MNDO Study of the Site of Protonation in Methylsydnone

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The electronic and geometric structures of the parent methylsydnone and its conjugate acids were studied by the semiempirical MNDO method. Protonation at the exocyclic carbonyl oxygen yields the most stable acid in agreement with some findings obtained for FSO_3H-SbF_5 solution. Since other experimental evidence indicates that protonation in aqueous acid occurs at the N(5) position, it appears that the influence of solvent cannot always be neglected. It is found that protonation at the endocyclic oxygen site leads to formation of an acyclic chain possessing a keten-like fragment.

SYDNONES are prototypes of a large class of interesting mesoionic compounds for which a single valence bond structure cannot be drawn without invoking two formal charges of opposite sign ($\mp$). They have attracted considerable attention from both experimental and theoretical standpoints due to their zwitterionic character. Much of the chemistry of sydnones may be found in reviews by Baker and Ollis [1] and Stewart.[2] Theoretical papers involve CNDO/2,[3] INDO, and *ab initio* [4] calculations. A MINDO/3 study of the related oxazoles and imidazoles has been reported.[5] The protonated species were, however, treated only by an early application of a rather crude ω-HMO technique.[6] As a part of our larger project of investigating the structure and properties of protonated compounds [7,8] we applied the MNDO scheme [9] to methylsydnone and its conjugated acids. This is of some importance because experimental evidence on the structure of alkysydnones and their protonated counterparts is partial, indirect, and controversial.[10-12] The MNDO method seems to be particularly suitable for this purpose because it describes systems possessing two neighbouring atoms with lone pairs significantly better than other semiempirical approaches.

RESULTS AND DISCUSSION

All independent geometrical parameters are varied, and computationally optimal structures are given in Table 1. Experimental data on compounds with sydnone rings are not very abundant. The structure of methylsydnone is compared with values obtained for 3,3′-ethylenebissydnone (dimer) by the *X*-ray technique.[13] The MNDO bond angles are in good accord with experiment, a feature which was noted earlier in studying the electronic structure of ascorbic acid and its anions.[14] The estimated interatomic distances are in qualitative agreement with the *X*-ray data. Part of the discrepancy arises from crystal packing forces and dimerization of this model compound while the rest appears to be due to inherent imperfections of the MNDO scheme. The structural characteristics of methylsydnone are best interpreted in terms of re-hybridization and π-electron bond orders. The former provides rationalization for the gross variations in geometry of organic molecules.[15-17] The latter can be conveniently considered as a perturbational correction of the mobile π-electrons which is imposed on the σ-molecular skeleton.[16] The closed shell single-configuration Slater determinant wavefunction is invariant to orthogonal transformations of the basis set and yet it contains information about hybridization stored in the charge density matrix.[18,19] The *s*-character of the hybrid placed on the nucleus A pointing to an atom B is given by equation (1) where equation (2) applies and

$$W_s^{AB} = 100\, W_{s(AB)}/[W_{s(AB)} + W_{px(AB)} + W_{py(AB)} + W_{pz(AB)}] \quad (1)$$

$$W_{\mu(AB)} = (1/2) \sum_{\nu}^{B} P_{\mu\nu}^2 \quad (2)$$

$P_{\mu\nu} = 2 \sum_{i=1}^{occ.} c_{\mu i}\, c_{\nu i}$ are conventional bond orders.

