Localized Molecular-orbital Representation of the Bonding in *N*-Sulphinosulphimides

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Localized molecular orbitals for the simplest *N*-sulphinosulphimide, H_2SNSO_2H, and of its conjugated acid have been calculated using the semiempirical CNDO/2 method. To understand the special features of the different bonds, a comparison is made with simpler molecules such as H_2S, Me_2SNH, Me_2SO, and Me_2SO_2. A three-centre $S^{IV}NS^{VI}$ π bond is formed in *N*-sulphinosulphimides which is localized mainly on the nitrogen atom. The $S^{IV}N$ and $S^{VI}N$ σ bonds as well as the nitrogen lone pair are considerably delocalized on to the neighbouring sulphur atoms. In all cases, the sulphur *d*-orbital participation in bonding is important. In Me_2SNH, Me_2SO, and Me_2SO_2, hyperconjugation of the CH bonds with the sulphur *d* orbitals occurs.

THE classical concept of the chemical bond serves as a valuable tool in understanding molecular phenomena. The description of bonds from the theoretical as well as from the experimental point of view forms an important part of structural chemistry. Several theoretical models of the chemical bond exist.[1-4] In this work we use localized molecular orbitals (l.m.o.). Thus, for example, lone pairs or σ and π bonds are related to l.m.o.s of the appropriate local symmetry, mainly localized on one or two atoms of a molecule. The transferability and additivity of bond properties correspond to those of the given l.m.o. Similarly, just as chemical bonds are used to build up the whole molecule, the l.m.o.s serve to construct the total molecular wavefunction. We feel that the use of the l.m.o. makes possible a didactic discussion of the chemical bond. It has to be said that the transferability and additivity of l.m.o.s is, by no means, quantitative. However, in many cases a qualitative or semiquantitative discussion can also yield valuable information.

The present work deals with *N*-sulphinosulphimides, $H_2SN(SO_2H)$, and related compounds. We hope to give an adequate description of the special bond types present in this class of molecules.

THEORY

Localized orbitals can be obtained in several ways.[3,4] We have used the Edmiston–Ruedenberg procedure [4] with the CNDO/2 approximation.[5,6] Standard computer programs were employed for the numerical calculations.[7,8]

An important quantity, $l_A{}^i$, characterizing the steric extension of the *i*th l.m.o., is the localizability on atom A.[9] Within the CNDO/2 approximation this is written as in (1).

$$l_A{}^i = 100\sum_a c_{ai}{}^2\ \% \qquad (1)$$

Here c_{ai} denotes the coefficient of the *a*th atomic orbital, centred on atom A, in the *i*th l.m.o. The localizability of different bond types is defined, in %, as in (2a) and (2b):

$$\text{for a lone-pair l.m.o. } L_A{}^{lp} = l_A{}^{lp} \qquad (2a)$$

$$\text{for a two-centre } \sigma \text{ and } \pi \text{ l.m.o. } L_{AB}{}^{\sigma \text{ or } \pi} = l_A{}^{\sigma \text{ or } \pi} + l_B{}^{\sigma \text{ or } \pi} \qquad (2b)$$

Other useful quantities are the *s* and *d* characters, where $c_{2s,A,i}$ is the coefficient of the 2*s* orbital in the *i*th l.m.o. on atom A and the summation in (4) includes all 3*d* orbital coefficients on atom A.

$$s_A{}^i = 100c_{2s,A,i}{}^2/l_A{}^i \qquad (3)$$

$$d_A{}^i = 100\Sigma c_{3d,A,i}{}^2/l_A{}^i \qquad (4)$$

Bond localizabilities, as defined in equation (2a) and (2b), are useful in treating the aromaticity of monocyclic heteroconjugated molecules.[10]

In the case of the ethylene molecule, the *ab initio* localization procedure yields two equivalent CC 'banana' bonds in place of the canonical σ and π m.o.s.[11] CNDO/2 calculations do not reproduce this result: the π orbital remains unchanged through localization.[6] It is known that the search for the optimum l.m.o.s may converge to one of the local minima. Symmetry constraints are of assistance in finding these local minima as was illustrated earlier [12] for the σ–π mixing of $:C\equiv O:$. We feel that this feature of the semiempirical method is advantageous because the concept of the σ and π bonds is maintained.

