Cyclic Sulphones. Part XVIII.[1] Probes for Conjugation of the Sulphonyl Group: Thiopyrano[3,2-*b*]quinoline 1,1-Dioxides

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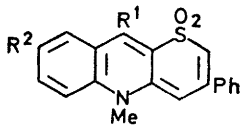
Three *N*-methyl-3-phenyl-5*H*-thiopyrano[3.2-*b*]quinoline 1,1-dioxides have been synthesized; the parent compound underwent bromination, nitration, azo-coupling, and Vilsmeier reaction in the thiopyran residue. Moderate bathochromic displacements of the sulphonyl stretching vibrations relative to normal values were observed. The results are discussed in the light of a preliminary *X*-ray report: it is concluded that in the title compounds 'one-side' conjugation of the sulphonyl group occurs without involvement of the sulphur–oxygen bonds. Structural analogies conferred on similar cyclic unsaturated frameworks by incorporation of sulphonyl and carbonyl groups are also discussed.

In continuation of the investigation reported in the preceding paper, we describe here the synthesis and properties of compounds (1)—(3). In view of the results obtained previously we expected to discover (i) the occurrence of electrophilic attack on the thiopyran ring, already shown to be electron-rich; (ii) a modest, if any, involvement of the sulphonyl group in 'through' conjugation; (iii) involvement of the sulphonyl group in



(1) $R^1 = R^2 = H$
(2) $R^1 = Me, R^2 = H$
(3) $R^1 = Ph, R^2 = Cl$

one-side' conjugation; and (iv) a similarity with carbonyl analogues of the 1-methyl-5-quinolone type. The results fulfilled our expectations: monosubstitution products were obtained by the action of a number of electrophiles on compound (1) and interpretation of sulphonyl stretching vibrations in the light of preliminary *X*-ray results confirmed points (ii) and (iii). In the light of a literature report on a 5-quinolone the structural analogies conferred on similar cyclic carbon frameworks by incorporation of sulphonyl and carbonyl groups have been assessed.

EXPERIMENTAL

I.r. spectra were recorded as previously.[1] Solutions were dried over Na_2SO_4.

3-Phenyl-2H-thiopyrano[3,2-b]quinoline 1,1-Dioxides (5)—(7).—An intimate equimolar mixture of 5-phenyl-2*H*-thiopyran-3(6*H*)-one 1,1-dioxide (4) [2] and *o*-aminobenzaldehyde, *o*-aminoacetophenone, or 2-amino-5-chlorobenzophenone (and a trace of toluene-*p*-sulphonic acid in the last two cases) was heated at 180° for 15—30 min. The residue was treated with methanol and the *solid* was collected, washed with aqueous 5% sodium hydroxide, and crystallized (yields 70—92%).

N-Methyl-3-phenyl-2H-thiopyrano[3,2-b]quinolinium 1,1-Dioxide Salts (8)—(10).—The thiopyrano[3,2-*b*]quinoline 1,1-dioxide (5), (6), or (7) (2—3 g) was treated with dimethyl sulphate (20 ml) at 110—120° for 1 h. After cooling, diethyl ether was added to complete precipitation of the methosulphate, which was collected, washed with ether, and dried in a desiccator. The crude methosulphates (8)—(10) (X = $O{\cdot}SO_2{\cdot}OMe$) were generally used for preparing com-

[1] Part XVII, G. Pagani, preceding paper.
[2] G. Pagani, *Gazzetta*, 1967, **97**, 1518.

pounds (1)—(3), respectively, without further purification. *5,10-Dimethyl-3-phenyl-2H-thiopyrano*[3,2-b]*quinolinium chloride dihydrate* [(9; X = Cl), $2H_2O$] was prepared by adding small samples of the methosulphate (9; X = $O{\cdot}SO_2{\cdot}OMe$) to hot 7% hydrochloric acid; the solid was collected and dried ($CaCl_2$). The same chloride dihydrate was obtained by analogous treatment of the anhydro-base (2). *5-Methyl-3-phenyl-2H-thiopyrano*[3,2-b]*quinolinium 1,1-dioxide fluoroborate* (8; X = BF_4) was prepared by adding the anhydro-base (1) (0·2 g) to 40% fluoroboric acid (5 ml) and boiling the solution for 2 min; the solid was collected, dried, and crystallized. *8-Chloro-5-methyl-3,10-diphenyl-2H-thiopyrano*[3,2-b]*quinolinium 1,1-dioxide fluoroborate* (10; X = BF_4) was analogously prepared from (3).