It is well known that an increase in *s*-character of two geminal hybrid orbitals opens up their mutual angle. This explains the asymmetry in bond angles at positions C(2) and C(3) where the experimental bond angles O(1)C(2)C(3) and C(2)C(3)H(11) are 136.5 and 135.0°, respectively. The hybrid *s*-characters (in %) are $W_s^{C(2)C(3)}$ 43.9 and $W_s^{C(2)O(1)}$ 30.9, indicating significant increase in the average *s*-character as compared to the canonical sp^2 value. The bond angle O(1)C(2)C(3) is therefore larger than 120°. Hence a distortion of the bond angles around the carbonyl group is to be ascribed to the rehybridization at C(2) indicating that the intramolecular ' charge transfer interaction ' between the carbonyl oxygen and bromine atom in 3-*p*-bromophenylsydnone is of little importance in determining the geometry of the latter molecule.[20] Similar conclusion holds for the C(2)C(3)H(11) angle where the relevant hybrids have the *s*-characters of $W_s^{C(3)C(2)}$ 32.8 and $W_s^{C(3)H(11)}$ 42.0, respectively. The large *s*-content in a localized orbital describing the C(3)–H(11) bond is reflected in the relatively short bond distance of 1.077 Å which should be compared with the distance *d*[C(7)–H(8)] of 1.111 Å of the methyl group as calculated by the MNDO method. The corresponding *s*-character of $W_s^{C(7)H(8)}$ is 27.2%, compatible with the increase in bond length. Another bond of interest is C(2)–O(6) described by 33.7—11.4 (in %) non-integer hybridization parameters. The large difference in the site of carbon and oxygen hybrid orbitals ψ[C(2)–O(6)] and ψ[O(6)–C(2)] leads to rather inefficient overlap according to Maccoll's theorem.[21] This rather poor overlap is in addition a consequence of the large disparity in hybrid compositions. It was shown that the optimal bonding interaction is achieved when the bonding partners have similar hybridizations.[22] It is, therefore, not surprising that the C(2)–O(6) bond is relatively long and weak. One concludes on the grounds of the same qualitative arguments that the N(5)–O(6) bond is stronger than C(2)–O(6), which is reflected in the difference in their bond distances. Comparison of the bonding parameters for methylsydnone with those found in the model compounds formaldehyde, keten, acetic acid, and penta-2,4-

TABLE 1

Comparison of the MNDO geometries with available experimental data [a]

