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MNDO calculations of systems with hydrogen bonds S–H

Alexander A. Voityuk and Andrey A. Bliznyuk

Institute of Bioorganic Chemistry, Sibirian Branch of the USSR Academy of Sciences, Lavrentyev Prospect 8, 630090 Novosibirsk, USSR

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The MNDO method has been modified for the calculation of the properties of complexes with hydrogen bonds S-H-X, X = N, O, F, S. The results obtained are in good agreement with the experimental data.

Key words: MNDO — Hydrogen bonds

1. Introduction

Recently, interest has sharply increased in the theoretical research on intermolecular interactions and on the effect of the medium on the physical properties and the reactivity of molecules. Particular attention has been paid to systems with hydrogen bonds (H-bonds) which play a significant role in bioorganic chemistry and which are essential for an understanding of processes occurring in aqueous solutions. *Ab initio* calculations employing extended basis sets and correlation energy estimates are known [1-3] to permit reliable data to be obtained for the structures and energies of *simple* complexes with H-bonds. But it is not practical to use them for relatively large molecular systems. On the other hand, the application of semiempirical methods is also limited, since the widely used schemes CNDO/2 [4], MINDO/3 [5] and MNDO [6] fail to describe hydrogen bonds. The modified methods CNDO/2H and MINDO/3H developed in [7] are intended for investigating neutral systems. Quite recently a version of the MNDO model has been suggested which is designed for calculating systems with H-bonds S-H-X [8] that play an essential role in a number of enzymatic processes and in acid-base catalysis. Since this MNDO method underestimates the energy of the H-bonds S-H-X significantly and yields incorrect data for the geometry of complexes involving these bonds, an attempt is made in the present paper to extend the scheme proposed in [8] to the calculation of systems with the H-bonds S-H-X where X = S, N, O and F.

2. Theory of the modified MNDO model

In the MNDO method the energy of core-core repulsion between the cores of atoms A and B is calculated according to [6]:

$$E^{n}_{AB} = Z_A Z_B g_{AB}(1 + f_3(R_{AB})) \tag{1}$$

where Z_A and Z_B are core charges, g_{AB} is the two-centre two-electron repulsion integral for *s*-orbitals of the atoms A and B; the empirical function $f_3(R_{AB})$ is dependent on the atomic parameters and tends to zero as the R_{AB} distance increases. In the MNDO/H method for the atom pairs HX and HY participating in an H-bond X-H-Y, the function $f_3(R_{AB})$ is replaced by $f'_3(R_{AB})$ which for the HX bond can be written in the form [8]:

$$f'_3(R_{HX}) = f_3(R_{HX}) - A_X \exp(-(R_{HX} - R_{HY})^2), \tag{2}$$

where the empirical parameter A_X equals 0.015, 0.012 and 0.009 for X = N, O and F, respectively.

An analysis of the data obtained in [8] and those presented in Table 1 shows that the calculation with $A_N = 0.015$ overestimates the H-bond energy for charged complexes. The best agreement with experiment is reached for $A_N = 0.010$ (cf. Table 1). With this value the results for neutral systems, e.g., for the dimer $(NH_3)_2$, are however unsatisfactory.

From general considerations it is clear that if the covalent radii of X and Y atoms participating in the H-bond are appreciably different, the application of the function $f'_3(R_{AB})$ may yield incorrect results. Indeed, consider the transition from the system X-H-Y to the system X-H-Y′, where the Y and Y′ atoms possess the same basicities but different covalent radii. Clearly the energy of the H-bond HX must be the same in both cases. However, since the equilibrium distances R_{HY} and $R_{HY'}$ are different, the substitution of Y′ for Y will lead to a change in the value of the function $f'_3(R_{HX})$ (cf Eq. (2)) and of the HX bond energy. For the N, O and F atoms the covalent radii are close to one another, so the scheme of [8] yields correct results for the X-H-Y bond. But if the X and Y atom radii

Table 1. Values of H-bond energy in complexes with N-H-X bond for parameter $A_N = 0.015$ and 0.010 (energies in kcal/mol)

System	$A_N = 0.015^a$	$A_N = 0.010^b$	Experiment^a
NH_4^+—NH_3	32.3	24.2	24.8
$NH_4NH_3^+$—NH_3	20.5	17.2	17.5
NH_4^+—H_2O	21.0	17.6	17.3
NH_3—NH_3	2.1	0.4	4.5

[a] [8]
[b] This work

differ greatly, Eq. (2) has to be modified so that the HX bond energy will be independent of the covalent radius of the Y atom. This condition is met by the empirical function $f_3''(R_{AB})$ which, for the HX bond, has the form:

$$f_3''(R_{HX}) = f_3(R_{HX}) - A_X \exp\left(-((R_{HX} - R_{HY}) - (R^0_{HX} - R^0_{HY}))^2\right) \qquad (3)$$

where R^0_{HX} and R^0_{HY} are the bond length values in the corresponding molecules XH_n and YH_n equal to 1.016, 0.957, 0.917, 1.336 [9] for X, Y = N, O, F and S, respectively. It can be seen that in the case of X-H-X type bonds Eq. (3) turns into (2), therefore the values of A_X found in [8] remain unchanged. The experimental value of the H-bond energy in a charged complex $(H_3S\text{-}H_2S)^+$ is reproduced best by choosing $A_s = 0.0025$. The energy of the H-bond in the dimer $(H_2S)_2$ remains practically unchanged if the A_s parameter varies in the range of $0-0.004$. Taking into account the results of the H-bond energy calculations in $(H_2S)_2$ by MNDO (0.5 kcal/mol) and by *ab initio* methods with a 6-31G basis and inclusion of CI (0.6 kcal/mol) [1], the optimal value of A_s can be deduced to equal 0.0025. This value has been used in the present calculations.

