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Semiempirical MNDO Study of Phenyl-sydnone and its Protonated Forms

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The electronic and geometric structure of the phenylsydnone and its conjugated acids is investigated by the semiempirical MNDO method. A comparison of the interatomic bond distances and bond angles with available experimental data for the parent compound reveals only qualitative accordance. It appears that the MNDO method is unable to reproduce finer details of the molecular geometry of sydnones. The gross changes caused by protonation are described, however, in agreement with chemical intuition and available experimental data. The variation in geometric parameters is interpreted in terms of rehybridization and π-electron bond orders. The most stable conjugated acid is that with a proton bonded to the keto-oxygen in accordance with the highest electron density concentration.

INTRODUCTION

Sydnones, discovered as early as 1935 by Earl and Macknay,[1] are archetypes of a broad class of mesoionic compounds which exhibit unusual physico-chemical features. Conceptually speaking, they cannot be characterized by a single VB structure without imposing formal ± 1 charges belonging either to the five membered ring or to the attached keto-oxygen. Concomitantly, sydnones aroused a long lasting interest which resulted in a large number of papers devoted to their structure and properties. The experimental findings were discussed at length in several review articles.[2–4] A normal coordinate analysis of 3-methyl-sydnone[5] and X-ray investigation of several sydnone-derivatives[6] have been reported recently. Theoretical studies of the sydnones range in their levels of sophistication from simple π-electron theories to versatile *ab initio* calculations. They involve HMO,[7] IHMO,[8] PPP[9] treatments with explicit consideration of π-electrons only, CNDO/2,[10,11] EHT and IEHT all-valence electrons calculations performed on the parent sydnone molecule.[10] The IEHT approach was used in order to get some insight into the electron

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distribution over the ring by computing the density maps.[12] The semiempirical schemes based on the ZDO approximation include further,[13] INDO-CI[6] studies of some alkyl- and aryl-substituted sydnones and MINDO/3 calculations on related oxazoles and imidazoles.[14] The *ab initio* calculations of the approximate DZ-quality were carried out on 3-methyl-sydnone.[13] Substantially less theoretical work has been devoted to conjugated acids of sydnones. Roche and Kier[8] considered protonated alkyl-sydnones employing the simple IHMO technique. Continuing our interest in structural and energetic properties of protonated organic bases[15,16] we investigated protonated species of 3-methyl-sydnone by the MNDO method.[16] This paper is an outgrowth of the previous work and describes the results of the MNDO computations on 3-phenyl-sydnone and its conjugated acids. The MNDO method[17] seems to be well suited to this purpose because it is capable of optimizing all independent geometric parameters within the approximate framework of the adopted semiempirical scheme. This is of some importance because »standard« bond distances and valence angles may introduce unnecessary bias. The limited accuracy of the MNDO method does not play a significant role in this connection because the relative values of structural parameters along the family of similar molecules are substantially better reproduced than the true geometric parameters. Hence, one can expect a fairly consistent picture for the series of closely related compounds. Furthermore, the choice of the MNDO approach is quite appropriate because this method describes systems involving two nearest-neighbour heteroatoms possessing lone pair(s) better than any other current semiempirical scheme. Last but not least, the MNDO procedure is a reasonable compromise between the accuracy of the results and computational costs. Hence, we believe that this work will throw some more light on the structure of sydnones. The improved version[18] of the sandard programme[17] was used in the present study.

RESULTS AND DISCUSSION

The calculated interatomic bond distances, valence and dihedral angles are presented in Table I. A comparison with the X-ray data for 3-phenyl-sydnone[19] reveals that agreement with the experiment is only moderate. Since the X-ray structural parameters for related 3-phenyl-sydnone, 4-(4-methyl-1-buten-2-yl)-3-phenylsydnone and 4-(cyclohexen-1-yl)-3-phenylsydnone compounds are fairly consistent[6] the one concludes that discrepancies between the experiment and MNDO method should be ascribed to the imperfections of the latter and (to a lesser extent) to the solid state crystal and/or hydrogen bonds effects. It is noteworthy that molecular shape (bond angles) is somewhat better reproduced by the MNDO procedure than its size (bond distances). In this respect MNDO shows improvement over the MINDO/3 method.[20] The sydnone ring is found to be planar in accordance with the experimental findings in phenylsydnone[19] and a number of other derivatives.[6] The dihedral angle between the phenyl and sydnone rings is estimated to be ~10° against 30° obtained by X-ray measurements.[19] It should be mentioned, however, that dihedral angles in the closely related compounds span a range between 30°—64°, indicating that the low value in *1* is probably a consequence of the crystal effects, particularly because the calculated rotation barrier is low (3 kcal/mol). On the other hand, the O(1)—C(2)—C(3) angle, which has the characteristic value of 136° for a large number of substituted sydnones,

