# Cyclic Sulphones. Part XVI.[1] Probes for Conjugation of the Sulphonyl Group: Thiopyranylidenedihydropyridine *SS*-Dioxides

By **GiorgioPagani,**† Istituto di Chimica Industriale dell'Università, C.N.R. Centro di studio sulla sintesi e stereochimica di speciali sistemi organici, via Saldini 50, 20133 Milano, Italy

The thiopyran group in the title compounds (7)—(10), which have been synthesized, may represent a reasonable model for the thiopyran *SS*-dioxide anion. Dipolar forms contribute to the ground state of these compounds as shown by $^1$H n.m.r. correlations and from reactions with electrophiles. I.r. stretching vibrations of the sulphonyl group of these molecules show considerable bathochromic displacements relative to the standard values, indicating that the sulphonyl group encounters the most favourable conditions for case I conjugation.

THIOPYRAN *SS*-dioxide anions are of interest because of the presence of a $\pi$ electron sextet potentially available for the formation of an aromatic shell: indeed these species are delocalized [2] and have been shown to be specially stabilized.[3] To account for this, two different situations have been discussed;[3a] (i) a 1,3-$\pi$ overlap occurs between the carbon atoms $\alpha$ and $\alpha'$ to the $SO_2$ without the involvement of the sulphonyl group (homosulphonyl aromaticity) and (ii) the sulphonyl group is involved in the stabilization and delocalization mechanism. If so, for symmetry considerations, the sulphonyl group would fall in the case I conjugation category described by Koch and Moffitt [4] for which it was predicted that the sulphur–oxygen and carbon–sulphur bonds would be appreciably affected. More information could be expected to come from i.r. spectral and *X*-ray studies of the sulphonyl group in the above species. Because of the inherent difficulties in studying anionic species, neutral structures in which the thiopyran *SS*-dioxide function could be expected to be anionic in character [(1a) ⟷ (1b) and (2a) ⟷ (2b)] were considered as structural probes for the thiopyran *SS*-dioxide anion. The situation is comparable to the case of cyclopentadienyl anion, for which sesquifulvalene and its heterocyclic congeners (3) [5] are useful structural probes.

† *Present address:* Department of Chemistry, Northwestern University, Evanston, Illinois 60201, U.S.A.

[1] S. Bradamante and G. Pagani, *J.C.S. Perkin I*, 1973, 163.

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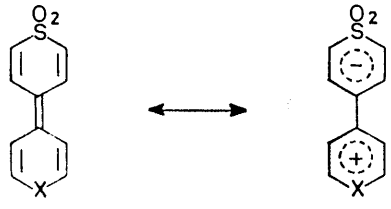
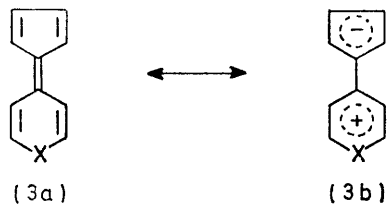
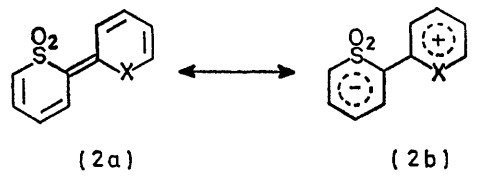
[5] (*a*) D. Lloyd, 'Carbocyclic Non-benzenoid Aromatic Compounds,' Elsevier, London, 1966; (*b*) H. Prinzbach, D. Seip, and G. Englerts, *Annalen*, 1966, **698**, 57; (*c*) F. Kröhnke, K. Ellegast, and E. Bertran, *ibid.*, 1956, **600**, 176; (*d*) J. A. Berson, E. M. Elveth, jun., and Z. Hamlet, *J. Amer. Chem. Soc.*, 1965, **87**, 2887; (*e*) J. A. Berson, E. M. Elveth, jun., and S. L. Manatt, *ibid.*, p. 2901; (*f*) E. M. Elveth, jun., J. A. Berson, and L. S. Manatt, *ibid.*, p. 2908; (*g*) G. V. Boyd, A. W. Ellis, and M. D. Harms, *J. Chem. Soc.* (*C*), 1970, 800; (*h*) G. V. Boyd and L. M. Jackman, *J. Chem. Soc.*, 1963, 548; (*i*) G. V. Boyd and N. Singer, *J. Chem. Soc.* (*B*), 1966, 1017; (*j*) J. H. Crabtree and D. J. Bertelli, *J. Amer. Chem. Soc.*, 1967, **89**, 5384; (*k*) A. Lüttringhaus, E. Futterer, and H. Prinzbach, *Tetrahedron Letters*, 1963, 1209.