When using the CNINDO [7] and LOCAL [8] computer programs together, non-equivalent lone-pair l.m.o.s were obtained on the oxygen atom. To get closer to classical chemical terms we transformed these into equivalent orbitals. Since the CNDO/2 method overestimates *d* orbital participation in molecular wavefunctions for second-row atoms,[13] the numerical results must be manipulated carefully. On the other hand, we feel that the qualitative conclusions, drawn from the semiempirical l.m.o.s, are in this case also close to reality.

SIMPLE MODELS

Comparative studies on the bonding in some simple molecules (H_2S, Me_2SNH, Me_2SO, and Me_2SO_2), related to *N*-sulphinosulphimides were carried out and the results are summarized in Table 1 and Figure 1. Data for bonds of the same type (*e.g.* for CH bonds in Me_2SO) were averaged. The deviations from the mean values were found to be negligible. For all molecules, experimental geometries [14] were used in the calculations.

The CS bonds in the methyl-substituted molecules, as well as the corresponding SH bonds in H_2S, are almost perfectly localized. These bonds are slightly polarized towards the carbon atom in Me_2SNH and in Me_2SO, while they are practically 'neutral' in H_2S and in Me_2SO_2 [Figure 1(*a*)]. The observed minor importance of sulphur *d* orbitals is in accordance with the results of Streitwieser and Williams [15] who have stated that *d* orbitals do not play any role in bonding in MeSH. Similarly, the SN(σ)

TABLE 1

Parameters characterizing the l.m.o.s in H_2S, Me_2SNH, Me_2SO, and Me_2SO_2

Bond type	Molecule	Localizability	Participation of A and B atoms in AB bond: A[a]	Participation of A and B atoms in AB bond: B[b]	Delocalization on to neighbouring sulphur atom[c]
SH(σ)	H_2S	100.0	S 50.2 (7.4, 9.3)	H 49.8 (100)	
CS(σ)	Me_2SNH	99.9	S 45.7 (9.4, 16.0)	C 54.2 (25.7)	
	Me_2SO	99.9	S 46.4 (10.2, 15.4)	C 53.5 (25.4)	
	Me_2SO_2	99.4	S 50.7 (36.1, 16.3)	C 48.7 (23.1)	
SN(σ)	Me_2SNH	99.7	S 51.4 (13.6, 10.6)	N 48.3 (22.5)	
SO(σ)	Me_2SO	99.9	S 46.7 (11.2, 12.7)	O 53.2 (19.7)	
	Me_2SO_2	99.4	S 46.1 (30.8, 15.2)	O 53.3 (21.1)	
S(*lp*)	H_2S	100.0	S 100.0 (48.4, 0.0)		
	Me_2SNH	99.7	S 99.7 (67.4, 1.4)		
	Me_2SO	99.8	S 99.8 (68.9, 1.5)		
CH(σ)	Me_2SNH	98.1	C 50.2 (26.0, 0.0)	H 47.9 (100)	S 1.9 (87.2)
	Me_2SO	98.0	C 50.5 (26.3, 0.0)	H 47.5 (100)	S 1.9 (82.1)
	Me_2SO_2	98.6	C 51.2 (27.0, 0.0)	H 47.4 (100)	S 1.1 (78.2)
NH(σ)	Me_2SNH	95.2	N 51.9 (28.7, 0.0)	H 43.3 (100)	S 4.6 (80.3)
N(*lp*)	Me_2SNH	89.8	N 89.8 (54.9, 0.0)		S 9.8 (79.5)
O(*lp*)	Me_2SO	90.4	O 90.4 (43.4, 0.0)		S 9.3 (82.9)
	Me_2SO_2	89.5	O 89.5 (43.7, 0.0)		S 10.3 (71.9)
SN(π)	Me_2SNH	99.5	S 23.9 (0.6, 79.3)	N 75.6 (0.0)	
SO(π)	Me_2SO	99.6	S 19.3 (0.3, 77.9)	O 80.3 (0.0)	
	Me_2SO_2	99.6	S 20.0 (0.2, 71.8)	O 79.6 (0.0)	

[a] *s* and *d* characters are given in parentheses. [b] *s* characters are given in parentheses. [c] *d* characters are given in parentheses.

bond in Me_2SNH is polarized towards sulphur and the SO(σ) bonds in Me_2SO or Me_2SO_2 are polarized towards oxygen [Figure 1(*b*)]. The sulphur lone pair is practically completely localized with negligible *d*-orbital participation [Figure 1(*c*)].