TABLE I

The Structural Parameters and Heats of Formation of Phenyl-sydnone and its Protonated Forms as Calculated by the MNDO Method[a]

	Bond distances/Å			
Bonds	*1*	*2*	*3*	*4*
O_1—C_2	1.219 (1.221)	1.315	1.164	1.205
C_2—C_3	1.454 (1.413)	1.410	1.356	1.517
C_3—N_4	1.382 (1.347)	1.413	1.416	1.328
N_4—N_5	1.314 (1.313)	1.306	1.273	1.424
N_5—O_6	1.289 (1.373)	1.288	1.281	1.332
O_6—C_2	1.419 (1.411)	1.382	2.718	1.402
N_4—C_7	1.447 (1.438)	1.456	1.477	1.452
C_7—C_8	1.415 (1.391)	1.416	1.416	1.417
C_8—C_{10}	1.405 (1.394)	1.405	1.405	1.406
C_{10}—C_{11}	1.407 (1.394)	1.410	1.409	1.410
C_{11}—C_{12}	1.406 (1.393)	1.409	1.408	1.411
C_{12}—C_{13}	1.408 (1.394)	1.406	1.407	1.405
C_{13}—C_7	1.413 (1.394)	1.415	1.415	1.414
C_{13}—H_{14}	1.091	1.091	1.091	1.091
C_{12}—H_{15}	1.091	1.092	1.092	1.092
C_{11}—H_{16}	1.091	1.092	1.092	1.092
C_{10}—H_{17}	1.091	1.091	1.091	1.092
C_3—H_{18}	1.076	1.083	1.096	1.091
C_8—H_9	1.091	1.091	1.091	1.091
O_1—H_{19}	—	0.956	—	—
O_6—H_{19}	—	—	0.967	—
N_5—H_{19}	—	—	—	1.046
$O_1C_2C_3$	137.9 (135.7)	131.9	176.1	134.1
$C_2C_3N_4$	103.6 (105.9)	102.1	125.6	105.3
$C_3N_4N_5$	112.4 (114.9)	111.3	129.9	111.6
$N_4N_5O_6$	109.0 (104.4)	109.3	116.4	107.3
$N_5N_4C_7$	120.6 (118.1)	121.4	113.1	120.0
$N_4C_7C_8$	119.2 (118.8)	118.7	118.8	118.9
$C_7C_8H_9$	121.6	122.1	122.2	122.0
$C_7C_8C_{10}$	118.9 (120.3)	118.5	118.5	118.7
$C_8C_{10}C_{11}$	120.5 (119.0)	120.4	120.5	120.5
$C_{10}C_{11}C_{12}$	120.1 (120.5)	120.2	120.2	120.1
$C_{11}C_{12}C_{13}$	120.4 (120.9)	120.7	120.6	120.5
$C_{12}C_{13}H_{14}$	119.3	119.5	119.4	119.0
$C_{11}C_{12}H_{15}$	120.0	119.9	119.9	120.0
$C_{10}C_{11}H_{16}$	120.0	119.9	119.9	120.0
$C_{11}C_{10}H_{17}$	120.0	120.0	120.0	119.9
$C_2C_3H_{18}$	130.4 (134.0)	132.9	117.8	127.3
$C_2O_1H_{19}$	—	117.1	—	—
$N_5O_6H_{19}$	—	—	110.3	—
$O_6N_5H_{19}$	—	—	—	108.9
	Dihedral angles (in degrees)			
Planes	*1*	*2*	*3*	*4*
$C_8C_7N_4 < C_7N_4N_5$	109.9	117.7	116.7	114.1
$C_7N_4N_5 < N_4N_5O_6$	180.0	180.0	179.7	178.1
$H_{19}O_1C_2 < O_1C_2O_6$	—	0.2	—	—
$H_{19}O_6N_5 < O_6N_5N_4$	—	—	180.0	—
$H_{19}N_5O_6 < N_5O_6C_2$	—	—	—	—118.6
Atoms	Nonbonded distances (in Å)			
$H_9 \ldots H_{18}$	3.265	3.098	2.804	3.226
$H_{14} \ldots H_{19}$	—	—	—	3.674
Heats of formation (in kcal/mol)	30.3	183.8	201.4	210.7

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[a] Experimental structural data are given in parentheses.

