Some Structural Observations on Molecules with Short Sulphur–Oxygen Intramolecular Contacts

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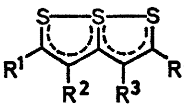
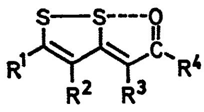
Summary The very short S · · · O distance observed in analogues of thiathiophthens containing a nitroso-group is not found in those containing a nitro-group.

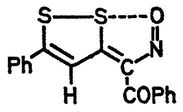
X-RAY studies[1] on a number of molecules of the thiathiophthen class (I) have shown that the S–S distances can range in length from 2·16 to 2·56 Å. In the oxygen analogues (II)[2,3] of the thiathiophthen system where one of the terminal sulphur atoms is replaced by oxygen, the S–S distances are much shorter (2·10—2·12 Å), while the S · · · O distances are considerably less than the sum of the appropriate van der Waals' radii.[4] The 3,5-epidithio-2-nitroso-1,5-diphenylpenta-2,4-dien-1-one molecule (III)[5] has the nitroso rather than the carbonyl group in close contact with the sulphur[6] and the resulting S–S and S · · · O distances are 2·178 and 2·034 Å, respectively; the latter distance being very short for an S · · · O contact.[7] We now report results of *X*-ray studies on 2,4-epidithio-1-nitro-1-nitroso-4-phenylbutadiene (IV) and on 1-bromo-2,4-epidithio-1-nitro-4-phenylbutadiene (V).[8]‡



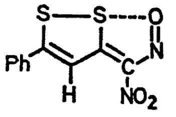
(I)



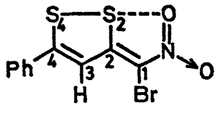
(II)



(III)



(IV)



(V)

The crystals of (IV) were very fine red needles. *Crystal data*, $C_{10}H_6N_2O_3S_2$, *M* 266·3, monoclinic, *a* = 3·944(3), *b* = 16·420(7), *c* = 16·492(7) Å, β = 96°27′(4′), D_m = 1·61(5) g cm^{-3}, *Z* = 4, space group: $P2_1/c$. All the crystals examined were twinned, (001) being the twinning plane. While the crystal selected had the minimum weight for the twinning component there was considerable overlapping of reflections other than those in the 0*kl* zone, making it impossible to refine the structure fully in three-dimensions. The structure was solved by the symbolic addition method[9] and a refinement (isotropic temperature factors) on the 274 non-zero reflections in the 0*kl* zone gave an *R*-factor of 0·108. Refinement with isotropic temperature factors on 1813 three-dimensional data measured on a diffractometer stopped at an *R*-factor of 0·29. S · · · O and S–S bond lengths calculated using the *x* co-ordinate from the latter refinement and the *y* and *z* co-ordinates from the two dimensional refinement were 2·10 and 2·14 Å (the corresponding bonds after the three-dimensional refinement were 2·11 and 2·13 Å). These distances are consistent with those found in (III). The results clearly demonstrate that the nitroso-group rather than the nitro-group is in close contact with sulphur.[8]

(V) forms red needles elongated along the *b* axis. *Crystal data*: $C_{10}H_6BrNO_2S_2$, *M* = 316·2, monoclinic, *a* = 9·281(3), *b* = 12·457(9), *c* = 12·713(9) Å, β = 132°7′(8′), D_m = 1·88 g cm^{-3}, *Z* = 4, space group: $P2_1/c$. The structure was solved by the heavy-atom method and has been refined to an *R*-factor of 0·075 on 1677 reflections measured on a diffractometer (Cu-K_α radiation). A view of the molecular structure is shown in the Figure.

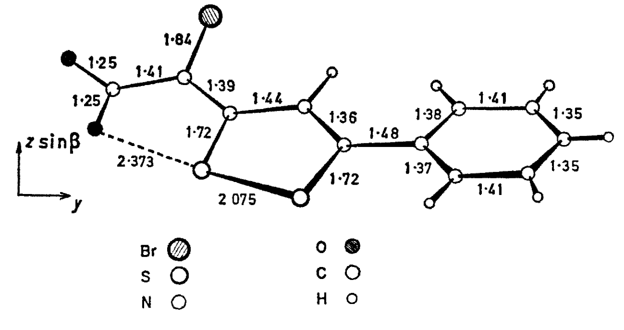


FIGURE. *Bond lengths in* (V). *The e.s.d. of the* C–C *bonds range from* 0·01—0·02 Å, *while those for the other bonds are close to* 0·01 Å.

The S(2)–S(4) bond length [2·075(3) Å] is within the range of normal covalent S–S distances, (2·00—2·10 Å),[10] and is thus somewhat shorter than the values reported for compounds (II)[2,3] and (III).[6] The S(2) · · · O distance [2·373(7) Å] is effectively the same as those reported in two compounds (II)[2,3] (2·41 and 2·382 Å, respectively), but is considerably longer than that found in the nitroso-derivative (III). An S · · · O (nitro) intramolecular distance

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‡ The crystals of (IV) and (V) were generously supplied by Dr. R. J. S. Beer and Mr. R. J. Gait, University of Liverpool.

of 2·44 Å was reported for the methyl ester of *o*-nitrobenzenesulphenic acid.[11] The bond angle S(4)–S(2) · · · O is 172·6°, in keeping with the observed linearity in these systems.

The bond lengths in the sequence C(1)–N–O in (V) are 1·41(1) and 1·26(1) Å, compared with 1·31 and 1·31 Å for the same sequence in (III). The corresponding bond sequence C–C–O in (II; $R^1 = R^3 = Ph$, $R^2 = R^4 = H$)[3] has lengths 1·43 and 1·26 Å. The N–O bond lengths in (V) are equal within experimental error and the C(1)–N–O angles are 117 and 120°. Further parallelling the behaviour of compounds (II), (V) exhibits alternate long and short C–C bonds, whereas the pattern of C–C lengths in (III) does not appear to be so regular.

From χ^2 tests, the central eight atoms of (V) [N, O, C(1), C(2), S(2), C(3), C(4), S(4)] are non-planar whereas both "5-membered rings" [N, O, C(1), C(2), S(2) and C(2), S(2), C(3), C(4), S(4)] are planar and inclined at an angle of 6°43′ to each other. The phenyl ring closely approximates a plane and is twisted 10° away from the plane through the 5-membered ring to which it is attached.

The work of Maeda[12] and of Gleiter and Hoffmann[13] indicates that in the thiathiophthen system the bonding can be considered as an electron-rich three-centred bond incorporating *d*-orbitals of the nearly linear S–S–S chain in a 10π system. SCF–MO calculations based on a 10π system have provided a theoretical basis for the u.v. spectra of thiathiophthens.[14] Kapecki and Baldwin,[15] on the basis of MO calculations on (II), concluded that *covalent* bonding between sulphur and oxygen in this class of compounds must be very weak or virtually non-existent, despite the short S · · · O contact. Preliminary observations of the bond distances in (V) tend to support a similar view of the bonding when a nitro-group replaces the carbonyl group.

The structural work on compounds (III) and (IV) serves to establish an order of preference in the S · · · O co-ordination, *i.e.*, nitro < nitroso > carbonyl.[8] The relationship between carbonyl and nitro-groups has yet to be determined.

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