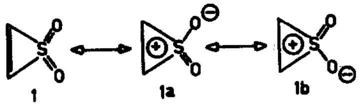
Tetrahedron Letters No. 13, pp 1209 - 1212, 1974. Pergamon Press. Printed in Great Britain.

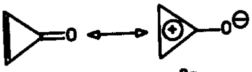
BONDING IN THIIRENE DIOXIDES

F. de Jong, A.J. Noorduin, Miss T. Bouwman and M.J. Janssen,
Department of Organic Chemistry, The University,
Zernikelaan, Groningen, The Netherlands.

(Received in UK 1 February 1974; accepted for publication 15 February 1974)

Our continuing interest in unsaturated sulfones[1], led us into a study of the properties of thiirene-1,1-dioxides (1). The structural resemblance with cyclopropenones (2) has induced the idea[2-4] that thiirene-dioxides are stabilized by the same type of cyclopropenium resonance structures (1a and 1b) as are cyclopropenones (2a). The participation of 3d-orbitals of sulfur is often thought to be responsible for this analogy. Indeed one does obtain a conjugated system as in cyclopropenones, when the $3d_{yz}$-orbital (fig. 1) of sulfur is used. This Hückel system demands the presence of 2 π electrons for aromaticity and stabilization is obtained by a weakening of the SO bond and an increase in charge density on oxygen (as depicted by resonance structures 1a and 1b).


1 1a 1b


2 2a

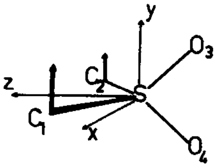
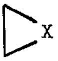
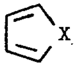


Fig. 1

However, participation of the $3d_{xy}$ orbital creates a Möbius-system with exactly opposite demands for stabilization[5], namely the presence of 4 π electrons in the ring. This is achieved by a decrease in charge on oxygen and a stronger SO bond. Obviously the total effect of 3d orbital resonance on the SO_2 group is difficult to estimate.

In order to have a more quantitative measure for the (in)validity of ketone-sulfone analogies, we carried out a series of CNDO/2 calculations on a number of model sulfones. In addition to the three-numbered rings, also the five-membered thiophene dioxide was calculated, in which molecule the inclusion of the $3d_{yz}$ orbital leads to capture of electrons from the SO bonds into the ring (6 π Hückel aromatic system) and the $3d_{xy}$ orbital to expulsion from the ring (4 π Möbius stable system). Some of the calculated molecular characteristics are compared with literature data of CNDO/2 calculations on corresponding ketones (table I).

Table I CNDO/2 results[11]

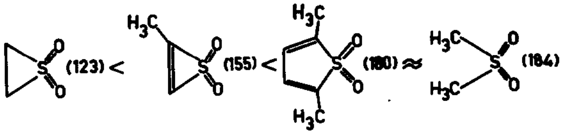
Compound	μ calcd (D)		q_o		X-O bond index[6]	
	X = SO_2	X = CO	X = SO_2	X = CO	X = SO_2	X = CO
CH_3-X-CH_3	4.26	3.03(a)	-0.256	-0.267(a)	2.196	1.878(a)
	3.72	2.63(b)	-0.220	-0.256(b)	2.191	1.880(b)
	4.54	4.52(c)	-0.225	-0.365(c)	2.112	1.689(c)
	5.35	2.37(d)	-0.245	-0.196(d)	2.192	1.912(d)

a) ref. 7; b) ref. 8; c) ref. 9; d) ref. 10.

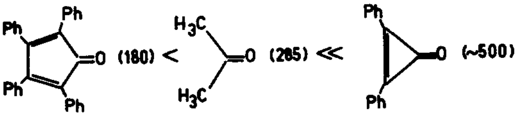
Whereas the calculated dipole moment for cyclopropenone is much larger than the moment of acetone, the dipole moment of thiirene dioxide is about the same as that of dimethyl sulfone. This indicates that little charge separation occurs in thiirene dioxides, which is in excellent agreement with Carpino's results[12]: the dipole moment of diphenylthiirene dioxide (5.63 D) was only slightly greater than that of diphenylsulfone (5.12 D), in sharp contrast with the corresponding ketones.

The differences in charge density on oxygen in the series of ketones are not reproduced by the sulfones either, since thiirene dioxide bears considerably less charge on oxygen than does dimethyl sulfone. We have obtained evidence for the calculated trends, assuming that differences in charge density on oxygen within a series are reflected in the hydrogen bonding ability. Therefore we measured the frequency shift $\Delta\nu_{OH}$ of p-nitrophenol in the presence of a number of stable compounds. For the series of sulfones, the order of hydrogen bonding ability was found to be

($\Delta\nu_{OH}$ values in cm^{-1} given in parenthesis):



whereas for ketones:



In good agreement with theory, we find cyclopropenone to be a strong, thiirene-dioxide to be a weak acceptor in hydrogen bonding.