is well reproduced by the calculation (137.9°). The endocyclic angles are in reasonable agreement with experimental ones (Table I). The valence angles of the phenyl ring are of some interest. Domenicano *et al.* have shown by comprehensive study that the benzene ring is deformed by substitution.[21-23] The electronegative N(4) atom at ipso position, which in turn carries substantial positive formal charge (vide infra), should increase the value of the C(8)—C(7)—C(13) angle according to the Walsh-Bent rule.[24,25] This is a consequence of rehybridization at the C(7) atom, since the σ-electron withdrawing substituent prefers *vis a vis* hybrids possessing high p-content (vide infra). Hence, the increased s-character of the hybrids describing C(7)—C(8) and C(7)—C(13) bonds tends to open up the corresponding bond angle. This is borne out by X-ray measurements[19] which give 122.6° for this angle. The MNDO value of 121.4° is compatible with the experimental finding and the simple Walsh-Bent model. Other bond angles are in fair agreement with the X-ray data. The largest discrepancy was found for $N_4N_5O_6$ angle (4.6°) with three adjacent heteroatoms, presumably due to the far too short N_5—O_6 distance. This indicates limitations of the MNDO scheme in revealing subtle structural facets of organic molecules. The calculated interatomic bond angles and distances are probably best understood in terms of the rehybridization of local atomic orbitals and changes in π-bond orders. We have provided conclusive evidence that hybridization gives a rationale for a large body of organic stereochemistry.[26-28] It is interesting that hybridization indices are immanently contained in the charge density matrix[29,30] although the total wavefunction is invariant to all orthogonal transformations of basis functions. The s-character of the hybrid placed on the nucleus A forming the A—B bond is defined:[29]

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

where

$$W_{\mu\,(AB)} = (1/2) \sum_{\nu}^{B} P_{\mu\nu}^{2} \; (\mu = s,\, px,\, py,\, pz) \tag{2}$$

and $P_{\mu\nu}$ are conventional charge density matrix elements introduced by Coulson[31] in his treatment of π-electron charge distributions. The formula (1) can be easily interpreted as a portion of the properly normalized mixed (active) charge arising due to the mixing of s_A orbital with the valence-shell AOs of the neighbouring atom B. The effect of mobile π-electrons in planar conjugated systems can be conveniently considered in Coulson's sense[31] as a perturbation imposed on the molecular σ-skeleton. The s-characters and π-bond orders obtained by the MNDO wave functions are given in Table II. One observes that the hybrid placed at the atom C_7 and directed toward N_4 nitrogen of the sydnone ring has s-content of 24.0%. This is substantially lower than 33.3% characterizing the canonical sp^2 state in accordance with the Walsh-Bent rule as discussed above. Since the χ (C_7—N_4) hybrid is practicaly of the sp^3 type, it follows that the remaining two hybrids centered at C_7 have s-characters significantly higher than 33%, implying that C_7—C_8 and C_7—C_{13} bonds are bent. This has been actually observed by Hope[19] who found that electron density maxima are placed outside the straight lines passing through C_7—C_8 and C_7—C_{13} centers. This is a consequence of the competition between the angle opening forces at C_7 and a tendency of other angles of the phenyl ring

TABLE II

S-characters of the Local Hybrid Orbitals (in %) and π-Electron Bond Orders in Phenyl-sydnone and its Protonated Forms, as Obtained by the MNDO Method

s-characters bonds	*1*	*2*	*3*	*4*
O_1—C_2	10.1—30.9	12.5—31.3	14.3—40.6	10.1—31.2
C_2—C_3	44.0—32.8	44.9—32.6	55.6—34.5	40.7—29.8
C_3—N_4	23.9—28.3	22.9—26.5	27.0—28.4	25.2—27.9
N_4—N_5	25.1— 8.7	23.4— 9.3	25.7—11.5	21.4— 8.7
N_5—O_6	8.7— 9.1	10.3—10.1	8.4— 8.8	10.8— 7.8
N_4—C_7	29.7—24.0	31.8—22.5	29.3—22.4	31.6—22.4
C_2—O_6	23.8—11.4	23.0—10.9	6.6—12.7	27.3—10.9
C_3—H_{18}	42.2	43.5	39.3	41.7
O_1—H_{19}	—	15.7	—	—
O_6—H_{19}	—	—	14.9	—
N_5—H_{19}	—	—	—	17.0
		π-bond orders		
O_1—C_2	0.802	0.427	0.682	0.911
C_2—C_3	0.408	0.710	0.663	0.180
C_3—N_4	0.592	0.524	0.376	0.884
N_4—N_5	0.650	0.711	0.804	0.192
N_5—O_6	0.343	0.446	0.378	0.114
C_2—O_6	0.358	0.449	0.112	0.323
C_7—N_4	0.144	0.165	0.154	0.157