N-Methyl-3-phenylthiopyrano[3,2-b]*quinoline 1,1-Dioxides* (1)—(3).—The crude methosulphates (8)—(10) (X = $O{\cdot}SO_2{\cdot}OMe$) were treated with boiling 10% potassium carbonate solution; the purple *precipitate* was collected, dried, and crystallized [yields 60—70% from (5)—(7)].

Reactions with Electrophiles.—(a) *Bromination.* A solution of bromine (1·4 g) in chloroform (10 ml) was slowly added to a stirred solution of compound (1) (1·2 g) in the same solvent (50 ml). After 1 h the solvent was removed and the residue was treated with warm (80°) saturated sodium hydrogen carbonate solution; the solid was collected, dried, and chromatographed [Al_2O_3 (150 g); CH_2Cl_2]. Fractions containing the monobromo-derivative (11) and some starting material (1) were chromatographed on silica gel (40 g; CH_2Cl_2). Fractions showing a single spot on t.l.c. gave *2-bromo-5-methyl-3-phenyl-5H-thiopyrano*[3,2-b]*quinoline 1,1-dioxide* (11) (0·3 g), which was thoroughly washed with methanol and dried. Attempted crystallization led to decomposition.

(b) *Nitration.* Tetranitromethane in ethanol (0·5M; 4 ml) was added to a solution of (1) (0·5 g) in pyridine (5 ml). After 1 h the solid was collected, dried, and chromatographed [Al_2O_3 (40 g); CH_2Cl_2]. The red fraction (one spot on t.l.c.) gave a residue which upon crystallization from dimethylformamide afforded *5-methyl-2-nitro-3-phenyl-5H-thiopyrano*[3,2-b]*quinoline 1,1-dioxide* (12).

(c) *Azo-coupling.* A solution of *p*-nitrobenzenediazonium fluoroborate (0·390 g) in water (200 ml) at 0 °C was slowly added to a stirred cold solution of (1) (0·520 g) in acetone–water (1 : 1; 2 l). After 30 min, sodium chloride (500 g) was added; the solvent was removed from the organic layer and the residue was dissolved in chloroform. The solution was filtered and chromatographed [SiO_2 (50 g); $CHCl_3$–AcOEt, 90 : 10). Blue fractions gave a residue which upon crystallization from chloroform afforded *5-methyl-2-p-nitrophenylazo-3-phenyl-5H-thiopyrano*[3,2-b]*quinoline 1,1-dioxide* (13) (0·2 g).

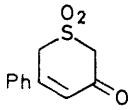
(d) *Vilsmeier reaction.* Phosphoric trichloride (1·15 g) was added to dimethylformamide (10 ml) and the solution was set aside for 1 h; the quinoline (1) (1·0 g) was then added in small portions with stirring. After 10 min the solution was treated with an excess of fluoroboric acid (40%). The precipitate was collected and crystallized to give *2-dimethylaminomethylene-5-methyl-3-phenyl-2H-thiopyrano*[3,2-b]*quinolinium 1,1-dioxide fluoroborate* (15). Treatment of (15) (0·29 g) with 10% sodium hydroxide (10 ml) at reflux for 10 min gave a solid (0·18 g) which, upon crystallization from dimethylformamide, afforded *2-formyl-5-methyl-3-phenyl-5H-thiopyrano*[3,2-b]*quinoline 1,1-dioxide* (14).

