

X-Ray Structural Evidence of Conjugation involving the Sulphonyl Group in Cyclic Sulphonyl Enamines

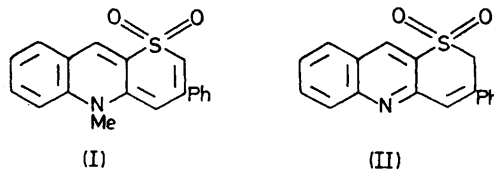
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Summary Comparison of X-ray structural data for 5-methyl-3-phenyl-5*H*-thiapyrano[3,2-*b*]quinoline SS-dioxide (I) and 3-phenyl-2*H*-thiapyrano[3,2-*b*]quinoline SS-dioxide (II) shows that extended π -delocalisation involving the sulphonyl group is present in the first compound.

Crystal data. Compound (I): $C_{19}H_{15}NO_2S$, $M = 309.2$, monoclinic, space group $P2_1/n$, $a = 11.29(1)$, $b = 9.31(1)$, $c = 14.55(1)$ Å, $\beta = 91.9(1)^\circ$, $U = 1528.5$ Å³, $Z = 4$, $D_c = 1.40$ g cm⁻³. 3019 intensities, of which 2517 were used in the crystal analysis, were measured diffractometrically.

THE probable involvement of sulphonyl conjugation in the special stabilisation of the thiapyranil anion has been studied recently.¹ Structural and i.r. data supported the involvement of the sulphonyl group in the delocalisation occurring within the π -framework. The problem has also been considered theoretically by Kock and Moffitt² and has been discussed in connection with thiopin SS-dioxide.³ In order to compare the bonding situation in cyclic sulphones in which conjugation of the SO₂ group is possible through an unsymmetrical system of π -orbitals (one-way conjugation) as, for example, in thiapyran SS-dioxide, the crystal and molecular structures of compounds (I) and (II)⁴ have been studied.



The structure was solved by direct methods and refined by block-diagonal least-squares down to a conventional R factor of 0.087 for the reflections which were considered observed and 0.095 for all reflections. Compound (II): $C_{18}H_{13}NO_2S$, $M = 295.2$, monoclinic, space group $P2_1/c$, $a = 12.41(1)$, $b = 6.16(1)$, $c = 20.03(1)$ Å, $\beta = 106.7(1)^\circ$, $U = 1466.6$ Å³, $D_c = 1.39$ g cm⁻³. 2883 intensities, of

which 1953 were used in the analysis, were measured as before. The final R was 0.053 for the reflections considered observed and 0.105 for all reflections.

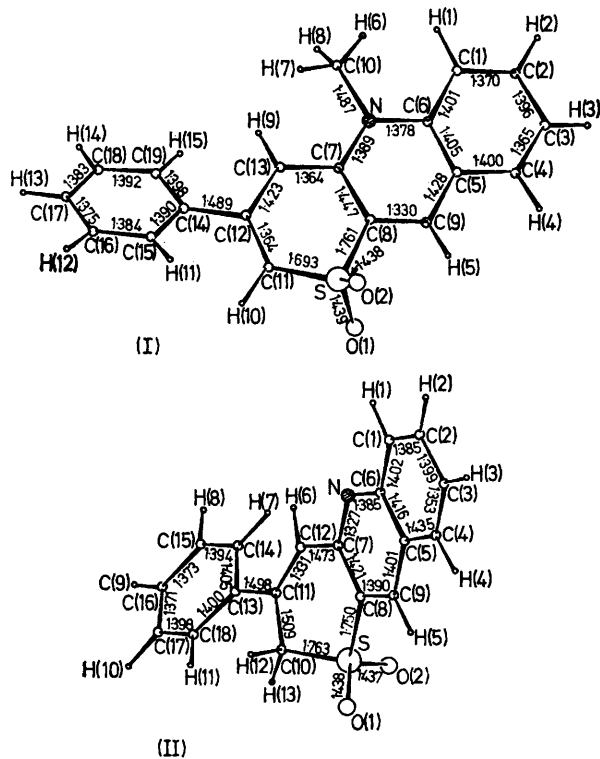


FIGURE. X-Ray structures of compounds (I) and (II). Bond distances are given in Å; standard deviations are 0.005 for bonds involving sulphur and 0.007 for the others.

As shown in the Figure, the bonding situation for the thiapyran ring is rather different in the two compounds. In compound (I) the diene system connecting the quinoline nitrogen atom and the sulphonyl group shows less bond

alternation than in compound (II), in which the diene system cannot interact with the sulphonyl group.

As a consequence of the possible conjugation in compound (I), S-C(11) [1.693(5) Å] is significantly shorter, this value being the shortest S-C distance observed in cyclic sulphones of known structure. On the other hand the S-C(8) distance, which connects the sulphonyl group to the quinoline system, is very similar in the two compounds and the values agree with the S-C(Ar) distances found in many aromatic sulphones. As already pointed out³ unsymmetric conjugation of the sulphonyl group seems to be favoured.

In compound (I) the thiapyran ring is not planar and the dihedral angle formed by the planes defined by C(8),S,C(11) and C(8),C(7),C(13),C(12),C(11) is 168.7° (136.0° in compound (II)). The S-O bonds are almost equal in the two compounds [1.439(4) and 1.438(4) Å] and are slightly shorter than those in thiapyranilidenedihydropyridine SS-dioxide.¹

Comparing the results obtained for other cyclic sulphones, for which there is strong evidence of conjugative interactions, it seems that the requirements of case I conjugation (π -orbitals normal to the C-S-C plane), in the Koch and Moffitt notation, are seldom observed. As a possible explanation, considering the well known ability of the sulphonyl group to stabilize adjacent carbanion centres,⁵ we assume that ionic structures with negative charge localized on the α -carbon atoms, significantly contribute to the overall electronic structure of the molecule. In compounds (I) and (II) and in thiapyranilidenedihydropyridine SS-dioxides,¹ the presence of the nitrogen atom of the enamino-group would favour this process. The α -carbon atomic orbitals would probably partially modify their hybridisation and the σ -bond network would be dominant in determining the non-planar conformations of this type of molecule, even in the presence of rather strong conjugative interactions.

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¹ G. D. Andreotti, G. Bocelli, and P. Sgarabotto, *J.C.S. Perkin II*, 1973, 1189; G. Pagani, *ibid.*, p. 1184.

² H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, 1951, **47**, 7.

³ H. L. Ammon, P. H. Watts, and J. M. Stewart, *Acta Cryst.*, 1970, **B26**, 1079.

⁴ G. Pagani, *J.C.S. Perkin I*, 1974, in the press.

⁵ D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 71.