to remain as close as possible to the 120° value. The hybrids at C_2 pointing toward O_1 and C_3 possess s-characters of 30.9% and 44.0%, respectively, being thus on average significantly richer in s-orbital than pure sp^2 hybrids. Hence, the O_1—C_2—C_3 angle is larger than 120° assuming the value of 138°. The more electronegative atoms use higher p-character in hybrids due to the more pronounced difference between ns and np atomic levels, the former being more stable. The hybridization of N_5 and O_6 is of some interest. The N_5 atom employs ~9% s-content hybrids to form N_5—O_6 and N_4—N_5 bonds. This means that the lone pair lying in the plane of the sydnone ring has a very high s-character. The same holds for O_6 oxygen which uses 9.1% and 11.4% s-character in N_5—O_6 and C_2—O_6 bonds. The high s-content of the lone pairs is in accordance with the high electron density found behind N_5 and O_6 atoms by IEHT calculations[12] and by X-ray measurements.[19] The small s-character involved in the N_5—O_6 bond is compatible with the low electron density in the bond region established by X-ray analysis.[19] The variation in hybridization of the same atom in various environments is of some interest. We found that in hydrocarbons hybrids forming the same bond tend to possess the same composition as close as possible.[28] This tendency is observed in heteroatomic situations too. For example, the hybrids emanating from the O_6 atom toward C_2 and N_5 atoms have s-characters 11.4% and 9.1%, respectively. Hence, the $\chi(O_6—C_2)$ hybrid has a slightly increased s-content because its *vis-a-vis* partner has the s-character of 23.8% which is considerably higher than the $\chi(N_5—O_6)$ hybrid possessing only 9%. A slight increase in s-content is found in the $\chi(O_1—C_2)$ hybrid (10.1%) because its partner orbital $\chi(C_2—O_1)$ has the relatively high s-character of 30.9%. The hybrid orbitals centered on carbon and nitrogen atoms follow the same pattern. It appears that the rule of maximum possible similarity of hybrids belonging to the same bond,[28] Maccoll's theorem[32] and Walsh-Bent rule[24,25] are intimately related. Some caution is, however, necessary if bonds possessing widely different bond energies compete for s-characters. Nevertheless, the rule of maximum similarity is very useful in discussing rehybridization. Finally, it is interesting to mention that the C_3—H bond is represented by a hybrid with s-content of 42.2% indicating that this bond is significantly stronger than those in ethylene. The remaining hybridization indices exhibit only small variation along the 1—4 series.

Examination of the π-bond orders (Table II) reveals that O_1—C_2 exo-bond is to a large extent localized, exhibiting a relatively high π-bond order of 0.80 which should be compared with the bond order of 0.95 found in formaldehyde.[16] Hence, the O_1—C_2 bond participates in the delocalization which is extended over the O_1—C_2—C_3—N_4—N_5 fragment. The extent of the π-electron delocalization over the O_6 centre and across the N_4—C_7 bond is very small, if not negligible. This is best illustrated by comparison with the model penta-2,4--dienoic acid which is a classical polyene and consequently has small conjugation. The bond-order of the hydroxy oxygen and the neighbouring carbon atom in this compound is 0.39,[16] being thus slightly higher than in C_2—O_6 bond (0.36) of the sydnone ring. Therefore, the participation of the O_6 atom in π-electron delocalization can be neglected at least in the first approximation. This is in accordance with the findings of other workes.[6,10,12,13] The most appropriate structural formula of phenyl-sydnone is depicted in Figure 1.

Although this structural formula is not free from criticism, because dashes do not give the extent of delocalization over the system, it is more realistic than earlier representations by betaine form,[33] resonance stabilized azo-methine imines,[3] or the original »meso-ionic« structure.[2] Therefore, our results support earlier theoretical calculations.[6,10,12,13] However, we feel that the phenyl-sydnone should not be characterized as semiaromatic[6] because aromaticity is by definition a cyclic conjugation.