Interestingly enough, the smaller calculated polarity of the SO bond in thiirene dioxides is accompanied by a decrease in bondorder (Table I). This property causes thiirene dioxides to be a unique class of sulfones, since in a series of dialkyl sulfones a less polar SO bond (as judged from dipole moments or from hydrogen bonding ability) is accompanied by a strengthening of the SO bond[13] (as judged from the SO stretching frequency) (fig. 2). The relationship between $\Delta\nu_{OH}$ and $\nu_{SO_2}^{asym}$ that we used before[1b] to distinguish between dialkyl sulfones and thiophene dioxides, clearly demonstrates the different electronic configuration of the SO_2-group in thiirene dioxides, resulting in abnormally low values of ν_{SO_2}.

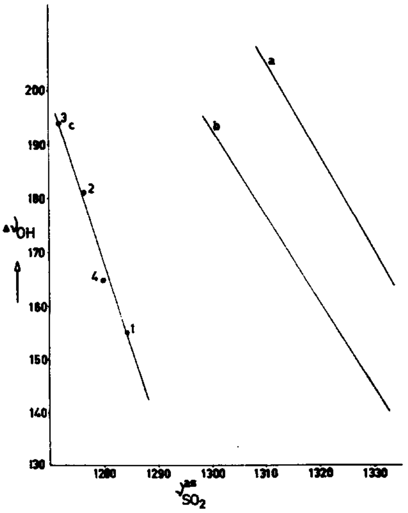
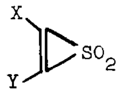


Fig. 2 Plot of $\Delta\nu_{OH}$ versus $\nu_{SO_2}^{asym}$ for

a: dialkyl and diaryl sulfones

b: thiophene dioxides

c: thiirene dioxides



1: X=H; Y=CH_3

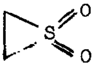
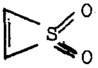
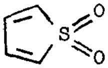
2: X=Y=C_6H_5

3: X=Y=C_6H_4.pCH_3

4: X=Y=C_6H_4.pCl

The origin of the small SO bondorder can be traced by breakdown of the calculated total bondorder into the symmetry components of the C_{2v} symmetry group (Table II). The Hückel-type resonance (b_2) is subdivided into the contributions involving the sulfur 2_{py} and the $3d_{yz}$ orbitals. Considering the sulfur d orbitals, it follows that the decrease of the SO bondorder by the Hückel-type of resonance (b_2) is opposed by an increase due to Möbius-type of resonance (a_2). The Hückel-type of resonance of the sulfur 3_{py} orbital gives rise to a further decrease in SO bondindex for thiirene-dioxide. As can be seen from the values for dimethylsulfone and thiirane dioxide, differences in CSC angle hardly effect the SO bondorder.

Table II SO bondorder decomposed into symmetry components

Compound	a_1	a_2	b_1	b_2		total
				p_y	d_{yz}	
CH_3-SO-CH_3	0.856	0.292	0.329	0.450	0.270	2.196
	0.844	0.305	0.344	0.449	0.249	2.191
	0.837	0.319	0.350	0.409	0.197	2.113
	0.852	0.278	0.351	0.450	0.262	2.193

In conclusion we can state that a comparison of cyclic unsaturated sulfones and ketones is of little value. Although the d_{yz} orbital of the sulfur atom can -and does- promote resonance structures analogous to the predominant polar resonance structures in ketones, the d_{xy} orbital has a contrary effect of comparable magnitude. The effect is a nice demonstration of the importance of Möbius aromaticity as compared to the more popular Hückel aromaticity.

References:

1a. F. de Jong, M.J. Janssen, J.Chem.Soc. Perkin Trans II, 572 (1972).
b. Ibid., Rec.Trav.Chim. 92, 1073 (1973).
2. M.E. Volpin, Yu. D. Koreshkov, V.G. Dulova, D.N. Kursanov, Tetrahedron 18. 107 (1962).
3. L.A. Carpino, L.V. McAdams, III, J.Amer.Chem.Soc. 87, 5804 (1965).
4. L.A. Paquette, L.S. Wittenbrook, Ibid. 89, 4483 (1967).
5. M.J.S. Dewar, Angew.Chem. 83, 859 (1971).
6. K.B. Wiberg, Tetrahedron 24, 1083 (1968).
7. F. Ijima, Bull.Chem.Soc.Jap. 43, 1049 (1970).
8. H.L. Ammon, J.Amer.Chem.Soc. 95, 7093 (1973).
9. R.C. Benson, W.H. Flygare, M. Oda, R. Breslow, Ibid. 95, 2772 (1973).
10. D.J. Bertelli, T.G. Andrews, Jr., Ibid. 91, 5280 (1969).
11. J.A. Pople, G.A. Segal, J.Chem.Phys. 44, 3289 (1966).
12. L.A. Carpino, L.V. McAdams, III, R.H. Rynbrandt, J.W. Spiewak, J.Amer.Chem.Soc. 93, 476 (1971).
13. P. Biscarni, G. Galloni, S. Ghersetti, Spectrochim. Act. 20, 261 (1964).