TABLE 1

Physical and analytical data

Compound	M.p. (°C)	Solvent	Found (%) C	H	N	Formula	Required (%) C	H	N
(1)	236 (decomp.)	PhMe	71·25	4·7	4·3	$C_{19}H_{15}NO_2S$	71·0	4·7	4·35
(2)	227	PhMe	71·5	4·9	4·0	$C_{20}H_{17}NO_2S$	71·6	5·1	4·2
(3)	265 [a]	PhMe	69·9	4·1	3·0	$C_{25}H_{18}ClNO_2S$	69·5	4·2	3·2
(5)	202	AcOH	70·7	4·2	4·5	$C_{18}H_{13}NO_2S$	70·3	4·3	4·55
(6)	237	AcOH	71·0	4·35	4·2	$C_{19}H_{15}NO_2S$	71·0	4·7	4·35
(7)	250	AcOH	68·9	3·95	3·2	$C_{24}H_{16}ClNO_2S$	69·0	3·85	3·35
(8; X = BF_4)	248	AcOH	55·7	3·6	3·4	$C_{19}H_{16}BF_4NO_2S$	55·8	3·9	3·4
(9; X = Cl)	205 (decomp.)	7% HCl	59·1	5·2	3·6	$C_{20}H_{18}NO_2S,2H_2O$	58·9	5·4	3·4
(10; X = BF_4)	266	AcOH	57·4	3·3	2·3	$C_{25}H_{19}BClF_4NO_2S$	57·7	3·7	2·7
(11)	>315		56·6	3·1	3·5	$C_{19}H_{14}BrNO_2S$	57·0	3·5	3·5
(12)	254	$Me_2N{\cdot}CHO$	62·2	3·9	7·5	$C_{19}H_{14}N_2O_4S$	62·3	3·85	7·65
(13)	250	$CHCl_3$	63·5	3·65	11·6	$C_{25}H_{18}N_4O_4S$	63·8	3·85	11·9
(14)	281 (decomp.)	$Me_2N{\cdot}CHO$	68·5	4·1	3·8	$C_{20}H_{15}NO_3S$	68·75	4·3	4·0
(15)	280 (decomp.)	AcOH	55·0	4·7	5·6	$C_{22}H_{21}BF_4N_2O_2S,C_2H_4O_2$	55·0	4·8	5·3

[a] After chromatography of the crude product (Al_2O_3: product, 20 : 1; methylene chloride as eluant) and crystallization.



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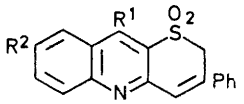

(5) $R^1 = R^2 = H$
(6) $R^1 = Me, R^2 = H$
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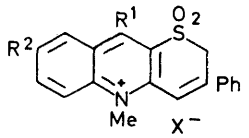
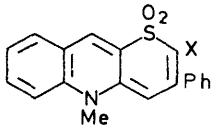
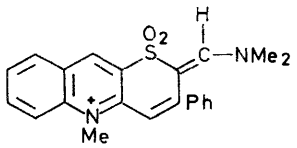


(8) $R^1 = R^2 = H$
(9) $R^1 = Me, R^2 = H$
(10) $R^1 = Ph, R^2 = Cl$



(11) X = Br
(12) X = NO_2
(13) X = $N{=}N{\cdot}C_6H_4{\cdot}NO_2{-}p$
(14) X = CHO



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RESULTS

Synthesis and Reactions with Electrophiles of Thiopyrano[3,2-b]*quinoline 1,1-Dioxides* (1)—(3).—Condensations of 5-phenyl-2*H*-thiopyran-3(6*H*)-one 1,1-dioxide

(4) with *o*-aminobenzaldehyde, *o*-aminoacetophenone, and 2-amino-5-chlorobenzophenone gave the quinoline derivatives (5)—(7), respectively. These quinolines could be *N*-methylated with dimethyl sulphate, giving the crude quinolinium methosulphates (8)—(10) (X = $O{\cdot}SO_2{\cdot}OMe$); the salts were characterized as either fluoroborates or chlorides. The quinolinium salts (8)—(10) were transformed into the corresponding purple anhydro-bases (1)—(3) by a mild base such as potassium carbonate; the reaction is reversible since strong acids protonate the anhydro-bases to give the starting quinolinium salts [see ^{1}H n.m.r. (Table 2) and u.v. and visible spectra (Table 3)]. The anhydro-bases (1)—(3) are sparingly soluble in common solvents; the quinolinium halides and fluoroborates (8)—(10) (X = Cl, Br, or BF_4) are insoluble.