Analysis of the protonated species shows that the proton attached to the exo-oxygen (*2*) (Table IV) yields the most stable conjugated acid. It appears also that protonation has a pronounced effect on geometry and charge distribution of the sydnone ring. In addition, it slightly affects the dihedral angle between rings, which in compounds *2*, *3* and *4* assumes values between 114—118°. This is compatible with the increased delocalization in protonated species (vide infra). A survey of the bond distances and π-bond orders in *2* reveals that π-electrons are delocalized over the whole sydnone ring, including the O_6 oxygen atom (Figure 1). Therefore, the protonation at the carbonyl oxygen yields a sydnone ring with a significant aromatic character. The second most stable cation is obtained by the proton attack at the O_6 site (*3*). This leads to cleavage of the weak C_2—O_6 bond and a formation of the ketene-like fragment C(3)=C(2)=O(1) and the localized N(4)=N(5) double bond (Figure 1). The ketene structural group exhibits considerable rehybridization. The $\chi\,(C_2$—$O_1)$ and $\chi\,(C_2$—$C_3)$ hybrids have s-characters of 40.6% and 55.6%, respectively. The former has a lower s-content because it is directed toward the more electronegative oxygen atom. The sum of s-characters at the C_2 atom is lower than 100% (96%) indicating the presence of σ-delocalization

TABLE III

Energy Partitioning of the MNDO Energy Expectation Value in Phenyl-sydnone and its Protonated Forms (in eV)

Bonded atoms	*1*	*2*	*3*	*4*
O_1—C_2	—26.9	—19.6	—30.9	—27.9
C_2—C_3	—18.1	—20.6	—21.9	—14.5
C_3—N_4	—18.8	—17.5	—17.0	—22.7
N_4—N_5	—18.8	—19.7	—21.4	—13.7
N_5—O_6	—16.7	—16.9	—17.1	—14.9
O_6—C_2	—14.5	—16.4	—0.5	—15.0
N_4—C_7	—15.2	—14.6	—14.3	—14.6
C_7—C_8	—19.9	—19.7	—19.7	—19.5
C_8—H_9	—12.9	—12.9	—12.9	—12.9
C_8—C_{10}	—20.1	—20.2	—20.1	—20.3
C_{10}—H_{17}	—12.9	—12.9	—12.9	—12.9
C_{10}—C_{11}	—19.9	—19.8	—19.8	—19.7
C_{11}—H_{16}	—12.9	—12.9	—12.9	—12.8
C_{11}—C_{12}	—20.0	—19.9	—19.9	—20.0
C_{12}—H_{15}	—12.9	—12.9	—12.9	—12.9
C_{12}—C_{13}	—20.0	—20.1	—20.1	—20.0
C_{13}—H_{14}	—12.9	—12.9	—12.9	—12.9
O_1—H_{19}	—	—13.7	—	—
O_6—H_{19}	—	—	—13.7	—
N_5—H_{19}	—	—	—	—12.0
Nonbonded atoms	*1*	*2*	*3*	*4*
$H_9 \ldots H_{18}$	0.05	0.08	0.08	0.07
$H_{14} \ldots N_4$	0.07	0.07	0.11	0.05
$H_{14} \ldots N_5$	—0.01	0.07	0.06	0.02
$H_{14} \ldots H_{19}$	—	—	—	0.07

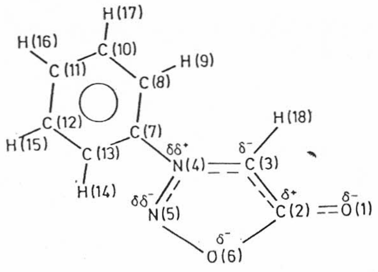
along the chain. One observes also a redistribution of the s-character among the bonds formed by the C_3 atom. Some of the s-character of the C(3)—H(18) bond is transferred into the χ (C_3—C_2) and χ (C_3—N_4) hybrids. The increase of the s-content of the (O_1—C_2) hybrid orbital is in accordance with the maximum similarity rule.

The least stable conjugated acid is obtained by the attachment of the proton to the N_5 nitrogen (*4*) in the plane of the ring. This form has highly localized O(1)=C(2) and C(3)=N(4) double bonds. It is interesting to point out that the pyramidal configuration of the N_5 atom with the out of plane H_{19} hydrogen (sp^3) is even less stable. The calculation gives the heat of formation of 222.9 kcal/mol for this isomer, which means that in-plane protonation (*4*) is by 12 kcal/mol more favourable.