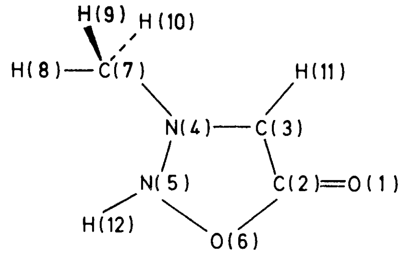
Compound	Bond distances (Å)			Bond angles (°)		
	Bond	MNDO	Experimental	Angle	MNDO	Experimental
(3), ΔH_f 1.4 kcal mol^{-1}	C(1)–C(2)	1.219	1.218	O(1)–C(2)–C(3)	137.9	136.5
	C(2)–C(3)	1.455	1.403	C(2)–C(3)–N(4)	104.0	106.5
	C(3)–N(4)	1.381	1.342	C(3)–N(4)–N(5)	112.1	115.3
	N(4)–N(5)	1.313	1.318	N(4)–N(5)–O(6)	109.3	103.6
	N(5)–O(6)	1.288	1.381	C(2)–C(3)–H(11)	130.3	135.0
	C(2)–O(6)	1.420	1.421	N(5)–N(4)–C(7)	121.0	117.9
	N(4)–C(7)	1.484	1.477	N(4)–C(7)–H(8)	110.8	
	C(7)–H(8)	1.111		N(4)–C(7)–H(9)	109.0	
	C(7)–H(9)	1.112				
	C(3)–H(11)	1.077				
(4), ΔH_f 156.8 kcal mol^{-1}	O(1)–C(2)	1.313		O(1)–C(2)–C(3)	131.9	
	C(2)–C(3)	1.412		N(4)–C(3)–C(2)	102.3	
	C(3)–N(4)	1.410		N(5)–N(4)–C(3)	111.3	
	N(4)–N(5)	1.305		O(6)–N(5)–N(4)	109.3	
	N(5)–O(6)	1.286		N(5)–N(4)–C(7)	121.8	
	C(2)–O(6)	1.382		N(4)–C(7)–H(8)	110.0	
	N(4)–C(7)	1.511		N(4)–C(7)–H(9)	107.0	
	C(7)–H(8)	1.110		N(4)–C(7)–H(10)	107.7	
	C(7)–H(9)	1.111		C(2)–C(3)–H(11)	132.7	
	C(7)–H(10)	1.112		C(2)–O(1)–H(12)	117.4	
	C(3)–H(11)	1.083				
	O(1)–H(12)	0.957				
(1), ΔH_f 186.0 kcal mol^{-1}	O(1)–C(2)	1.204		O(1)–C(2)–C(3)	134.1	
	C(2)–C(3)	1.520		C(2)–C(3)–N(4)	105.5	
	C(3)–N(4)	1.326		C(3)–N(4)–N(5)	111.3	
	N(4)–N(5)	1.423		N(4)–N(5)–O(6)	107.6	
	N(5)–O(6)	1.331		N(5)–N(4)–C(7)	119.3	
	O(6)–C(2)	1.401		N(4)–C(7)–H(8)	108.1	
	C(7)–N(4)	1.509		N(4)–C(7)–H(9)	109.3	
	C(7)–H(8)	1.112		N(4)–C(7)–H(10)	108.4	
	C(7)–H(9)	1.112		C(2)–C(3)–H(11)	126.9	
	C(7)–H(10)	1.111		O(6)–N(5)–H(12)	108.8	
	C(3)–H(11)	1.092				
	N(5)–H(12)	1.048				
(2), ΔH_f 173.6 kcal mol^{-1}	O(1)–C(2)	1.163		O(1)–C(2)–C(3)	176.2	
	C(2)–C(3)	1.358		C(2)–C(3)–N(4)	125.7	
	C(3)–N(4)	1.414		C(3)–N(4)–N(5)	129.9	
	N(4)–N(5)	1.271		N(4)–N(5)–O(6)	116.7	
	N(5)–O(6)	1.279		C(7)–N(4)–N(5)	113.7	
	C(2)–O(6)	2.722		N(4)–C(7)–H(8)	110.7	
	O(6)–H(12)	0.968		N(4)–C(7)–H(9)	107.7	
	C(3)–H(11)	1.095		C(2)–C(3)–H(11)	117.7	
	N(4)–C(7)	1.531		N(5)–O(6)–H(12)	110.4	
	C(7)–H(8)	1.111				
	C(7)–H(9)	1.111				

[a] The experimental data refer to the *X*-ray structure of 3,3′-ethylenebis-sydnone (dimer) reported in ref. 13.

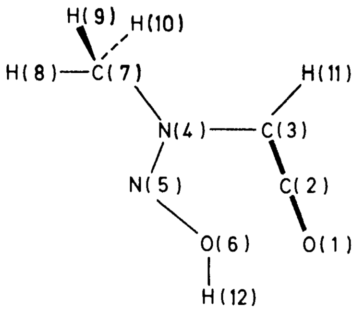
dienoic acid is illuminating. The exocyclic C=O bond seems to be longer in sydnone relative to that in formaldehyde due to a slight decrease in *s*-character ($s_{C(2)O(1)}$ 30.9% in sydnone and s_{CO} 39.0% in formaldehyde) and additional decrease in π-electron mixed charge density. The values of the π-bond orders are 0.81 and 0.95 for sydnone and formaldehyde, respectively (Table 2). It should be pointed out here that the MNDO bond orders cannot be directly compared with the *ab initio* ones [4] because the latter involve overlap integrals. Therefore the MNDO values are considerably higher. Nevertheless, both *ab initio* and MNDO results exhibit significant π-electron delocalization over the sydnone skeleton. The smallest π-bond orders are found in C(2)–O(6) and N(5)–O(6) bonds. It is interesting to observe that MNDO bond orders for these bonds are comparable to the value calculated for the C(10)–O(12) bond in the model compound penta-2,4-dienoic acid. Taking into account other relevant data one concludes that the π-electron delocalization is more pronounced over the chain of O(1)–C(2)–C(3)–N(4)–N(5) in sydnone than over the acyclic counterpart in penta-2,4-dienoic acid. It should be pointed out, however, that the π-delocalization in the latter compound is small because it belongs to a class of classical polyenes which have a dominant single valence bond scheme.[16,23] In any case, the present results support the conclusion of Barber *et al.*[4] that the sydnone ring is best represented by formula c in the Figure, if the dashes are to be used at all.