The n.m.r. signal due to the 9-proton in compound (3) is further upfield than that in its precursor (7); this must be due to the diamagnetic effect of the 10-phenyl group. Molecular models show that whereas in compound (7) puckering of ring A can accommodate a quasi-coplanar arrangement of the 10-phenyl group and the quinoline residue, flattening of ring A in compound (3) prevents such a disposition and induces twisting of the phenyl group (Figure 1).

Chemical shifts of the 2- and 4-protons of compounds (1)—(3) are analogous to those found for the thiopyrano-[3,2-*b*]pyridine *SS*-dioxide (16); it can be similarly argued that the thiopyran ring in compounds (1)—(3) is also electron-rich. The higher field resonance is assigned to the 4-proton on the basis of the following considerations: (i) the analogous assignment for the

TABLE 2

^{1}H N.m.r. spectra (τ values)

Compound	Solvent	Aromatic	2-H	4-H	10-H	NMe	*J*/Hz
(1)	$(CD_3)_2SO$	1·80—2·90	3·55 (d)	4·18 (q)	1·30 (d)	6·22 (s)	$J_{2,4}$ *ca.* 1
	$(CF_3CO_2H$ [a]	1·70—2·70	5·31 (s)	*b*	0·70 (s)	5·52 (s)	
(2)	$(CD_3)_2SO$	2·00—2·80	3·63 (d)	4·30 (d)	6·98 (Me)	6·28 (s)	$J_{2,4}$ *ca.* 1
(3)	$(CD_3)_2SO$	2·20—2·70 [c]	3·68br (s)	4·12br (s)		6·22 (s)	
(5)	$(CD_3)_2SO$	1·70—2·70	5·04br (s)	*b*	0·95br (s)		
	C_5D_5N	1·70—2·70	4·98 (d)	*b*	1·04 (s)		$J_{2,4}$ *ca.* 1
(6)	$(CD_3)_2SO$	1·60—2·65	5·06 (d)	*b*	6·89 (s) (Me)		$J_{2,4}$ *ca.* 1
(7)	$(CD_3)_2SO$	1·80—2·70	5·15 (d)	*b*			$J_{2,4}$ *ca.* 1
(11)	$(CD_3)_2SO$	2·00—2·60		4·41br (s)	1·20br (s)	6·33 (s)	
(12)	$(CD_3)_2SO$	1·70—3·00		3·84br (s)	0·55br (s)	5·82 (s)	
(13)	$(CD_3)_2SO$	1·68—3·20		3·78br (s)	0·86br (s)	5·92 (s)	
(14)	$(CD_3)_2SO$ [d]	1·65—2·60		4·02 (d)	0·82 (d)	5·93 (s)	$J_{4,10}$ *ca.* 1·2
(15)	$(CD_3)_2SO$ [e]	1·39—2·50		2·64br (s)	0·42br (s)	5·40 (s)	

[a] $MeCO_2H$ was added as internal standard; Me at τ 8·00. [b] Covered by aromatic signals. [c] H-9 at τ 3·22 (m). [d] HC=O at τ 0·92 (s). [e] =CH·N at τ 1·99; NMe_2 at τ 7·62 and 8·12.

TABLE 3

U.v. and visible spectra

Compound	Solvent	$\lambda_{max.}$/nm [a] (log ε)								
(1)	MeOH	524 (3·88)		*344*		321 (4·25)	292 (4·15)	274 (4·27)		234 (4·19)
	MeOH–2N-HCl (20 : 80)		396 (4·59)			319 (4·12)		269 (3·92)		
(2)	MeCN	525 (3·86)		*365*	350 (4·02)	316 (4·17)	292 (4·25)	277 (4·33)	*268*	236 (4·43)
	MeCN–2N-HCl (20 : 80)		390 (4·44)			315 (4·17)		264 (4·45)		
(5)	MeOH			*346*		322 (4·37)	295 (4·42)	260 (4·28)	*240*	231 (4·37)
	MeOH, 0·452M in MeONa	535 (3·26)	400 (3·64)			*318*	300 (4·40)	260 (4·32)		236 (4·42)
(6)	MeOH					325 (4·40)	298 (4·47)	264 (4·30)	*242*	238 (4·39)
(7)	MeOH					328 (4·36)	307 (4·40)	*260*	*246*	239 (4·40)
(11)	MeOH	535 (3·81)		354 (4·05)		315 (4·11)	292 (4·10)	282 (4·10)		234 (4·39)
	MeOH–2N-HCl (60 : 40)		402 (4·40)			328 (3·99)		276 (4·29)		
(12)	MeOH–$Me_2N{\cdot}CHO$ (96 : 4)	530 (4·40)	408 (3·73)	345 (4·08)				274 (4·02)	255 (4·40)	
(13)	MeCN	610 (4·61)	480 (4·24)			*320*	292 (4·23)	261 (4·41)		235 (4·43)
(14)	MeCN	521 (4·29)	385 (4·20)			325 (4·15)		*273*	245 (4·55)	
	MeCN–2N-HCl (60 : 40)		402 (4·35)			322 (4·20)		270 (4·49)	*260*	
(15)	MeOH	504 (4·31)	*380*	353 (4·46)		314 (4·04)		255 (4·39)		236 (4·35)