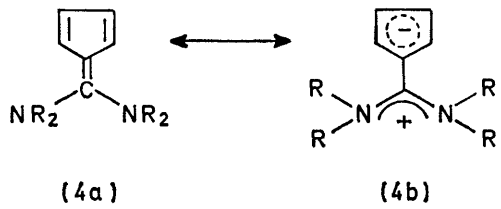
Spectroscopic properties,[5e,5j,6] molecular parameters,[7] and reactivity [5d,g] in heterocyclic congeners of sesquifulvalene (3), in diaminofulvenes (4) and related systems [8] have been interpreted on the basis of the mesomerism [(3a) ⟷ (3b), (4a) ⟷ (4b)].

In an attempt to discriminate between the two different electronic situations envisaged above for the thiopyran 1,1-dioxide anion and in order to assess experimentally the theoretical predictions on case I conjugation, we describe in this paper the syntheses of four compounds related to structures (1) and (2) (X = NMe).




Evidence is presented for their dipolar character which supports the hypothesis that these compounds may be used as neutral structural probes for inferring the role of the sulphonyl group in the thiopyran SS-dioxide anion. I.r. data obtained for the sulphonyl function of these compounds are correlated with those for other sulphones and are interpreted as evidence for the involvement of this group in the conjugation within the thiopyranyl frame. In the accompanying paper [9] the crystal and molecular structures of two compounds related to structures (1) and (2) are described and the results are compared with those of the present investigation.

## EXPERIMENTAL

I.r. spectra were recorded on Perkin-Elmer 621 or 625 instruments, $^1$H n.m.r. spectra on Varian A60-A or HA-100D instruments, and u.v. spectra on a Beckman DB-GT instrument.

*Condensation of Thiopyran* SS-*Dioxides* (5) *and* (6) *with* 2- *and* 4-*Halogeno*-N-*methylpyridinium Iodides*.—1,4-*Dihydro*-1-*methyl*-4-(3-*phenylthiopyran*-4-*ylidene*)*pyridine* SS-*dioxide* (7), 1,4-*dihydro*-1-*methyl*-4-(2-*methyl*-5-*phenylthiopyran*-4-*ylidene*)*pyridine* SS-*dioxide* (8), 1,2-*dihydro*-1-*methyl*-2-(5-*phenylthiopyran*-2-*ylidene*)*pyridine* SS-*dioxide* (9), *and* 1,2-*dihydro*-1-*methyl*-2-(6-*methyl*-3-*phenylthiopyran*-2-*ylidene*)*pyridine* SS-*dioxide* (10). Dry acetone (100 ml) was added, with stirring and under nitrogen, to an intimate mixture of the sulphone (5) or (6) (5 mmol), 4-bromo-*N*-methylpyridinium iodide [10] or 2-chloro-*N*-methylpyridinium iodide [11] (5 mmol), and finely powdered potassium carbonate (15 mmol). After 48 h at room temperature, the solution was filtered and evaporated to dryness and the residue was taken up with hydrochloric acid (10—12%; 20—30 ml), filtered, and cautiously neutralized with sodium hydrogen carbonate. The solid was collected, chromatographed through a short column [alumina (15 g); chloroform–ethyl acetate (9 : 1)], and crystallized. The anhydro-base (7) (200 mg) was dissolved in 40% fluoroboric acid (2 ml): upon addition of a few drops of water the *pyridinium fluoroborate* (11) slowly crystallized (30%).