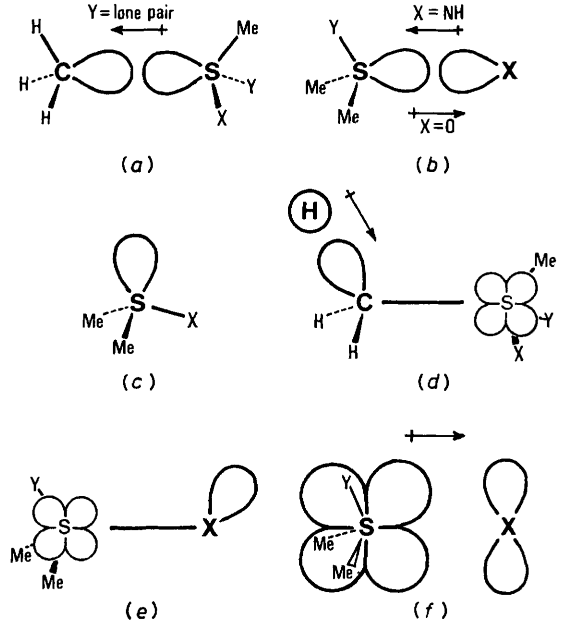

FIGURE 1 Schematic representation of the l.m.o. in Me_2SNH (X = NH, Y = lone pair), Me_2SO (X = O, Y = lone pair), and Me_2SO_2 (X = Y = O). Basic components of a bond are drawn as full lines; arrows indicate the direction of bond polarization. (*a*) CS σ; (*b*) SX σ; (*c*) S lone pair; (*d*) CH σ; (*e*) X lone pair; (*f*) SX π bond orbital

Owing to delocalization on to the sulphur *d* orbitals, the localizability of the CH bonds is anomalously low, indicating appreciable hyperconjugation [see final column in Table 1 and Figure 1(*d*)]. This is in agreement with the results of Knoll *et al.*[16] who discussed H–D exchange in Me_2SO by taking hyperconjugation into account.

The nitrogen and oxygen lone pairs are markedly delocalized on to the sulphur *d* orbitals [Figure 1(*e*)]. A similar effect, owing to hyperconjugation, can be observed for the NH bond which is polarized towards the nitrogen atom in Me_2SNH. The lone-pair delocalization indicates that resonance structures of type $Me_2\overset{-}{S}(Y)\equiv\overset{+}{X}$ (X = NH or O; Y = lone pair or O) cannot be neglected when depicting the total distribution of electrons in sulphimides, sulphoxides, and sulphones.

Sulphur *d* orbitals seem to play a decisive role in SN and SO π bonding as shown schematically in Figure 1(*f*). SN(π) and SO(π) bonds are strongly localized, but considerably polarized towards the nitrogen or oxygen atom. These facts are usually illustrated by the resonance structures $Me_2S(Y){=}X \longleftrightarrow Me_2\overset{+}{S}(Y){-}\overset{-}{X}$ (*cf.* refs. 17 and 18).

As a result of strong *d*-orbital participation, the localizability of the SN π bond is expected to be practically independent of the CSNH dihedral angle in Me_2SNH. This view gains support from the calculation of the l.m.o. for two different conformations of Me_2SNH. In one of them the CSNH moiety was planar while in the other the CSN and SNH planes were perpendicular to each other. The values in Table 1, showing the localizability of the SN(π) bond, were found to vary by only $\pm 0.5\%$. On the other hand, the difference in energy between the two conformations is also relatively small (4.6 kcal mol^{-1}) * with the planar arrangement being more stable. These findings are in qualitative agreement with *ab initio* results.[19] Thus, it is suggested that the relative positions of the sulphur *d* and nitrogen *p* orbitals in all conformations are almost equally favourable in ensuring maximal overlap (*cf.* ref. 20).

N-*Sulphinosulphimides.*—The structure of *SS*-dimethyl-*N*-methylsulphonylsulphimide (Me_2SNSO_2Me) has been studied extensively by *X*-ray[21] and extended-Hückel[20] methods. On the basis of further studies, the present work gives an account of the bond localizabilities in such systems. To avoid difficulties in computations, a simplified model having hydrogen atoms instead of methyl groups was investigated where convergence in the localization procedure

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* Throughout this paper: 1 cal = 4.184 J.

could be reached. The geometry was taken from *X*-ray measurements [21,22] and standard SH and NH bond lengths [14] were used.