[a] Inflections in italics.

strictly related substrate (16) has already been proved; [1] and (ii) the high-field proton shows long-range coupling with H-10. Although a five-bond coupling between H-2

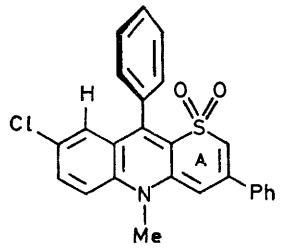
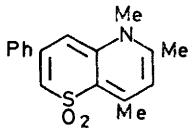


FIGURE 1

and H-10 cannot be excluded, coupling between H-4 and H-10 seems more reasonable and is not unprecedented.[3] This interpretation is supported by experiments (see later) which show that deuteriation occurs at C-2: the low-field proton signal disappears and the high-field one maintains its coupling with H-10.

Electrophiles attack the thiopyran ring of the anhydro-base (1). The number of possible electrophiles is limited since the reactions must be carried out in non-acidic media; otherwise the anhydro-base suffers preferential attack by the hydronium ion. Besides protonation the anhydro-base (1) underwent bromination, nitration, azo-coupling, and the Vilsmeier reaction. Monosubstitution was by far the major pathway of the reactions, and since one of the two protons of the thiopyran ring disappears upon substitution (n.m.r.), the electrophiles must enter the thiopyran ring. The site of attack is not rigorously proved. We had hoped to use the long-range coupling of H-4 with H-10 to elucidate this, but in all cases but one the coupling was poorly resolved, owing to the very low solubilities of the substitution products. However, on the basis of the following facts and arguments we strongly favour structures (11)—(15) for the substitution products (*i.e.* electrophilic attack takes place at C-2). (i) Strong acids protonate compound (1) at C-2: evidence for this is offered by the similarity of the ^1H n.m.r. spectrum of (1) in trifluoroacetic acid to that of the precursor (5). There is other circumstantial evidence: thiopyran 1,1-dioxide anions carrying a 2,3-fused aromatic residue {*e.g.* benzo[*b*]thiopyran 1,1-dioxide anion [4] and thiopyrano[3,2-*b*]pyridine *SS*-dioxide anion (17) [1]} always undergo protonation and react with electrophiles [5] at a position α to the sulphonyl group. (ii) Compound (1) suffers instantaneous deuteriation when treated with $CD_3{\cdot}CO_2D$ in dimethyl sulphoxide: a slower deuteriation occurs upon treatment with D_2O in the same solvent. Since compound (1) is a very weak base, acetic acid cannot give a stable quinolinium acetate (8; X = AcO^-); no doubt, however, small amounts of this salt are reversibly formed and, if the acid is the source of deuterium, deuteriation occurs at the same position as protonation takes place, that is C-2. With D_2O, a far weaker acid than $CD_3{\cdot}CO_2D$, deuteriation requires a longer time. (iii) Compound (1) did not give the expected formyl derivative under Vilsmeier conditions but gave instead a dimethylaminomethylene quinolinium salt, isolated as the fluoroborate (15); the formyl derivative (14) could be obtained by alkaline hydrolysis of (15). Since in the formyl derivative (14) the thiopyran proton resonating at τ 4·02 is clearly coupled with H-10, substitution must have occurred at C-2. The chemical



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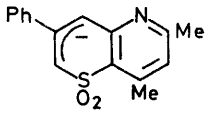

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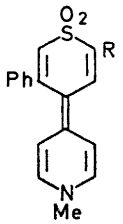

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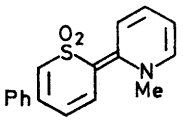


(19)

shift of H-4 in (14) is similar to that in the other substitution products (11)—(13): this is strong evidence for 2-substitution in the latter.

