Spectrochemical Study of Aminoiminomethanesulphinic Acid and Related *NN'*-Substituted Derivatives

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Aminoiminomethanesulphinic acid and some related *NN'*-substituted derivatives have been prepared and characterized by i.r. and ^1H n.m.r. spectroscopy. The presence of strong hydrogen bonds has been observed; values of force constants, bond orders, and O–$\overset{\frown}{S}$–O angles have been measured. The assignment of all ^1H n.m.r. resonances has allowed full characterization of these compounds. In particular a conformational study of *o*-tolyl-amino-*o*-tolyliminomethanesulphinic acid and salt in [^2H]trifluoroacetic acid–[^2H]chloroform has been accomplished.

WE are interested in the study of sulphinic and seleninic acids from various points of view,[1-8] and report here the preparation and the spectrochemical characterization of aminoiminomethanesulphinic acid and some *NN'*-substituted derivatives (Table 1).

I.r. Analysis.—Because of the negligible solubility of these compounds in the usual solvents for i.r. studies, solid phase i.r. spectra only have been recorded. The assignments of the most important absorption bands in the range 4000—400 cm⁻¹ are listed in Table 2.

in the spectra of the corresponding deuterio-compounds [v(OD) 2360—2340 and 1900 cm⁻¹]. The v(NH) vibrations occur at 3290—3220 cm⁻¹ as strong sharp bands. The wave numbers of v(OH) and v(NH) suggest that a strong hydrogen bond is present.[9-12]

The v(OH) absorption is split in two distinct broad absorption zones, as previously observed for the benzene-sulphinic [13] and -seleninic [7] series. This could tentatively be attributed to two different types of hydrogen bond; however, on the basis of the i.r. results only, we cannot

TABLE 1

Analytical data and some physical properties of sulphinic acids and salts

No.	Compound	M.p. (°C)	Λ/ ohm⁻¹ cm² *a*	pH *a*	Required (%) C	H	N	Found (%) C	H	N
(I)	$(H_2N)(HN)CSO_2H$	129	12·3	5·45	11·5	3·7	25·9	12·5	3·7	25·9
(II)	$(PhNH)(PhN)CSO_2H$	132	11·1	4·07	60·0	4·7	10·8	59·2	5·5	10·6
(III)	$(PhNH)(PhN)CSO_2Na$	130(decomp.)	79·6 *b*	6·80 *b*	55·3	4·0	9·9	54·4	4·4	9·6
(IV)	$(p\text{-}MeC_6H_4NH)(HN)CSO_2H$	108	36·1	4·29	48·5	5·1	14·1	49·6	5·4	14·5
(V)	$(o\text{-}MeC_6H_4NH)(o\text{-}MeC_6H_4N)CSO_2H$	204	36·2	4·21	62·5	5·6	9·7	63·3	6·1	9·9
(VI)	$(o\text{-}MeC_6H_4NH)(o\text{-}MeC_6H_4N)CSO_2Na$	178	105 *b*	7·34 *b*	58·0	4·9	9·0	57·4	5·2	8·8

a For 10⁻³M solutions in H_2O unless otherwise noted.   *b* For 10⁻³M solutions in EtOH–H_2O (1 : 1 v/v).

TABLE 2

Assignments of the most important i.r. absorption bands in the range 4000—400 cm⁻¹

Compounds	(I)	(II)	(III)	(IV)	(V)	(VI)
v(NH)	3260vs	3260vs	3260vs	3270vs	3220vs	3290vs
v(OH)	3020s, 2765s	3000s, 2680s		3020s, 2780m	3020s, 2780s	
δ(OH)	1360m	1340m		1375w	1382m	
v(S=O)	1110vs	1095vs		1099vs, 1073vs	1111s	
v(SO₂) Sym.			1110sh			1110vs
Antisym.			1140vvs			1145vvs
v(SOH)	1025vs	1004ms		1004vs	1015s	
γ(OH)	960m	970w		939w	946w	
ρ(NH)	730ms	722sh	720sh	755sh	740sh	722m

OH and NH *Vibrations.*—By comparing the i.r. spectra of the acids with those of the corresponding salts, two broad absorption zones in the range 3020—2680 cm⁻¹ can be attributed to v(OH) vibrations. These assignments have been also confirmed by the expected shift

distinguish between the many possible *inter-* or *intra-*molecular bonds involving S=O, SOH, NH, or C=N groups.