Additional information about the strength of the covalent bonds is provided by the dissection of the total molecular energy into mono- and bicentric terms:[34–37]

$$E = \sum_{A} E_A + \sum_{A<B} \sum E_{AB} \qquad (3)$$

It was shown by Fischer and Kollmar that two centre terms E_{AB} are good measures of bond energies in hydrocarbons.[35] The same conclusion holds for



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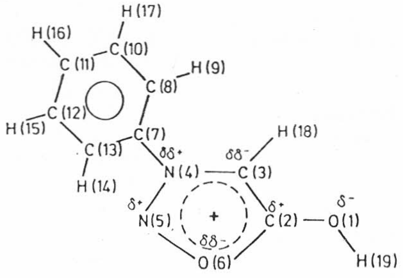

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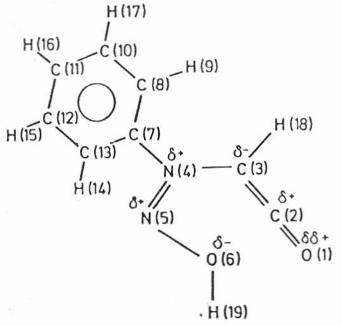

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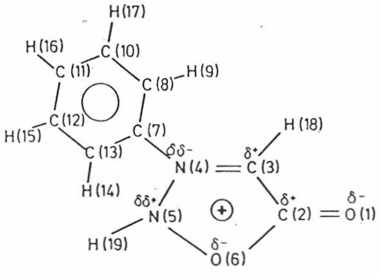

4

heteroatomic bonds.[37] The partitioning of the MNDO energy expectation values was made by using the ZDO approximation and the resulting two-centre terms are presented in Table III. Since they are closely related to bond energies we shall call them like that simply by changing their signs. Let us focus our attention to the O_1—C_2 bond first. The bond energy $E_{O(1)C(2)}$ drops appreciably in going from the parent compound *1* to the carbonyl protonated acid *2*. This is compatible with the change in the double bond character. The O_1—C_2 bond in *2* is essentially a single one while in *1* it has a high double bond character. The strongest O_1—C_2 bond is found in *3* due to the considerable increase in s-content of the local hybrid orbitals. It is interesting to observe that the O_1—C_2 bond in *4* is stronger than in parent phenyl-sydnone *1* as a consequence of a higher degree of localization (Figure 1). As mentioned earlier, the O_1—C_2 bond is delocalized in *1* over the O_1—C_2—C_3—N_4—N_5 fragment. The strength of the C_2—C_3 bond fits this picture. This bond is stronger in *1* than in *4*. The strongest C_2—C_3 bond is again found in *3* due to favourable hybridization. The highest C_3—N_4 bond energy is found in *4* again due to pronounced localization. On the other hand, the most stable N_4—N_5 bond is that in *3* for the same reason. The N_5—O_6 and C_2—O_6 bonds are weak. In particular, the $E_{C(2)O(6)}$ value is practically zero in *3* in accordance with the broken bond picture (Figure 1). It should be stressed that the N_5—O_6 bond in *1* is stronger than the C_2—O_6 bond though the average s-character is much higher in the latter. Hence, one has to be careful in discussing bond energies in terms of hybridization when bonds involving different atoms are in question. One observes also practically uniform distribution of C—C bond energies in the phenyl ring. The C—H bond energies of the phenyl are virtually the same. Finally, it should be mentioned that the nonbonded interactions between the H_{14} hydrogen and nitrogen atoms of the sydnone ring are very small. The same holds for the repulsions between H_9 and H_{18} atoms. To conclude this section, one can say that the energy partitioning technique gives useful information which is close to chemical intuition.

The formal atomic charges are of interest too, because they give good description of a number of molecular properties like diamagnetic susceptibility,[38] diamagnetic shielding,[39] ESCA shifts[40–42] etc. Their Coulomb interactions contribute significantly to the stability of molecules.[43] The formal atomic charges and π-electron densities of compounds *1*—*4* are given in Table IV. The largest negative charge in *1* is placed on the carbonyl oxygen while the C_2 bears the highest formal positive charge. Hence, the O_1=C_2 bond is

TABLE IV

Formal Atomic Charges and π-electron Densities (in Parentheses) in Phenyl-sydnone and its Protonated Forms, as Estimated by the MNDO Method (in | e | Units)

Atoms	*1*	*2*	*3*	*4*
O_1	—0.315	—0.149	0.013	—0.110
	(—1.453)	(—1.832)	(—1.607)	(—1.268)
C_2	0.334	0.245	0.403	0.295
	(—0.816)	(—0.911)	(—0.807)	(—0.832)
C_3	—0.246	—0.043	—0.242	0.191
	(—1.310)	(—1.132)	(—1.416)	(—0.725)
N_4	0.018	0.012	0.113	—0.025
	(—1.352)	(—1.318)	(—1.277)	(—1.350)
N_5	—0.030	0.142	0.129	0.060
	(—1.306)	(—1.147)	(—1.064)	(—1.396)
O_6	—0.148	—0.038	—0.206	—0.157
	(—1.763)	(—1.686)	(—1.847)	(—1.887)
C_7	0.030	—0.042	—0.044	—0.073
C_8	—0.022	—0.008	—0.011	—0.022
H_9	0.082	0.086	0.087	0.083
C_{10}	—0.058	—0.044	—0.044	—0.039
C_{11}	—0.028	0.019	0.013	0.024
C_{12}	—0.060	—0.046	—0.046	—0.046
C_{13}	—0.012	0.007	0.001	0.020
H_{14}	0.086	0.092	0.088	0.100
H_{15}	0.075	0.098	0.096	0.103
H_{16}	0.073	0.098	0.096	0.101
H_{17}	0.074	0.098	0.096	0.101
H_{18}	0.147	0.198	0.169	0.198
H_{19}	—	0.275	0.289	0.196