TABLE 4

Sulphonyl i.r. stretching vibrations [a]

Compd.	Phase	ν_{asym} (1350—1200 cm^{-1})	ν_{sym} (1160—1070 cm^{-1})
(1)	$CDCl_3$	*1274*m, 1210m	*1158*m, *1114*vs, 1076m
	Nujol	*1258*vs, 1212vs	*1160*m, *1109*vs, 1072s
(2)	$CDCl_3$	*1306*m, *1256*m, 1218w	*1128*m, *1111*s, 1086m
(3)	$CDCl_3$	*1318*vs, *1280*m, *1265*m	*1154*m, *1134*m, *1123*m, 1105m, 1074w
	Nujol	*1312*vs, *1306*vs, *1265*vs	*1139*s, *1130*m, *1103*vs, 1079m
(5)	$CDCl_3$	*1318*vs, 1236w	*1156*vs, 1137m, *1127*vs
(6)	$CDCl_3$	*1309*vs, 1222w	*1152*m, *1128*vs
	Nujol	*1296*vs, 1240w	1150w, *1122*vs
(7)	$CDCl_3$	*1320*vs, 1219vw	*1156*s, *1135*s, 1081m
	Nujol	*1310*vs	*1140*s, *1130*s, 1080w
(8; X = BF_4)	Nujol	*1326*vs, 1245m, 1220m	*1148*vs, *1135*vs
(10; X = BF_4)	Nujol	*1342*vs, 1226w	*1147*s, 1085m
(11)	Nujol	1321w, *1272*vs, 1222m	1159m, *1130*vs, 1102m
(14)	Nujol	1315w, *1269*s, 1209s	*1128*m, 1103w, 1077s
(15)	Nujol	*1346*s, 1325m, *1285*vs, 1257m, 1220m	*1134*vs

[a] Figures in italics refer to the most probable assignments.

Sulphonyl stretching vibrations (Table 4) for the anhydro-bases (1)—(3) are bathochromically displaced relative to the values observed for the precursors (5)—(7)

[3] J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 1964, 981; J. M. Cox, J. A. Elvidge, and D. E. H. Jones, *ibid.*, p. 1423.

[4] S. Bradamante, A. Mangia, and G. Pagani, *J. Chem. Soc.* (*B*), 1971, 545.

[5] S. Bradmante and G. Pagani, *J.C.S. Perkin I*, 1973, 163.

and the quinolinium salts (8) and (10). The extent of the shift is strictly analogous to that found for the thiopyrano[3,2-*b*]pyridine *SS*-dioxide (16) and its congeners, and though appreciable, is not as dramatic as in the case of the thiopyranylidenedihydropyridine *SS*-dioxides (18) and (19).

DISCUSSION

The Question of Sulphonyl Conjugation.—In order to assess the significance of the aforementioned electrophilic substitutions and to evaluate whether the variable sulphonyl stretching displacements are in better accord with mesomerism (1a) ◄► (1b) (' through ' conjugation at the sulphonyl group) or with the mesomerism (1a) ◄► (1c) or (1a) ◄► (1d) (' one-side ' conjugation at the sulphonyl group) we have compared preliminary *X*-ray