*Reaction with Electrophiles*.—(a) 1,4-*Dihydro*-1-*methyl*-4-(2,6-*dibromo*-3-*phenylthiopyran*-4-*ylidene*)*pyridine* SS-*dioxide* (15). Bromine (470 mg) in chloroform (2 ml) was added to a mixture of the anhydro-base (7) (400 mg) and triethylamine (424 mg) in chloroform (45 ml). After 2 h at room temperature the precipitate was removed by filtration, immediately washed with methanol, and then with hot methanol. The product decomposed readily in solution, particularly in dimethyl sulphoxide; thus the $^1$H n.m.r. spectrum could not be recorded.

(b) 1,4-*Dihydro*-1-*methyl*-4-(2,6-*diformyl*-3-*phenylthiopyran*-4-*ylidene*)*pyridine* SS-*dioxide* (16). Phosphoryl chloride (120 mg) was added to dimethylformamide (1 ml) and after 2 h the anhydro-base (7) (106 mg) was added to the solution. After 3 days this was diluted with a saturated solution of sodium hydrogen carbonate (5 ml); the precipitate (83 mg) slowly separates: crystallization gave pure (16).

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[8] (*a*) E. D. Bergmann, *Chem. Rev.*, 1968, **68**, 41; (*b*) K. Hartke and G. Salamon, *Chem. Ber.*, 1970, **103**, 133; (*c*) K. Hafner, K. H. Häfner, C. König, M. Krender, G. Ploss, G. Schultz, E. Sturm, and K. H. Vopel, *Angew. Chem. Internat. Ed.*, 1963, **2**, 123.

[9] G. D. Andreetti, G. Bocelli, and P. Sgarabotto, following paper.

[10] J. A. Berson, E. M. Elveth, jun., and Z. Hamlet, *J. Amer. Chem. Soc.*, 1960, **82**, 3793.

[11] H. L. Bradlow and C. A. Vanderwerf, *J. Org. Chem.*, 1951, **16**, 1143.

TABLE 1

Physical and analytical data

| Compound | M.p. (°C) | Yield (%) | Found (%) C | H | N | Formula | Calculated (%) C | H | N |
|---|---|---|---|---|---|---|---|---|---|
| (7) | 214 [a] | 50 | 68·4 | 5·1 | 4·5 | $C_{17}H_{15}NO_2S$ | 68·6 | 5·1 | 4·7 |
| (8) | 231—232 [a] | 50 | 69·2 | 5·7 | 4·3 | $C_{18}H_{17}NO_2S$ | 69·4 | 5·5 | 4·5 |
| (9) | 199—200 [a] | 42 | 68·3 | 5·1 | 4·5 | $C_{17}H_{15}NO_2S$ | 68·6 | 5·1 | 4·7 |
| (10) | 209—210 [a] | 38 | 69·1 | 5·5 | 4·35 | $C_{18}H_{17}NO_2S$ | 69·4 | 5·5 | 4·5 |
| (11) | 241 (decomp.) [b] | 30 | 53·0 | 4·2 | 3·6 | $C_{17}H_{16}BF_4NO_2S$ | 53·0 | 4·2 | 3·4 |
| (15) | 160 (decomp.) [c] | 70 | 45·1 | 3·0 | 3·1 | $C_{17}H_{13}Br_2NO_2S$ | 44·8 | 2·9 | 3·1 |
| (16) | 320 [d] | 66 | 64·0 | 4·1 | 4·2 | $C_{19}H_{15}NO_4S$ | 64·6 | 4·3 | 4·0 |
| (17) | 175 (sint) [e] 226 (decomp.) | 39 | 56·6 | 4·95 | 5·05 | $C_{26}H_{25}ClN_2O_7S,H_2O$ | 57·1 | 5·0 | 5·1 |
| (18) | 204 (decomp.) [e] | 30 | 59·2 | 5·0 | 5·2 | $C_{26}H_{25}BF_4N_2O_2S,0·5H_2O$ | 59·4 | 4·95 | 5·3 |

[a] From EtOH. [b] From 30% $HBF_4$. [c] From EtOH–acetone. [d] From dimethylformamide. [e] From water.