highly polar. Considerable concentration of negative charge is found around the C_3 carbon atom compatible with enhanced shielding of the attached proton.[44] At the same time HOMO has the largest coefficient at this position in full agreement with the susceptibility of this site to electrophilic attack of reagents like mercuric chloride.[45] The N_4 nitrogen has positive charge. It is, however, significantly lower than the positive charge of the carbonyl carbon in agreement with nucleophilic attack by reagents such as hydroxyde ion or piperidine which occurs exclusively at the C_2 site.[8] It should be noticed that the N_5 and O_6 atoms are negatively charged and their Coulomb repulsion contributes to the low stability of this bond. The charges of the sydnone ring alternate otherwise. Protonation of the sydnone ring causes dramatic changes of the charge distribution. The σ-electrons are affected by creation of the proton potential which induces σ-electron drift toward the positive »hole«. The π-electron system is also perturbed by the protonation due to the increased effective electronegativity of the attacked atom. The data presented in Table IV show clearly that the π-electron density of the latter is allways increased. The opposite is true for the σ-density which is transferred from the host atom to the proton during the formation of the new bond. It is interesting that the N_5 nitrogen charge changes sign upon protonation in all three conjugated acids. The C_3 atom undergoes a remarkable change when the proton is attached to the N_5 nitrogen (*4*). It becomes substantially positively charged, which explains the ^{13}C NMR data (downfield shift) obtained in aqueous sulphuric and trifluoroacetic acid.[46] On the other hand, the charge distribution in *2* is in accordance with NMR measurements performed in $FSO_3H—SbF_5$ solution,[45] which unequivocally show that protonation occurs at the carbonyl oxygen. Hence, it seems that solvents strongly influence the site of protonation. The formal charge distributions can be introduced in the structural formulas in a qualitative way, as shown in Figure 1. It is noteworthy to observe the π-electron population of various fragments in *1—4*. The conjugated O(1)—C(2)—C(3)—N(4)—N(5) fragment in parent molecule *1* has 6.2 e of the π-electron density. The same π-population is found in the delocalized sydnone cycle of *2*. Therefore, the most stable conjugated acid possesses the full aromatic sextet. The ketene-like fragment in *3* has 3.8 π-electrons, while the localized O(1)=C(2) and C(3)=N(4) bonds in *4* have $\sim$ 2 π-electrons each.

The formal atomic charges and π-bond orders of the sydnone and its substituted derivatives, as obtained by various theoretical methods, are collected in Table V. Apart from the EHT approach, which apparently exaggerates the intramolecular charge transfer, the calculated atomic charges are fairly consistent, being in qualitative agreement despite the fact that the applied semiempirical schemes were at different levels of sophistication. The MNDO charges for N(4) substituted methyl- and phenyl-sydnones are practically equal, excluding of course the site of substitution. The same holds for INDO results on other substituted sydnones. The estimated π-bond orders are in qualitative accordance with the empirical ones obtained from force constants.[5] A comparison of the semiempirical formal atomic charges with the *ab initio* ones shows qualitative accordance, except for the N_5 atom which is positive if the STO-3G basis set is employed.[13] These *ab initio* charges, however, are not in agreement with the ESCA measurements.[13] It would be worthwhile to examine semiempirical atomic densities by the calculation of ESCA chemical shifts.