3. Results

Table 2 compares calculated and observed data for complexes with S-H-S bonds. It can be seen that the modified MNDO model gives reasonable results for these systems.

As has been noted earlier, Eq. (2) and (3) coincide for complexes with the H-bond of the X-H-X type. Let us compare the parameters of the H-bond S-H-X (X = N, O and F) obtained by using Eq. (2) and (3). From the data of Table 3 it follows that the application of Eq. (3), i.e. taking into account the difference between the covalent radii of the atoms S and X, allows the energies of the H-bonds in the complexes to be obtained more accurately.

Recently, the *ab initio* data for the dependence of the proton-transfer energy barrier upon the length of the H-bond has been collected [12]. To test the modified MNDO method, the same systems have been calculated. In Fig. 1 the *ab initio* data and the MNDO results are compared. The barrier (E^t) for transfer from X

Table 2. Calculated and observed properties of complexes with S-H-S bond

	E (kcal/mol)			R_{SS} (Å)	
Complex	MNDO	*ab initio*[a]	Exp.[b]	MNDO	*ab initio*[a]
$H_2S—H_2S\ C_S$	0.52	0.6	1.7	4.571	4.514
$H_2S—H_2S\ C_{2V}$	0.54	0.6		4.516	
$H_3S^+—H_2S$	15.53	10.5	15.4	3.107	3.747
$H_3SH_2S^+—H_2S$	7.70		9.1	3.144	
$H_3S2H_2S^+—H_2S$	5.82		8.4	3.252	

[a] [2] and [1]
[b] [10]

Table 3. Energy and distance R_{SX} of H-bond S-H-X

	E (kcal/mol)			R_{SX} (Å)	
System	Calculations by Eq. (2)	Calculations by Eq. (3)	Exp.	Calculations by Eq. (2)	Calculations by Eq. (3)
H_3O^+—H_2S	11.36	17.43	17.0[a], 21.9[b]	2.873	2.892
$H_3OH_2S^+$—H_2S	10.24	15.08	13.3[b]	3.118	3.114
$H_3OH_2O^+$—H_2S	25.65	22.32	20.4[b]	3.651	3.572
NH_4^+—H_2S[c]	8.38	11.55	11.4[a]	3.226	3.207
HF—H_2S	0.91	4.27	(4.17)[d]	3.604	3.427

[a] [11]
[b] [10]
[c] Calculations were made with $A_N = 0.010$
[d] *Ab initio* result, [3]

to Y in the $(H_nX-H-YH_m)^+$ system is denoted as $XH \rightarrow Y$. For example, the transfer barrier from amine (NH_3) to hydroxyl (OH_2) is labeled $NH \rightarrow O$. For all systems, except for $OH \rightarrow S$, the *ab initio* and MNDO data are in good agreement.

Comparison of the modified method with the original method

The main difference between the modified and the original method lies in the treatment of the core-core repulsion. The function for the interaction between H and X and H and Y in the H-bond X-H-Y has been modified. To calculate the system, it is necessary to determine in advance the atoms participating in the H-bond. Dewar's expression (1) is used for all other atomic pairs. The standard parameterisation is used. The modified method has several advantages over the original one in the calculation of interatomic distances and energies for systems with an H-bond. It appears to give comparable results in calculating other properties, e.g., bond lengths and bond angles between atoms, which are not

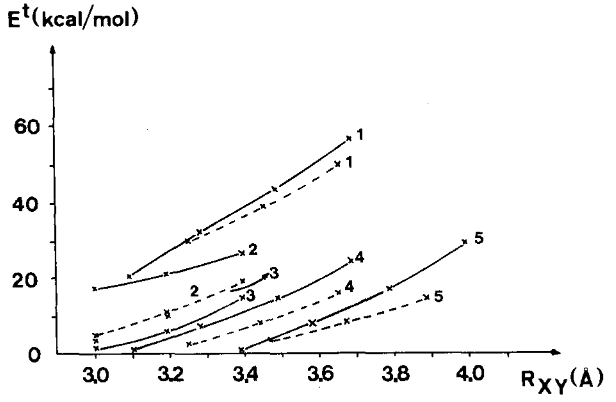

Fig 1. Energy barriers to proton transfer as a function of the H-bond length R_{XY}. *Full line*: MNDO data, *dotted*: *ab initio* data 12. Systems examined are: 1 $NH \rightarrow S$, 2 $OH \rightarrow S$, 3 $SH \rightarrow O$, 4 $SH \rightarrow N$, 5 $SH \rightarrow S$

involved in the H-bond, dipole moments, ionization potentials, charge distributions etc. Obviously, the modified version is equivalent to the original MNDO model when calculating molecules without H-bonds.

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