TABLE 2

$^1H$ N.m.r. data [a]

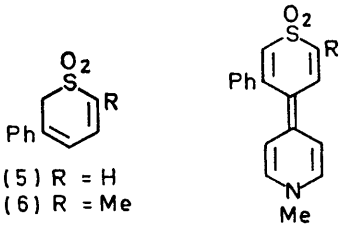
| Compd. | Solvent | 2′ | 3′ | 4′ | 5′ | 6′ | Pyridine | NMe | J/Hz |
|---|---|---|---|---|---|---|---|---|---|
| (7) | DMSO | 4·50 (d) | 2·70 (m, Ph) | | 2·60 (d) | 4·11 (dd) | 2·40—3·33 [b] | 6·32 (s) | $J_{2',6'}$ 3·75 $J_{5',6'}$ 10·0 |
| (8) | DMSO | 4·61 (s) | 2·75 (m, Ph) | | 2·75 [c] | 7·90 (s, Me) | 2·53—3·45 [b] | 6·40 (s) | $J_{CH.Me}$ 0·5 |
| (9) | DMSO | 3·83 (d) | 2·50 (m, Ph) | 4·13 (dd) | 3·07 (d) | | 1·80—3·00 [d] | 5·87 (s) | $J_{2',4'}$ 1·75 $J_{4',5'}$ 9·5 |
| (10) | DMSO | | 2·75 (m, Ph) | 4·16 (d) | 3·44 (dq) | 7·90 (d, Me) | 1·70—3·20 [d] | 6·05 (s) | $J_{4',5'}$ 7 $J_{5',Me}$ 1·25 |
| (11a) | | 5·47 (s) (30%) | | | | [c] | | 5·75 (s) (30%) | |
| (11b) | $CF_3CO_2H$ | [c] | 2·60—3·20 (m, Ph) | | [c] | 5·63 (d) (70%) | 1·60—2·40 [b] | 5·77 (s) (70%) | $J_{5',6'}$ 5·0 |
| (12) | $CF_3CO_2H$ | 5·48 (s) | 2·60—3·20 (m, Ph) | | 3·35 (m) | [e] | 1·60—2·40 [b] | 5·73 (s) | |
| (13) | $CF_3CO_2H$ | 5·27 (s) | 2·60 (m, Ph) | | 3·15 (d) | | 1·10—2·75 [d] | 5·53 (s) | |
| (14a) | | 5·35 (s) (70%) | | 3·50 (d) (70%) | 3·15 (d) (70%) | [e] | | | |
| (14b) | $CF_3CO_2H$ | | 2·65 (m, Ph) | 3·85 (d) (30%) | 3·45 (d) (30%) | 8·33 (d, Me) | 1·10—2·80 [d] | 5·85 (s) | $J_{CH.Me}$ 7·0, |
| (16) | DMSO | 0·45 (s, CHO) | 2·7 (m, Ph) | | 2·30 (s) | 1·02 (s, CHO) | 1·66—2·70 [d] | 5·97 (s) | |

[a] Chemical shifts are given in τ values (±0·02) relative to $Me_4Si$ as internal reference; d = doublet, dq = double quartet, m = multiplet, q = quartet, s = singlet. [b] AA′BB′ system. [c] Covered by aromatic peaks. [d] ABCD system. [e] Covered by solvent peak.