Analysis of the formal electronic densities (Table 2) reveals a large degree of charge alternation in sydnone. It also shows that the sum of effective charges of ring atoms is negative (−0.15) as well as the charge of the exocyclic oxygen (−0.31) indicating that bonding scheme a (Figure) is misleading. The highest electron density is found at C(3) compatible with the ^{13}C n.m.r. results. The measured C(3) chemical shift was considerably higher than that observed in other unsubstituted heterocycles.[24] We conclude that the distribution of charge fits the qualitative picture offered by the n.m.r. measurements.

Protonation is most favoured at the exocyclic oxygen O(1) (Table 1) consistent with chemical intuition and the high electron density at this position. Protonation is followed



(1)



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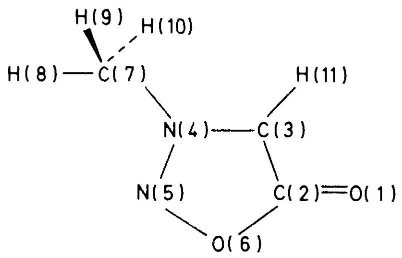
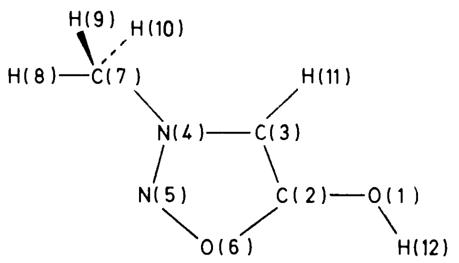


(3)



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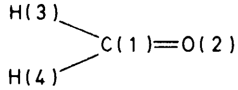
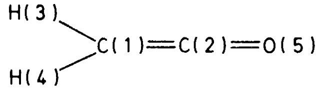
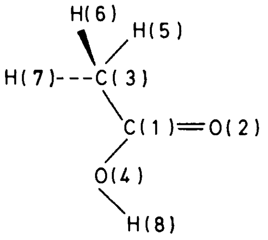


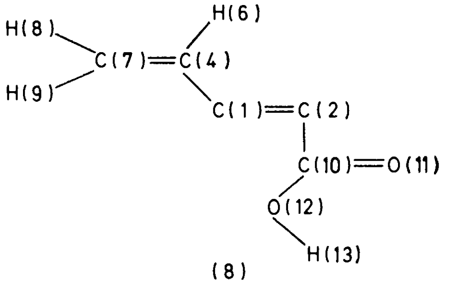
(5)



(6)

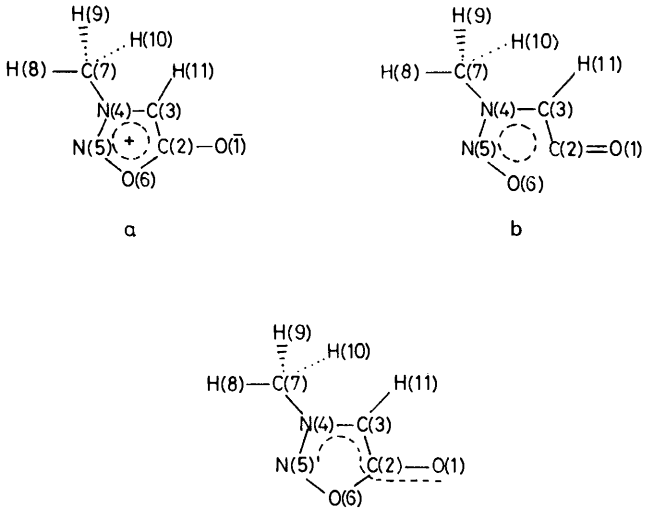


(7)



