Nitro- and Nitroso-derivatives of 3-Methylene-1,2-dithioles

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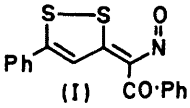
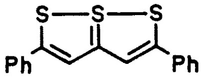
Summary In ω-nitroso-3-methylene-1,2-dithioles, the nitroso-group takes precedence over other groups (*e.g.* nitro-) in adopting the position *cis* to the dithiole S–S link.

STRUCTURE (I) was assigned to the product obtained by the action of nitrous acid on 2,5-diphenyl-6a-thiathiophthen (II) (and on 5-phenyl-1,2-dithiol-3-ylideneacetophenone) on the basis of spectroscopic evidence.[1] Subsequent study of the structure by *X*-ray crystallography[2] has shown that there is a very short "contact" (2·034 Å) between a sulphur atom and the oxygen atom of the nitroso-group, and it is clear that the dimensions suggested by a single classical structure of type (I) are considerably modified in the actual molecule.


(I)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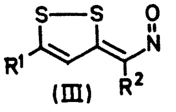
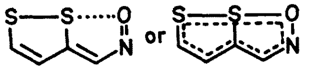
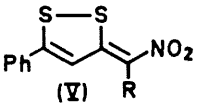

(III)

a; R^1 = Ph, R^2 = CS_2Me
b; R^1 = Ph, R^2 = H
c; R^1 = Ph, R^2. = CS·NMe_2
d; R^1 = MeS, R^2 = CS_2Me
e; R^1 = Ph, R^2 = NO_2


(IV)


(V)

R = H; λ_{max} 314, 464 nm (ε 10,000, 26,800)
R = Me; λ_{max} 316, 468 nm (ε 10,500, 23,600)
R = Br; λ_{max} 318, 477 nm (ε 6440, 15,600)

The three nitroso-compounds previously reported,[1] (I), (IIIa), and (IIIb), and two further compounds, (IIIc) and (IIId), obtained by nitrosation of 2-dimethylamino-5-phenyl-6a-thiathiophthen and of 2,5-bismethylthio-6a-thiathiophthen respectively, all have similar absorption spectra, with maxima at *ca.* 330 and *ca.* 420 nm. We infer that the five compounds are of the same structural type, *i.e.* derivatives of the system (IV).

We now report the preparation of structurally related nitro-compounds, (V; R = H) and (V; R = Me), obtained by condensation of 3-methylthio-5-phenyl-1,2-dithiolium methosulphate with nitromethane and nitroethane in acetic acid–pyridine. Compound (V; R = H), which is also produced by the action of mercuric acetate on 2-methylthio-3-nitro-5-phenyl-6a-thiathiophthen,[1] reacts readily with bromine in benzene solution giving the mono-substitution product (V; R = Br). The position of bromination can be inferred by comparison of n.m.r. spectra.

The three nitro-compounds clearly have similar structures, but the product obtained by nitrosation of compound (V; R = H) shows absorption maxima at 327 and 415 nm, closely resembling the nitroso-compounds (I) and (IIIa—d); it is therefore formulated as (IIIe).

This structure is confirmed by the *X*-ray crystallographic study described in the following communication,[3] which also gives definitive structural data for the nitro-compound (V; R = Br). It is of particular interest that the S–O contact in the nitro-compound is considerably longer than the S–O distances in the two nitroso-compounds for which data are available.

We conclude that the nitroso-group takes precedence over other groups (CO·Ph, CS·SMe, CS·NMe_2, NO_2) in competition for the apparently advantageous position adjacent to the dithiole S–S link.

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[1] R. J. S. Beer, D. Cartwright, R. J. Gait, R. A. W. Johnstone, and S. D. Ward, *Chem. Comm.*, 1968, 688.

[2] P. L. Johnson and I. C. Paul, *J. Amer. Chem. Soc.*, 1969, **91**, 781.

[3] K. I. G. Reid and I. C. Paul, following communication.