In Table 2 tentative assignments of in-plane and out-

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³ F. Momicchioli, G. Verani, and D. De Filippo, *Ann. Soc. Nat. e Mat. Modena,* 1968, **99**, 219.

⁴ D. De Filippo and C. Preti, *Ricerca Sci.,* 1969, **39**, 231.

⁵ D. De Filippo and F. Momicchioli, *Tetrahedron,* 1969, **25**, 5733.

⁶ F. Ferranti and D. De Filippo, *J. Chem. Soc. (B),* 1971, 1925.

⁷ D. De Filippo, F. Momicchioli, C. Preti, A. Rastelli, and G. Verani, *J. Chem. Soc. (B),* 1971, 1065.

⁸ B. J. Lindberg, *Acta Chem. Scand.,* 1967, **21**, 2215.

⁹ C. N. R. Rao, ' Chemical Applications of Infrared Spectroscopy,' Academic Press, New York and London, 1962, p. 178.

¹⁰ L. J. Bellamy, C. P. Conduit, E. L. Pace, and V. Z. Williams, *Trans. Faraday Soc.,* 1959, **55**, 1677.

¹¹ T. Gramstad, *Spectrochim. Acta,* 1963, **19**, 829.

¹² H. S. Ghersetti and M. Lusa, *Spectrochim. Acta,* 1965, **21**, 1067.

¹³ S. Detoni and D. Hadzi, *J. Chem. Soc.,* 1955, 3163.

of-plane OH deformations and of NH waggings are also reported.

SO$_2$, S=O, *and* S(OH) *Vibrations.*—If the CSO$_2$⁻ group of the salt is regarded as an isolated pyramidal molecule, giving a situation in which the specific vibrations of this group are not mixed with those of the remaining part of the molecule,[14] the following six absorption bands, characteristic of C_s symmetry in a ZXY$_2$ molecule, are predicted: ν_s(SC), δ_s(O$_2$SC), ν_s(SO$_2$), ν_{as}(SO$_2$), δ_s(OSO), and δ_{as}(O$_2$SC). Absorption bands due to ν(SC), ν(S=O), δ(OSOH), δ(CSO), ν(SOH), and δ(CSOH) are similarly expected in the i.r. spectra of the acids.

The sulphur–oxygen stretching vibrations, ranging between 1500 and 700 cm⁻¹,[15] have been assigned using the benzenesulphinic acids and salts as reference molecules;[8] they fall, in our compounds, between 1111 and 1004 cm⁻¹ (see Table 2).

The lack of complete structural data does not permit a rigorous evaluation of force constants; in any case, a

Miscellaneous Vibrations.—The medium–weak absorption band occurring near 630 cm⁻¹ could be tentatively assigned to the ν(CS) vibration. The very strong ν(C=N) absorption band occurs in our compounds at 1693—1656 cm⁻¹, in a typical range for oximo- or imino-derivatives.[19] The ν(C$_{ar}$-N) bands occur at 1315—1340 cm⁻¹, in very good agreement with published data for secondary aromatic amines;[20] the bands related to the aromatic ring are also found in the predicted range for mono- and di-substituted aromatic rings.

N.m.r. Measurements.—All ¹H n.m.r. resonances have been assigned on the basis of typical chemical shift, resonance area, and line width values (see Table 3). The resonances at δ 8·15—9·00 p.p.m. are due to the NH and NH$_2$ protons. It is surprising to observe that, although the NH protons are usually considered labile, in the cases of compounds (II), (III), (V), and (VI), these resonances do not undergo deuterium exchange in D$_2$O, [²H]trifluoroacetic acid, and CD$_3$OD even in the

TABLE 3 [a]