TABLE V

Comparison of the Formal Atomic Charges and π-electron Bond Orders of the Sydnone Ring as Obtained by Various Empirical and Semiempirical Methods

	Formal charges of the sydnone ring atoms					
Method	*O(1)*	*C(2)*	*C(3)*	*N(4)*	*N(5)*	*O(6)*
CNDO/2[a]	—0.37	0.41	—0.17	0.15	—0.05	—0.17
EHT[a]	—1.35	1.51	0.07	0.34	—0.12	—0.86
IEHT[a]	—0.35	0.17	—0.09	0.02	—0.09	—0.18
MNDO[b]	—0.31	0.34	—0.25	—0.05	—0.04	—0.15
MNDO[c]	—0.32	0.33	—0.25	0.02	—0.03	—0.15
INDO[d]	—0.63	0.77	—0.18	0.24	—0.11	—0.27
INDO[e]	—0.63	0.74	—0.15	0.26	—0.14	—0.28
INDO[f]	—0.63	0.74	—0.13	0.26	—0.14	—0.28

	π-bond orders in the sydnone ring[g]					
Method	*O(1)—C(2)*	*C(2)—O(6)*	*C(2)—C(3)*	*C(3)—N(4)*	*N(4)—N(5)*	*N(5)—O(6)*
»Exp.«[h]	0.77	0.46	0.62	0.70	0.70	0.37
HMO[i]	0.73	0.33	0.53	0.50	0.75	0.36
IHMO[j]	0.64	0.23	0.66	0.50	0.57	0.22
CNDO/2[a]	0.76	0.33	0.50	0.59	0.71	0.31
CNDO/2[k]	0.80	0.36	0.40	0.65	0.64	0.27
MNDO[b]	0.81	0.36	0.41	0.59	0.65	0.35
MNDO[c]	0.80	0.38	0.41	0.59	0.65	0.43

[a] Sydnone: ref. [10].
[b] CH$_3$-sydnone substituted at N(4): ref. [15].
[c] Phenyl-sydnone substituted at N(4): present results.
[d] Sydnone: ref. [6].
[e] 4-(4-methyl-1-buten-2-yl)-3-phenylsydnone: ref. [6].
[f] 4-(cyclohexen-1-yl)-3-phenyl-sydnone: ref. [6].
[g] Bond orders are given for CH$_3$-sydnone substituted at N(4), if not stated otherwise.
[h] Empirical bond orders estimated from force constants, ref. [5].
[i] Ref. [7].
[j] Ref. [8].
[k] Ref. [11].

FINAL REMARKS

A comparison of the MNDO results for N(4) substituted CH$_3$- and phenyl-sydnone shows that the sydnone ring is not very sensitive to the nature of the substituent. The interatomic bond distances and bond angles are to a high degree transferable between these two compounds. The same conclusion is valid for the corresponding bond parameters, like s-characters of the local hybrids and π-bond orders. The atomic charges are also very similar. Some differences are of course found at the substituted atom and in the bond linking the substituent. This finding is in accordance with that of Nešpurek *et al.*[6] Therefore, we can safely conclude that the sydnone ring is rigid and not susceptible to changes. The most stable conjugated acid is produced by the protonation of the carbonyl oxygen, which is compatible with the highest electron density found at that atom. The formation of the aromatic sextet in the sydnone ring contributes to the stability of *2* too. The ^{13}C NMR experiments in FSO$_3$H—SbF$_5$ acid conclusively show that protonation occurs at the carbonyl oxygen.[45] However, the change of the solvent and use of aqueous sulphuric and trifluoroacetic acids indicates the presence of the considerably less stable protonated form *4* with the hydrogen attached to the nitrogen atom.[46] It appears that solvents play an important role in the formation of conjugated acids. Finally, the much debated question of the structural formula of the sydnone ring seems to be satisfactorily answered. The O(1)—C(2)—C(3)—N(4)—N(5) fragment exhibits appreciable conjugation which, however, is interrupted by the intraring oxygen. Consequently, the parent compound *1* is not aromatic. The aromatic sextet is formed only upon protonation at the carbonyl oxygen. This bonding picture of phenyl-sydnone is obtained by the analysis of the MNDO π-bond orders and supported by the results of the energy partitioning technique.

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SAŽETAK

Semiempirijski MNDO studij fenilsidnona i njegovih protoniranih oblika

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Geometrijska i elektronska struktura fenilsidnona i njegovih protoniranih oblika proučavani su primjenom MNDO metode. Dobivene međuatomske udaljenosti i kutovi veza za ishodnu molekulu kvalitativno se dobro slažu s eksperimentalnim podacima. Ipak, finiji detalji strukture fenilsidnona ostali su izvan dosega aproksimativne MNDO metode. Unatoč tome, promjene izazvane protoniranjem u skladu su s kemijskim iskustvom i raspoloživim eksperimentalnim opažanjima. Ona se mogu racionalizirati s pomoću rehibridizacije i promjene redova veza mobilnih π-elektrona. Najstabilnija konjugirana kiselina jest ona s protonom vezanim na karbonilni kisik, što je u skladu s najvećom koncentracijom elektronske gustoće na tom atomu.