(c) 1-*Methyl*-2-*phenyl*-4-(2-p-*dimethylaminobenzylidene*-1,1-*dioxo*-5-*phenylthiopyran*-4-*yl*)*pyridinium perchlorate* (17) *or fluoroborate* (18). *p*-Dimethylaminobenzaldehyde hydrochloride (130 mg) in methanol (5 ml) was added to the anhydro-base (7) (200 mg) in methanol (15 ml) with stirring. After 2 days the solvent was removed and the residue was dissolved in water (20 ml). Upon treatment of this solution (10 ml) with water (5 ml) containing lithium perchlorate (800 mg) the *perchlorate* (17) was obtained. The corresponding *fluoroborate* (18) was prepared analogously by treatment with potassium fluoroborate (300 mg) in water (5 ml).

RESULTS AND DISCUSSION

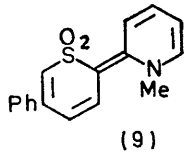
*Structure of Thiopyranylidenedihydropyridine* SS-*dioxides*.—Derivatives of thiopyran *SS*-dioxide and their benzologues behave as nucleophiles toward methyl iodide under mild basic conditions.[1] Analogously, the synthesis of thiopyranylidenedihydropyridines (7)—(10) was accomplished by treating the thiopyran derivatives (5) and (6) with 4-bromo-*N*-methylpyridinium iodide and with 2-chloro-*N*-methylpyridinium iodide, respectively, in the presence of potassium carbonate. Compounds (7) and (8) show similar spectroscopic properties [$^1H$ n.m.r. (Table 2), u.v. (Table 3), and i.r. spectra] offering evidence for condensation of the pyridine group at the same site of the thiopyran ring. Since structure (8) has been confirmed by *X*-ray analysis,[9] structure (7), for



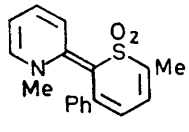

(5) R = H
(6) R = Me



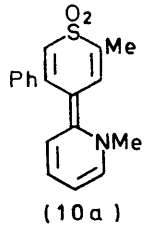

(7) R = H
(8) R = Me




(9)




(10)




(10a)

the product from (5) and 4-bromo-*N*-methylpyridinium iodide, is established by the above spectroscopic correlations. Structure (9) has been proved by *X*-ray analysis [9] and $^1$H n.m.r. parameters are consistent with it. Structure (10) was assigned to the product originating from (6) and 2-chloro-*N*-methylpyridinium iodide on the basis of an AB system due to the protons β and γ to the sulphonyl group in the heterocycle: the alternative structure (10a) was thus ruled out. It appears relevant that the thiopyran *SS*-dioxide anion shows greater reactivity at the γ-position toward 4-bromo-*N*-methylpyridinium iodide but greater reactivity at the α- or α′-position toward 2-chloro-*N*-methylpyridinium iodide. While it is difficult to account for this high regiospecificity, formation of (7)—(10) is in accord with a tridentate structure for thiopyran *SS*-dioxide anion derivatives.

*Dipolar Character of the Thiopyranylidenedihydropyridines.*—(a) $^1$H *N.m.r. evidence.* The protons in positions α, α′, and γ to the sulphonyl group in compounds (7)—(10) appear at unusually high field. This is analogous to the behaviour of the thiopyran *SS*-dioxide anion, and indicates that these protons are bonded to electron-rich trigonal carbon atoms.[12] This is consistent with the mesomerism indicated by the formulae (1a), (2a) ⟷ (1b), and (2b). The similarity of the $^1$H n.m.r. spectra of compounds (7)—(10) with that of the thiopyran *SS*-dioxide anion is not restricted to chemical shifts: the value of $J_{2',6'}$ in compound (7) is unusually high (3·75 Hz) and is analogous with the typical corresponding value of both thiopyran *SS*-dioxide anion [(unsubstituted, 4·43,[13] and 3-substituted 4·2 Hz [2a]) and benzo[*c*]thiopyran 2,2-dioxide anion, $J_{1,3}$ 4·15 Hz [2b]].* On the basis of the foregoing considerations it appears logical to assume that (i) the dipolar structures (1b), (2b) contribute to some extent to the ground state of compounds (7)—(10),† and that (ii) the thiopyran group in these compounds can therefore be considered an acceptable structural probe for the thiopyran *SS*-dioxide anion.