¹H N.m.r. parameters for various solvents

	(CD$_3$)$_2$SO				CD$_3$OD				D$_2$O				H$_2$O			
Compound	δ(Me)	δ(Ar)	δ(NH)	Δ(NH)	δ(Me)	δ(Ar)	δ(NH)	Δ(NH)	δ(Me)	δ(Ar)	δ(NH)	Δ(NH)	δ(Me)	δ(Ar)	δ(NH)	Δ(NH)
(I)			8·84 [c]	75		Insoluble				Insoluble					8·92 [c]	75
(II)		7·62	8·94	4		7·22	9·00	4		Insoluble				Insoluble		
(III)		7·48	8·39	3		7·20	8·15	2		Insoluble				Insoluble		
(IV)	2·54	7·42	b		2·33	7·20	b		2·69	7·61	b					
(V)	2·56	7·64	8·87	2	2·22	7·28	8·57	2	2·55	7·71	8·73	3				
									2·60		8·93	2				
(VI)	2·55	7·44	8·59	3	2·36	7·26	8·51	3		Insoluble				Insoluble		

[a] Chemical shifts in p.p.m. For multiplets the values reported refer to the mid-point of the multiplet; Δ = approximate line-widths in Hz. [b] NH Resonances not detectable by exchange and/or quadrupole broadening. [c] Single collapsed broad band for both NH and NH$_2$ resonances.

satisfactory approximation can be obtained, by a crude vibrational model, using the equation $k_{SO} = 0·6282$ ν_{SO}^2 where ν_{SO} is, in the salts, Lehmann's mean value.*[16]

According to the method of ref. 15 bond lengths, bond angles, and bond orders have been evaluated [bond lengths, r(Å) S=O 1·48—1·49, S–OH 1·51, and SO$_2$ 1·47; O–S⌢O angles 107—108° in the acids and 110° in the salts; bond orders $n_{S=O}$ 1·52—1·56; n_{SOH} 1·43—1·46, and n_{SO_2} 1·58—1·59]. The bond-order values of S=O and S–OH in the acids do not differ too much, in accordance with nearly complete resonance. A total bond-order value higher in the salts than in the corresponding acids has been observed. This increase is in agreement with an ionization process inducing an increment in the negative net charge on the SO$_2$ group.†

The O–S⌢O angle value is typical for sp^3 hybridized sulphur.

* For the ν(SOH) vibrations the equation $k_{SO} = 0·6547$ ν_{SO}^2 has been used.

† This interpretation is supported by quantum chemical calculations [17,18] previously carried out on benzenesulphinic acid and its salt,[5] where a net charge of −0·53 in the acid becomes −0·90 in the salt. Analogous results have been obtained for all the studied *meta*- and *para*-substituted benzenesulphinic acids and salts. The absolute value of the net charge increment is not so significant, because of a typical EHT overestimation of charge polarization, but it is important to point out that an increase of the charge on the SO$_2$ group always takes place on going from the acid to the corresponding salt.

presence of acid; moreover, the relative chemical shifts are concentration independent. On the contrary, a fast deuterium exchange occurs for D$_2$O, CD$_3$OD, and [²H]trifluoroacetic acid solutions of compounds (I) and (IV). The observed absence of exchange might be due to the two phenyl groups interfering with solvation. On the other hand, the presence of SO$_2$H and SO$_2$⁻ groups might play an important role in the determination of the exchange rates, since we have observed that the NH protons of diphenyl- and di-o-tolyl-thiourea quickly exchange in D$_2$O.

The spectra of the two di-o-tolyl derivatives [compounds (V) and (VI)] on passing from DMSO and CDCl$_3$ to the protic solvents D$_2$O and [²H]trifluoroacetic acid exhibit a great difference; in fact, the methyl singlet is split in three separate resonances (A$_1$, coincident with the singlet signal for CDCl$_3$, B$_1$, and B$_2$). Simultaneously

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[19] L. J. Bellamy, ' The Infrared Spectra of Organic Sulphur Compounds,' ed. N. Kharasch, Pergamon Press, Oxford, 1961, p. 54.

[20] N. B. Colthup, L. H. Daly, and S. E. Wiberley, ' Introduction to Infrared and Raman Spectroscopy,' Academic Press, New York, 1964, p. 279.

the absorption signal attributed to the NH resonance is split into two different resonances (A' and B').