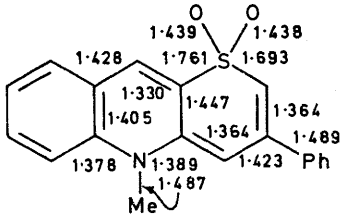


FIGURE 2

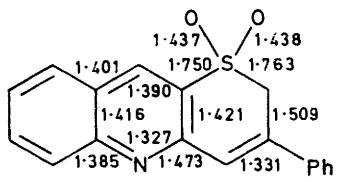


FIGURE 3

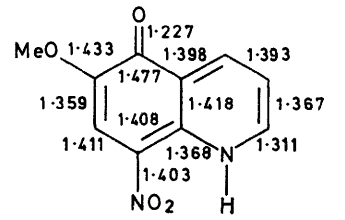


FIGURE 4

results * for the anhydro-base (1) and its precursor (5) (Figures 2 and 3, respectively) with those obtained for the thiopyranylidenedihydropyridine derivatives (18; R = Me) and (19);[7,8] also in view of the structural analogies which seem to be conferred on a cyclic unsaturated framework by incorporation of the sulphonyl and carbonyl functions,[1] it is instructive to compare some structural features of the anhydro-base (1) with those of the only 5-quinolone derivative for which an *X*-ray study has as yet been described, 6-methoxy-8-nitro-1*H*-5-quinolone (20) [9] (Figure 4).† The aforementioned results being kept in mind, inspection of Figures 2—4 gave rise to the following observations. (i) No variation in S–O bond length was observed on going from compound (5) to its anhydro-base (1); therefore the moderate bathochromic shift ($\Delta\nu_{as}$ *ca.* 40, $\Delta\nu_{sym}$ 0—25 cm^{-1}) of the sulphonyl stretching vibrations of (1) relative to (5) cannot be correlated with a variation in S–O bond order. This situation is different from that of the thiopyranylidene-1,4- or 1,2-dihydropyridines (18) and (19), where the remarkable bathochromic shift [7] ($\Delta\nu_{as}$ *ca.* 100, $\Delta\nu_{sym}$ *ca.* 40 cm^{-1}) is accompanied by a discernible elongation of the S–O bond [1·45 (av.) *versus* 1·44 Å (av) in the precursors].[8] (ii) While C(10a)–S does not vary appreciably, C(2)–S is markedly shorter in the anhydro-base (1) relative to the precursor (1·693 *versus* 1·763): this is unequivocal evidence for the occurrence of ' one-side ' conjugation and lack of ' through ' conjugation. The value of 1·693 Å for a C_{sp^2}–SO_2 bond is among the shortest, close to that observed in Ph_3P^{+}–CH^{-}–SO_2Ph.[10] The value of 1·72 Å for C_{sp^2}–SO_2 (average) in (18) and (19),[8] for which ' through ' conjugation was suggested, is intermediate between the value for ' one-side ' conjugation (1·69 Å) and C_{sp^2}–SO_2 standard values (1·75 Å).[11] It is tempting to argue that where ' through ' delocalization occurs the C_{sp^2}–SO_2 bond length is intermediate between that of a ' double bond ' corresponding to ' one-side ' conjugation and the standard ' single bond ' value: furthermore it seems relevant that where ' through ' delocalization is inferred from C_{sp^2}–SO_2 bond lengths, S–O bond lengths are also affected. (iii) Lack of ' through ' conjugation at the sulphonyl group in the anhydro-base (1), and hence the absence of a contribution from the mesomerism (1a) ◄► (1b), is not surprising since aromatization does not occur even in a structure such as (20) [mesomerism (20) ◄► (20a)] where the carbonyl group is far more likely than the sulphonyl group to be involved in aromatizing conjugation. In fact the C=O bond is a true double bond, only slightly elongated, and there is no appreciable conjugation between C-8 and C-9 (1·47 Å). Analogies between (16) and (21) in electronic distribution inferred from u.v. and visible spectra are confirmed from

* The detailed report and discussion of molecular parameters of compounds (1) and (5) is beyond the scope of the present investigation and will be published elsewhere.[6] I thank Professor Cavalca's group for performing these analyses and for allowing me to publish their results.