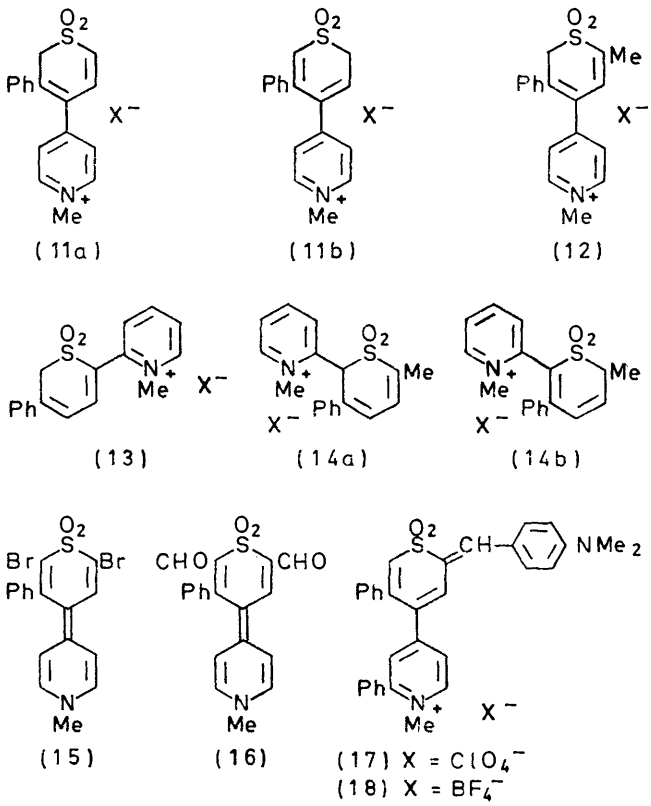
(*b*) *Reaction with electrophiles.* Thiopyranylidenedihydropyridine *SS*-dioxides (7)—(10) are basic compounds (anhydro-bases); with the simplest electrophile, a proton, they gave the corresponding *N*-methylthiopyranylpyridinium salts (11)—(14). The crystalline, analytically pure pyridinium fluoroborate (11) could be isolated by treating (7) with fluoroboric acid. Protonation is reversible since from the acidic solutions of the thiopyranylpyridinium salts the corresponding anhydro-bases (7)—(10) could be easily obtained by careful addition of sodium hydrogen carbonate. Upon acidification the intense orange or red-violet colour of the anhydro-bases was discharged allowing an easy monitoring of the reaction by u.v. spectroscopy (Table 3). $^1$H N.m.r. spectroscopy (Table 2) gave evidence for possible protonation at either of two different sites of the thiopyran ring. While protonation of anhydro-bases (8) and

TABLE 3

U.v. data

| Compound | Solvent | $\lambda_{max.}$/nm (log ε) | | | | | |
|---|---|---|---|---|---|---|---|
| (7) | MeOH | 457 (4·62) | | 333 (3·65) | 280 (3·46) | | 238 (4·22) |
| (8) | MeOH | 470 (4·61) | | 337 (3·72) | 285 (3·58) | | 240 (4·24) |
| (9) | MeOH [a] | 490 (4·25) | 380 (3·54) | *334* [b] | 306 (3·83) | 262 (3·99) | 245 (4·10) |
| (10) | MeOH | 483 (4·02) | | 341 (3·78) | *278* [b] | | 245 (4·12) |
| (11) | 4% $HClO_4$ (70%) in MeOH | | | 340 (3·38) | | 271 (4·13) | |
| (12) | 4% $HClO_4$ (70%) in MeOH | | | 340 (3·74) | | 271 (4·06) | 237 (4·14) |
| (13) | 4% $HClO_4$ (70%) in MeOH | | | 343 (4·19) | | 269 (3·87) | 245 (3·77) |
| (14) | 4% $HClO_4$ (70%) in MeOH | | | 310 (3·86) | | 275 (4·12) | |

[a] Unchanged in basic (0·004M-NaOH) solution. [b] Inflections.