Characteristic l.m.o. data for H_2SNSO_2H and for its conjugated acid, $H_2S\overset{+}{N}HSO_2H$, are collected in Table 2. In analogy with the CS^{IV} bonds in Me_2SO and with the CS^{VI} bond in Me_2SO_2 (see Table 1), the $S^{IV}H$ and $S^{VI}H$ bonds in H_2SNSO_2H are strongly localizable with small *d*-orbital participation. $S^{VI}O$ (σ and π) bonds, and oxygen lone pairs, in sulphimides are similar, almost equivalent, to those in Me_2SO_2, while the strongly localized sulphur(IV) lone pair has its analogue in Me_2SO.

Infrared spectroscopic,[23] *X*-ray,[21,24-26] and extended-Hückel [20] studies have indicated that the $S^{IV}NS^{VI}$ moiety is conjugated in *N*-sulphinosulphimides. This conclusion is supported by our finding that in H_2SNSO_2H there is a three-centre (*d–p–d*) $S^{IV}NS^{VI}$ π bond, which is strongly concentrated on to the central nitrogen atom. The π-electron delocalization and polarization may also be represented by the following resonance structures:

$$H_2\ddot{S}{=}\ddot{N}{-}SO_2H \longleftrightarrow H_2\overset{+}{\dot{S}}{-}\underset{\cdot\cdot}{\overset{-}{\ddot{N}}}{-}SO_2H \longleftrightarrow H_2\overset{+}{\dot{S}}{-}\ddot{N}{=}\overset{-}{S}O_2H$$

Due to the *d* orbitals of the neighbouring sulphur(IV) and sulphur(VI) atoms, the nitrogen lone pair cannot be localized [Figure 2(*b*)] as shown by the limiting structures:

$$H_2\ddot{S}{=}\ddot{N}{-}SO_2H \longleftrightarrow H_2\overset{-}{\ddot{S}}{\equiv}\overset{+}{N}{-}SO_2H \longleftrightarrow H_2\ddot{S}{=}\overset{+}{N}{=}\overset{-}{S}O_2H$$

For the same reason, neither the $S^{IV}N$(σ) nor the $S^{VI}N$(σ) bonds can be localized completely [see Figure 2(*c*) and 2(*d*) and the final column in Table 2]. This striking result for σ bonds involving sulphur atoms suggests the importance of the following unusual limiting structures:

$$S^{IV}{-}N{-}S^{VI} \longleftrightarrow \overset{+}{S}{}^{IV}\ N{=}\overset{-}{S}{}^{VI} \longleftrightarrow \overset{-}{S}{}^{IV}{=}N\ \overset{+}{S}{}^{VI}$$

It is possible that the important delocalization of the l.m.o. is, to a large extent, due to the overestimation of the *d*-orbital participation within the CNDO/2 approximation. However, the effect is so large that it should also be present when more sophisticated quantum-chemical methods are used.

There is no dramatic change in bonding characteristics when a proton is added to the H_2SNSO_2H structure (Table 2). The new NH bond in $H_2S\overset{+}{N}HSO_2H$, like the nitrogen lone pair in the conjugated base, is delocalized on to the adjacent sulphur *d* orbitals. As to the other bonds, the data in Table 2 show that *N*-protonation results in a somewhat greater localizability of bonds, except for oxygen lone pairs. *N*-protonation gives rise to inductive electron displacement towards sulphur(IV) and sulphur(VI) atoms in the terminal $S^{IV}H$(σ), $S^{VI}H$(σ), $S^{VI}O$(σ and π) bonds and to

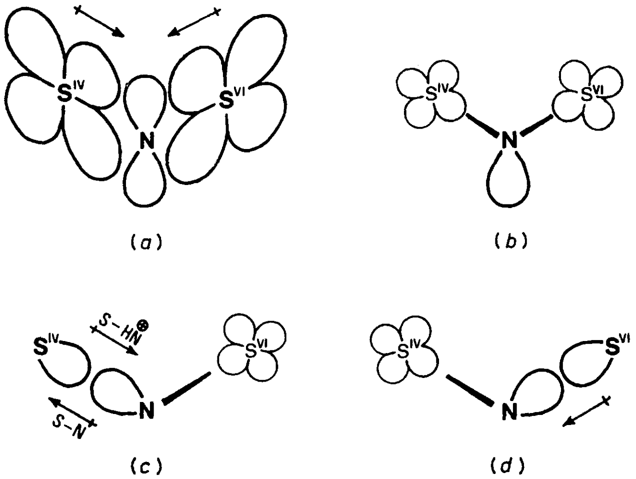

FIGURE 2 Schematic representation of SN l.m.o. in H_2SNSO_2H and in $H_2S\overset{+}{N}HSO_2H$. Basic components of a bond are drawn as full lines; arrows indicate the direction of bond polarization. (*a*) $S^{IV}NS^{VI}$ π; (*b*) N lone pair; (*c*) $S^{IV}N$ σ; (*d*) NS^{VI} σ bond orbital