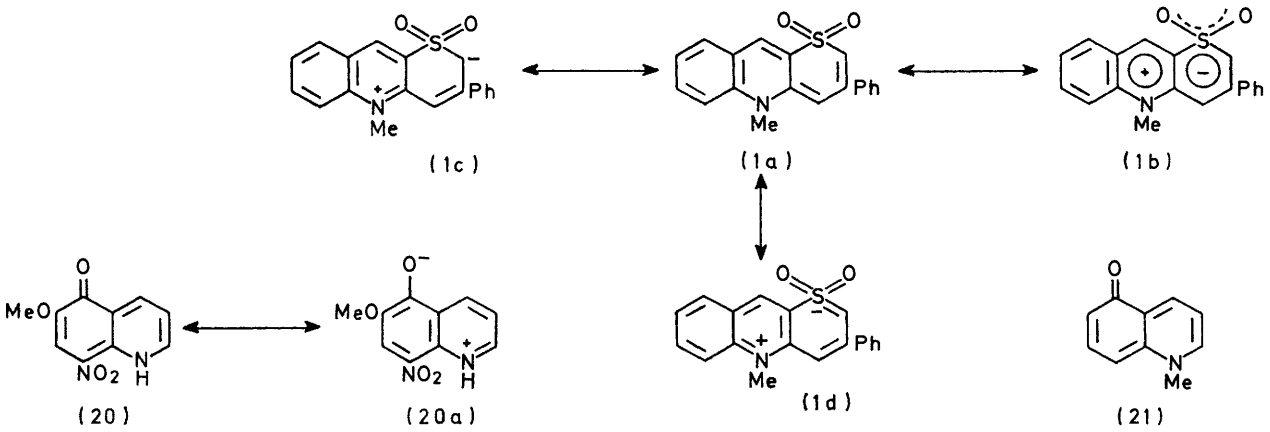
† A better comparison would have been between compound (16) and 1-methyl-1*H*-5-quinolone: unfortunately all attempts to grow suitable crystals of (16) failed. Since we are primarily concerned with the carbon–sulphur and sulphur–oxygen bond lengths and since sulphonyl stretching vibrations in compounds (1) and (16) are very similar, we assumed that the situation around the sulphur atom would be similar in the two cases. Compound (20) presents the disadvantage, as a keto-analogue of (1), of having a nitro-group in position (8), which withdraws electrons from the ring: we assume however that perturbation due to the nitro-group influences the situation at the carbonyl group only to a minor extent.

[6] G. D. Andreetti, G. Bocelli, and P. Sgarabotto, *Cryst. Struct. Comm.*, 1974, **3**, 309, 314.
[7] G. Pagani, *J.C.S. Perkin II*, 1973, 1184.
[8] G. D. Andreetti, G. Bocelli, and P. Sgarabotto, *J.C.S. Perkin II*, 1973, 1189.
[9] M. Sax and R. Desiderato, *Acta Cryst.*, 1969, **B25**, 362.
[10] A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, 1965, **87**, 5603.
[11] For 4,5-dihydrothiepin 1,1-dioxide C_{sp^2}–SO_2 is 1·753 Å: see H. L. Ammon, M. R. Smith, and E. Kelso, *Acta Cryst.*, 1972, **B28**, 246. For shorter C_{sp^2}–SO_2 bond lengths see thiopyran 1,1-dioxide (1·730 Å) [12a] and thiepin 1,1-dioxide (1·720 Å).[12b]
[12] (*a*) E. Boelema, G. J. Visser, and A. Vos, *Rec. Trav. chim.*, 1967, **86**, 1275; (*b*) H. L. Ammon, P. H. Watts, and J. M. Stewart, *Acta Cryst.*, 1970, **B26**, 1079.

comparison of molecular parameters of structures (1) and (2).

If the above considerations are accepted, we are led to the following conclusions:

(a) Anhydro-bases (1)—(3), once believed to be models for the thiopyran 1,1-dioxide anion by involvement of the mesomerism (1a) ⟷ (1b), are polyenic in character.



The thiopyran ring is electron-rich owing to the mesomerism (1a) ⟷ (1d): the criterion according to which success in performing electrophilic substitutions with retainment of structural type is evidence for aromatic behaviour is not valid in this case.

(b) Strong ' one-side ' conjugation at the sulphonyl sulphur atom with no involvement of the S–O bonds occurs in the anhydro-bases (1)—(3): this situation makes it possible for us to discriminate between ' one-side ' and ' through ' conjugation. Sulphonyl stretching vibrations are an insensitive measure of conjugation: only conspicuous bathochromic shifts relative to standard values can indicate an involvement of S–O bonds in conjugation.

(c) ' One-side ' conjugation of the sulphonyl group is possible when a strongly electron-donating residue is present: in this case structural effects due to incorporation of a sulphonyl group into a conjugated ring are analogous to those conferred by the incorporation of a carbonyl group.

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