* A discussion of $^4J$ values through heteroatoms or heteroatomic groups has recently appeared: [13] the most impressive values are for thiepin 1,1-dioxide, $J_{2,7}$ 2·3,[13] and pyrone, $J_{3,5}$ 2·7 Hz.[14]

† Unfortunately the low solubility of compounds (7)—(10) has so far prevented the measurement of their dipole moments.

[12] T. Schaeffer and W. G. Schneider, *Canad. J. Chem.*, 1963, **41**, 966; J. W. Burley and R. N. Young, *J.C.S. Perkin II*, 1972, 1006.

[13] M. P. Williamson, W. L. Mock, and S. M. Castellano, *J. Magnetic Resonance*, 1970, **2**, 50.

[14] E. W. Garbish, jun., *Chem. and Ind.*, 1964, 1715.

(9) occurred almost exclusively at the 6′-position giving the pyridinium salts (12) and (13) respectively, protonation of anhydro-bases (7) and (10) led to the isomeric mixtures (11a and b) and (14a and b). This behaviour is in line with previous findings: when a substituent is present at the 2-position of the thiopyran ring only the 6*H*-structures were detected [2a,15] while for 2-unsubstituted compounds both the 2*H*- and 6*H*-derivatives were formed.[16]

Since the electrophilic attack by a proton on anhydro-bases (7)—(10) is by far the fastest reaction in acidic media, electrophilic substitutions had to be carried out under neutral or basic conditions: this limited the number of electrophiles which could be considered. The anhydro-base (7) underwent bromination, Vilsmeier–Haack formylation, and condensation with *p*-dimethylaminobenzaldehyde hydrochloride. The products obtained gave correct analyses,* but the $^1$H n.m.r. spectrum could be recorded only for the formylation product, showing that the formyl groups entered the sulphur ring. Although so far no firm proof has been obtained for the site(s) of attack of the electrophiles on the anhydro-base (7), it is logical to assume that they attack sites which undergo protonation. Therefore the bromination, formylation, and condensation products are believed to have the structures (15), (16), and (17) and (18), respectively. Evidence has also been obtained for the occurrence of the azo coupling reaction between (7) and *p*-nitrobenzenediazonium fluoroborate though no satisfactory analytical figures could be obtained for the product isolated.

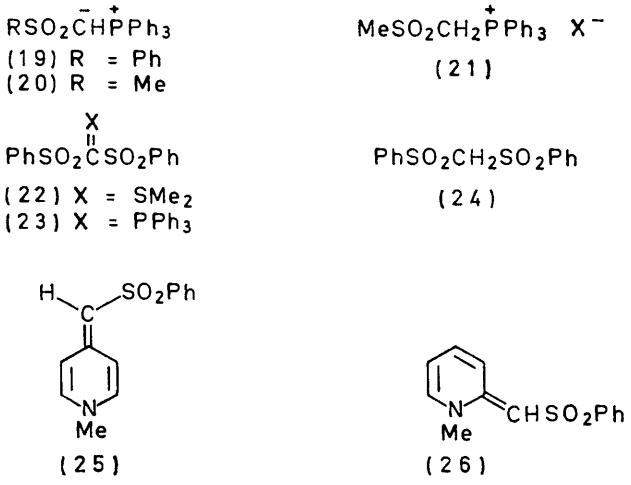
With the exception of the dibromo-compound (15), which could also arise from an addition–elimination, products (16)—(18) may be considered as arising from the attack of the pertinent electrophile on the anhydro-base (7). Protonation and electrophilic substitutions on the anhydro-base (7) are thus evidence that the thiopyran ring is the nucleophilic part of the molecule and that therefore there is some electron availability on this ring.