(8)

by the formation of a ' normal ' O–H bond and significant redistribution of the charges over the ring. A dramatic loss of electron density is observed at C(3), O(6), and N(5). The latter assumes in the protonated form a rather high positive atomic charge (+0.15). A survey of the data displayed in Table 2 shows a considerable decrease of the σ-population of the attacked atom O(1) due to a formation of the O(1)–H(12) σ-bond. The increased effective positive charge of the σ-core of O(1) causes a flow of mobile π-electrons toward the site of protonation. Thus the π-electron density at O(1) is increased by 0.38, the largest donors of π-electron charge being C(3) (0.18) and N(5) (0.17). The π-electron delocalization in this respect plays a decisive role. The geometric changes upon the protonation are most pronounced in the O(1)C(2)C(3)O(6) fragment. The O(1)–C(2) bond length is larger due to a decrease of π-electron bond order. There is an appreciable increase in double bond character of the C(2)–C(3) bond in the protonated form and also a strengthening of the C(2)–O(6) bond due to the increase of the bond order and average *s*-character. Finally, it should be mentioned that the charge flow does not completely neutralize the incoming proton. Thus the O–H bond exhibits the largest polarity. The considerable ionic character of the C(3)–H(11) bond is noteworthy. Protonation at O(6) leads to cleavage of the C(2)–O(6) bond, the interatomic distance being 2.72 Å. The proton produces a perturbation over the whole system yielding an acyclic chain with a C(3)=C(2)=O(1) keten-like structural group. It is of interest to compare the hybridization of C(2) with



a

b

c

Various representations of bonding in methylsydnone

TABLE 2

Charge and overlap population analysis of the compounds (1)—(8)

		Atomic charge			π Bond overlap charge	
Compound	Atom	Effective	σ	π	Bond	π-mixed charge
(3)	O(1)	−0.31	4.86	1.45	O(1)–C(2)	0.81
	C(2)	0.34	2.85	0.82	C(2)–C(3)	0.41
	C(3)	−0.25	2.94	1.31	C(3)–N(4)	0.59
	N(4)	−0.05	3.69	1.36	N(4)–N(5)	0.65
	N(5)	−0.04	3.73	1.31	N(5)–O(6)	0.35
	O(6)	−0.15	4.38	1.76	C(2)–O(6)	0.36
	C(7)	0.20	3.80			
	H(8)	0.05	0.95			
	H(9)	0.03	0.97			
	H(10)	0.03	0.97			
	H(11)	0.15	0.85			
(4)	O(1)	−0.14	4.32	1.83	O(1)–C(2)	0.44
	C(2)	0.26	2.84	0.90	C(2)–C(3)	0.70
	C(3)	−0.04	2.91	1.13	C(3)–N(4)	0.53
	N(4)	−0.09	3.75	1.34	N(4)–N(5)	0.71
	N(5)	0.15	3.71	1.14	N(5)–O(6)	0.46
	O(6)	−0.03	4.35	1.68	C(2)–O(6)	0.45
	C(7)	0.20	3.80			
	H(8)	0.08	0.92			
	H(9)	0.07	0.93			
	H(10)	0.07	0.93			
	H(11)	0.20	0.80			
	H(12)	0.28	0.72			
(2)	O(1)	−0.10	4.84	1.26	O(1)–C(2)	0.91
	C(2)	0.29	2.87	0.84	C(2)–C(3)	0.18
	C(3)	0.21	3.10	0.70	C(3)–N(4)	0.88
	N(4)	−0.13	3.76	1.37	N(4)–N(5)	0.19
	N(5)	0.07	3.54	1.39	N(5)–O(6)	0.12
	O(6)	−0.15	4.26	1.89	C(2)–O(6)	0.32
	C(7)	0.19	3.81			
	H(8)	0.07	0.93			
	H(9)	0.09	0.91			
	H(10)	0.06	0.94			
	H(11)	0.20	0.80			
	H(12)	0.20	0.80			
(1)	O(1)	0.02	4.38	1.60	O(1)–C(2)	0.69
	C(2)	0.41	2.79	0.80	C(2)–C(3)	0.65
	C(3)	−0.25	2.83	1.43	C(3)–N(4)	0.38
	N(4)	0.03	3.68	1.29	N(4)–N(5)	0.80
	N(5)	0.13	3.81	1.06	N(5)–O(6)	0.39
	O(6)	−0.20	4.36	1.84	C(2)–O(6)	0.11
	C(7)	0.20	3.81			
	H(8)	0.08	0.92			
	H(9)	0.07	0.94			
	H(10)	0.07	0.94			
	H(11)	0.17	0.83			
	H(12)	0.29	0.71			
(5)	C(1)	0.29	3.01	0.70	C(1)–O(2)	0.95
	O(2)	−0.29	4.99	1.30		
(6)	C(1)	−0.28	2.98	1.30	C(1)–C(2)	0.86
	C(2)	0.26	2.79	0.94	C(2)–O(5)	0.91
	O(5)	−0.17	4.42	1.75		
(7)	C(1)	0.33	2.94	0.74	C(1)–O(4)	0.40
	O(2)	−0.37	4.96	1.40	C(1)–O(2)	0.87
	O(4)	−0.31	4.43	1.88		
(8)	C(1)	0.04	3.06	0.91	C(10)–O(11)	0.85
	C(2)	−0.12	3.03	1.08	C(2)–C(10)	0.22
	C(10)	0.38	2.88	0.74	C(1)–C(2)	0.94
	O(11)	−0.37	4.96	1.41	C(1)–C(4)	0.26
	C(4)	−0.11	3.07	1.04	C(4)–C(7)	0.96
	C(7)	−0.02	3.08	0.94	C(10)–O(12)	0.39
	O(12)	−0.31	4.43	1.88		