On going from pure $CDCl_3$ to pure $CF_3 \cdot CO_2D$ through a series of mixed solvents we observe that the chemical shifts of A_1, B_1, and B_2 move towards lower field while those of A' and B' move in opposite directions so that plotting $\Delta\delta_{A_1-B_2}$ and $\Delta\delta_{B'-A'}$ versus $X_{CF_3 \cdot CO_2D}$ two straight lines (1) and (2) are obtained. $X_{CF_3 \cdot CO_2D}$ Is the

$$\Delta\delta_{A_1-B_2} = 0 \cdot 21 - 0 \cdot 03 \, X_{CF_3 \cdot CO_2D} \qquad (1)$$

$$\Delta\delta_{B'-A'} = 0 \cdot 66 - 0 \cdot 45 \, X_{CF_3 \cdot CO_2D} \qquad (2)$$

mol fraction of $CF_3 \cdot CO_2D$ in the mixed solvent.
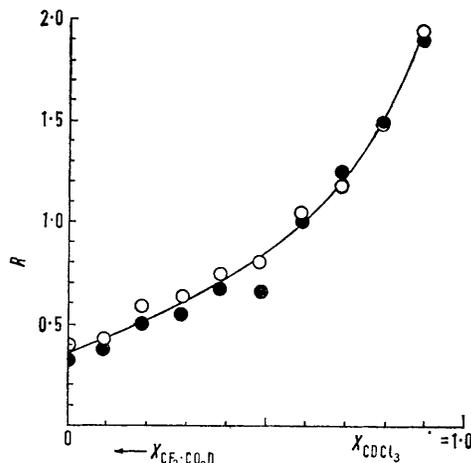
Variation of resonance area R with mol fraction for the mixed solvent $CF_3 \cdot CO_2D$–$CDCl_3$; ○ Me, ● NH

As far as the resonance areas are concerned (Figure) the relationships (3) and (4) obtain. Equation (4)

$$a_{B_1} = a_{B_2} \qquad (3)$$

$$R = \frac{a_{A_1}}{a_{B_1} + a_{B_2}} = \frac{a_{A'}}{a_{B'}} \qquad (4)$$

strongly supports the hypothesis that A and A' and B_1, B_2, and B' are respectively associated with two conformers in equilibrium. The results of experiments confirm the reversibility of the process. It seems that, on changing the solvent, the two methyl groups become magnetically non-equivalent. Moreover, the polar solvent trifluoroacetic acetic might play a role in the formation of conformer B. In fact, if the conformer B is an adduct formed between conformer A and a trifluoroacetic acid molecule, the equilibrium (5) is obtained.

$$A + CF_3 \cdot CO_2H \rightleftharpoons B \qquad (5)$$
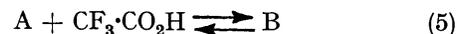
The apparent concentration equilibrium constant can be written as $K = 1/R \cdot X_{CF_3 \cdot CO_2H} = 2 \cdot 6 \pm 0 \cdot 3$.

EXPERIMENTAL

Preparation of Compounds.—The acids (I), (II), (IV), and (V) were prepared by low-temperature (0—6 °C) oxidation of the corresponding thiourea (5 g) in dioxan (70 ml) by dropwise addition with vigorous stirring of an excess of 33% H_2O_2 (*ca.* 5 ml) using sodium molybdate (30 mg) as catalyst. The product (*ca.* 70%) was twice recrystallized from water or methanol (not exceeding 50%). The compounds are stable under vacuum in a dry dark place. The salts (III) and (VI) were prepared by a quantitative reaction between the corresponding acid and sodium methoxide. The deuterio-acids were obtained from D_2O solutions.

I.r. Measurements.—All i.r. spectra were recorded in the range 4000—400 cm^{-1} with a Perkin-Elmer model 457 spectrophotometer for Nujol and hexachlorobutadiene mulls between KBr plates.

N.m.r. Measurements.—All ^1H n.m.r. spectra were taken with a Varian HA-100 spectrometer at 28 ± 1 °C, with tetramethylsilane as internal standard and, for the measurements in D_2O or $[^2H_6]$dimethyl sulphoxide, Hexamethyldisiloxane as external standard in Wilmad special coaxial cells (solvents, Fluka, had isotope purity of 99%).