*I.r. Spectra and the Question of Sulphonyl Conjugation.*—A dramatic bathochromic shift for the asymmetric and symmetric stretching vibrations of the sulphonyl group was observed for the anhydro-bases (7)—(10) relative to the normal values [17] found for the thiopyran *SS*-dioxides (5) and (6) and for the fluoroborate salt (11) (Table 4). The expected [17] linear correlation of the asymmetric and symmetric vibrations of the sulphonyl group of the anhydro-bases (7)—(10) indicates that the assignments of the bands are correct. These bathochromic shifts are analogous to the shifts observed for a number of sulphonyl stabilized ylides (19),[18] (20),[19] (22), and (23) [20] relative to the normal values for the corresponding ' onium ' salts [*e.g.* (21)] or neutral precursors [*e.g.* (24)]. Sulphonyl stretching displacements, both in the alkanesulphonate salts [21] and in the sulphonyl stabilized ylides have been accounted for by the stabilizing delocalization of the negative charge [19,20] and the consequent direct participation of the sulphonyl group.

TABLE 4

Sulphonyl stretching vibrations

| Compound | $\nu_{as}(SO_2)$/cm$^{-1}$ | $\nu_{sym}(SO_2)$/cm$^{-1}$ |
|---|---|---|
| (5) | 1308 | 1123 |
| (6) | 1300 | 1125 |
| (7) | 1205 | 1088 |
| (8) | 1202 | 1085 |
| (9) | 1237 | 1084 |
| (10) | 1234 | 1098 |
| (11) | 1300 | 1120 |
| (19) | 1267 | 1128 |
| (20) | 1252 | 1112 |
| (21) | 1320 | 1148 |
| (22) | 1302 | 1143 |
| | 1276 | 1131 |
| (23) | 1304 | 1140 |
| | 1280 | 1130 |
| (24) | 1329 | 1160 |
| | 1317 | |
| (25), (26) | 1295 | 1125 |
| | 1285 | 1130 |
| $RSO_2O^-$ | 1190 | 1050 |




Indeed, since the stretching vibrations for the anhydro-bases (7)—(10) are even more displaced than those of the ylides cited and approach the limiting value of the alkanesulphonate salts in which complete delocalization of the negative charge to the oxygen atoms occurs, it seems safe to conclude that the sulphonyl group in the anhydro-

* Considerable difficulties have also been encountered in the isolation of pure compounds from the reaction of aza-analogues of sesquifulvalene with electrophiles.[5d,g]

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bases (7)—(10) is somehow involved in the conjugation within the thiopyran *SS*-dioxide ring.

The strong bathochromic shifts of the sulphonyl stretching vibrations found for anhydro-bases (7)—(10) do not find analogy in the correspondingly small displacements observed for the formally related compounds (25) and (26).[22] Since the pyridine functions are identical in both series of compounds (7)—(10) and (25) and (26), the contrast may be accounted for by considering that through delocalization compounds (7)—(10) can attain stabilization both in the pyridine and in the thiopyran *SS*-dioxide rings. Apparently delocalization and stabilization of the thiopyran *SS*-dioxide anion are necessary to force the sulphonyl group into conjugation.

If one accepts that anhydro-bases (7)—(10) are reasonable models for the thiopyran *SS*-dioxide anion, then the sulphonyl group should participate in conjugation with this ring. We believe that both series of comparisons and correlations discussed above represent support for the hypothesis according to which the most favourable conditions for case I conjugation in sulphones are met when the sulphonyl group is incorporated into an unsaturated, electron-rich, cyclic, potentially aromatic frame.

Experimental assistance by S. Bradamante, G. Gaviraghi, and L. Valtorta is gratefully acknowledged. I am also indebted to Professor F. G. Bordwell for comments and to Dr. W. Matthews for help in correcting the manuscript.

[2/2198 *Received*, 20*th September*, 1972]

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