the equivalent atom in keten. The hybrid orbitals ψ[C(2)–O(1)] and ψ[C(2)–C(3)] have in O(6)-protonated methylsydnone *s*-characters of 40.6 and 55.6%, respectively, while in keten the corresponding values are 39.1 and 58.9%. One observes that the sum of *s*-characters in methylsydnone is significantly lower than 100% indicating a large degree of σ-delocalisation in this molecule. On the contrary, the sum of *s*-characters in keten is 98%. The delocalization of mobile π-electrons in the conjugate acid in question is noticeable. The N(4)–N(5) bond exhibts the largest double bond character. It is interesting that the electron density at O(6) is increased compared with the value for parent compound. Thus the electron flow overcompensates for the effect of the proton. C(3) again carries a large portion of electron density while the effective positive charge at C(2) has a particularly high value (0.41). Surprisingly enough, the O(1) becomes slightly positive. It should be strongly pointed out that all these values must be taken with due caution because of the inadequacies inherent in the Mulliken population analysis. Protonation at N(5) enchances delocalization along the sequence of atoms O(1)-C(2)-C(3)-N(4). O(1) is now negatively charged although the loss in π-electron density is considerable (*ca.* 0.2) compared with the parent methylsydnone. C(3) carried a high positive charge since its π-electron population becomes smaller by roughly $\frac{1}{2}$. This is compatible with ^{13}C n.m.r. data which show a downfield shift in the C(3) resonance when the solvent is changed from $CDCl_3$ to aqueous acid.[12] Since our calculations indicate that protonation at N(5) gives the most unstable conjugate acid we conclude that solvent plays an important role in its stabilization. This conclusion is supported by the finding of Olah *et al.*[11] according to which phenylsydnone is protonated at carbonyl oxygen in FSO_3H-SbF_5 solution in full agreement with our results for methylsydnone. It is also noteworthy that phenylsydnone is substantially protonated while it is suspected that protonation at N(5) is only partial.[12] This may well be the consequence of the smaller stability of the latter conjugate acid as evidenced by the MNDO calculations.

To conclude, the protonation of methylsydnone at the carbonyl oxygen yields the most stable conjugate acid but other protonated forms may well occur due to the stabilizing effects of the solvents employed.

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