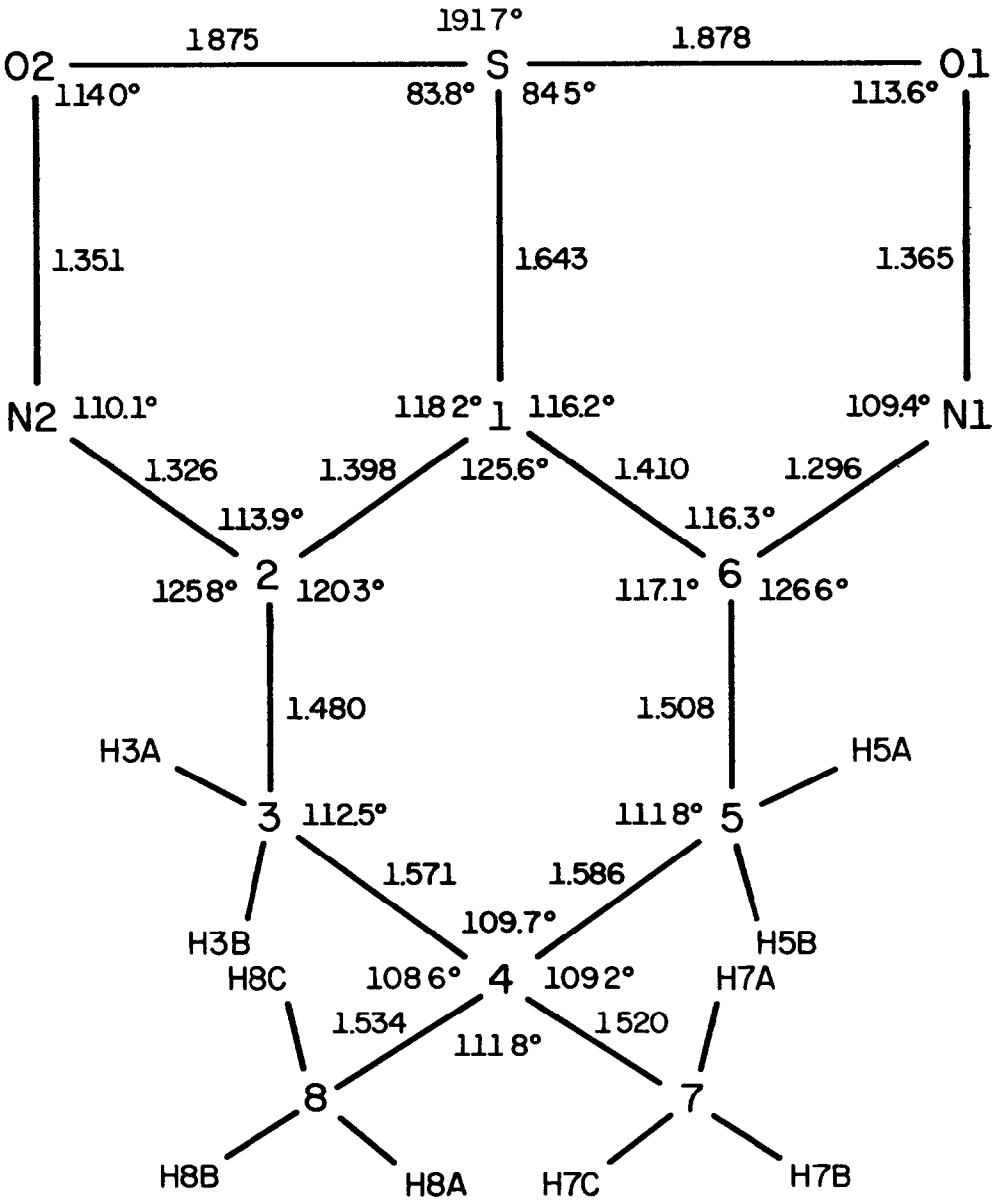


Figure 1 Bond lengths and bond angles in (II) The esd for the S-O, C-S, N-O, C-N, and C-C lengths are 0.007-0 008Å, 0.009Å, 0 012-0 014Å, and 0.013-0 017Å, respectively. The esd for the bond angles around the S and O atoms are 0 04°-0 05° and for those around the C and N atoms are in the range 0 5°-0 9°

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