TABLE 2

Parameters characterizing the l.m.o. in H_2SNSO_2H (upper row) and in $H_2S\overset{+}{N}HSO_2H$ (lower row)

		Participation of A and B atoms in AB bond		Delocalization on to neighbouring sulphur atom [c]
Bond type	Localizability	A [a]	B [b]	
$S^{IV}H$(σ)	99.8	S^{IV} 50.4 (11.1, 12.2)	H 49.4 (100)	
	99.9	S^{IV} 53.6 (12.4, 11.0)	H 46.3 (100)	
$S^{VI}H$(σ)	99.7	S^{VI} 50.3 (36.2, 17.5)	H 49.4 (100)	
	99.7	S^{VI} 54.1 (39.2, 16.0)	H 45.6 (100)	
S^{IV}(*lp*)	99.9	S^{IV} 99.9 (65.3, 0.8)		
	99.7	S^{IV} 99.7 (65.3, 0.6)		
$S^{VI}O$(σ)	99.4	S^{VI} 46.5 (31.9, 15.0)	O 52.9 (20.5)	
	99.4	S^{VI} 48.4 (32.4, 14.6)	O 51.0 (21.3)	
$S^{VI}O$(π)	99.7	S^{VI} 20.6 (0.8, 74.2)	O 79.1 (0.0)	
	99.6	S^{VI} 22.1 (0.3, 70.5)	O 77.5 (0.3)	
O(*lp*)	90.2	O 90.2 (43.5, 0.0)		S^{VI} 9.4 (73.6)
	89.3	O 89.3 (44.0, 0.0)		S^{VI} 10.2 (70.4)
$S^{IV}N$(σ)	96.3	S^{IV} 52.6 (11.5, 8.0)	N 43.7 (15.4)	S^{VI} 3.5 (75.4)
	97.8	S^{IV} 43.9 (9.4, 12.3)	N 53.9 (25.7)	S^{VI} 2.0 (79.8)
$S^{VI}N$(σ)	92.3	S^{VI} 38.1 (27.2, 19.1)	N 54.2 (20.6)	S^{IV} 7.2 (87.9)
	95.7	S^{VI} 29.0 (20.9, 25.4)	N 66.7 (40.3)	S^{IV} 4.2 (91.7)
N(*lp*)	90.5	N 90.5 (65.7, 0.0)		S^{IV} 5.8 (92.6) S^{VI} 3.4 (74.0)
NH(σ)	95.9	N 95.9 (39.5, 0.0)		S^{IV} 2.7 (91.6) S^{VI} 1.5 (79.0)
$S^{IV}N$(π)	87.8	S^{IV} 16.2 (0.0, 79.0)	N 71.6 (0.6)	S^{VI} 11.9 (76.2)
	90.9	S^{IV} 12.7 (0.1, 82.2)	N 78.2 (0.8)	S^{VI} 8.8 (78.7)

[a] *s* and *d* characters are given in parentheses. [b] *s* characters are given in parentheses. [c] *d* characters are given in parentheses.

a similar effect towards the nitrogen atom in the internal $S^{IV}N(\sigma$ and $\pi)$ and $S^{VI}N(\sigma)$ bonds. The lower localizability of the oxygen lone pairs is also due to the electron-withdrawing power of the proton bound to nitrogen. Values of the net atomic charge for $H_2S\overset{+}{N}HSO_2H$, when compared to those for the conjugated base, also point to a ' charge flow ' from all atoms towards the proton, so reducing its unit positive charge to about a quarter of an electron (Table 3).

TABLE 3

Net atomic charges in H_2SNSO_2H and in $H_2S\overset{+}{N}HSO_2H$

Net charge (in electrons)

Atom	H_2SNSO_2H	$H_2S\overset{+}{N}HSO_2H$	Difference
S^{IV}	0.319	0.557	0.238
S^{VI}	0.408	0.428	0.020
O^1	−0.250	−0.158	0.092
O^2	−0.276	−0.148	0.128
N	−0.214	−0.157	0.057
$H(S^{VI})$	−0.002	0.075	0.077
$H^1(S^{IV})$	0.003	0.067	0.064
$H^2(S^{IV})$	0.012	0.076	0.064
H(N)		0.261	0.261

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