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MNDO calculations of systems containing hydrogen bonds

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A modified MNDO method, which can be used in the studies on structures with hydrogen bonds X'-H-X'', X', X'' = N, O, is described. Results for a wide range of molecular complexes are reported. Energies of hydrogen bonds are reproduced with useful accuracy. The modified MNDO seems to give more reliable values of hydrogen bond energies and barrier heights of proton transfers than 4-31G *ab initio* model.

Key words: MNDO - Hydrogen bond - Proton transfer - Parametrisation

1. Introduction

Hydrogen bonding is an important phenomenon in many chemical and biological systems, and hydrogen-bonded complexes have been extensively studied in a wide range of experimental techniques. Only a small number of these complexes, however, have been well characterised at the molecular level. Quantum mechanical calculations have been shown to be useful for the supplementation of scarce experimental data available in this field.

Ab initio calculations employing an extended basis set and correlation energy estimates are used to obtain the hydrogen bond energy and geometry of relatively simple molecular systems. But recently calculations of some dimers $(XH_n)_2$ even by 6-31G** basis set with CI and a correction for zero point vibrational energy [1, 2] do not give the best results. For example, these calculations give for hydrogen bond energy in $(H_2O)_2$ and $(NH_3)_2$ values 3.8 and 2.2 kcal/mol respectively, while the experimental values are 5.4 and 4.0 kcal/mol. Moreover, such *ab initio* calculations require prohibitively large computational time and cannot practically be used for relatively large molecular systems.

The applications of semi-empirical methods are also restricted since the widely used schemes CNDO/2 [3], MINDO/3 [4] and MNDO [5] are known to fail to describe hydrogen bonded systems. Hydrogen bonding may be divided into two main categories: weak hydrogen bonding between neutral molecules (with interaction energy of a few kcal/mol) and strong hydrogen bonding in charged systems (with binding energy of 20-40 kcal/mol). The modified methods CNDO/2H and MINDO/3H developed in [6] are intended for investigating only neutral systems. The I-MNDO scheme [7] is applicable only to $(H_2O)_n$ clusters. The MNDO/H method [8] gives unsatisfactory results for geometry of charged complexes (e.g. this scheme predicts greatly nonsymmetric structures for $H_3O^+ \cdot H_2O$ and $H_2O \cdot OH^-$) and doés not permit to study hydrogen transfer reactions. In a new version of MNDO/H [9] these deficiencies are reduced, but this method is not satisfactory for calculation of some nitrogen containing species.

2. Parametrisation

In the present paper an attempt is made to modify the original MNDO scheme to calculate systems with weak and strong hydrogen bonds X′-H-X″, where X′, X″ = N and O.

In the MNDO method the energy of core-core repulsion between the cores of atoms A and B is calculated according to [5]:

$$E_{AB}^{N} = Z_A Z_B G_{AB}(1 + f_3(R_{AB})) \tag{1}$$

where Z_A and Z_B are core charges, G_{AB} is the two-centre two-electron repulsion integral for *s*-orbitals of A and B atoms; the empirical function $f_3(R_{AB})$ is dependent on the atoms parameters and tends to zero as R_{AB} distance increases. For the interaction between atoms H and X′ and H and X″ in the hydrogen bond X′-H-X″ the original function f_3 is replaced by function $f_3'(R_{AB})$:

$$f_3'(R_{HX}) = \sum_{i=1}^{2} A_{X,i} \exp\left(-C_X (R_{HX} - B_{X,i})^2\right) \tag{2}$$

where the parameters $A_{X,i}$, $B_{X,i}$ and C_X were determined by optimisation so as to reproduce the energy and geometry of hydrogen bonds for some simple systems.

The obtained values of parameters are listed in Table 1. The optimisation was carried out by programme [10].

Table 1. Optimised parameters

X	$A_{X,1}$	$A_{X,2}$	$B_{X,1}$	$B_{X,2}$	C_X
N	0.259	0.060	0.341	−0.046	1.700
O	0.289	7.077	0.327	−1.117	2.000

3. Results and discussion

The results of calculation by the modified MNDO method and available experimental data are compared in Table 2. For neutral systems $(H_2O)_2$ and $(NH_3)_2$ the experimental values of the binding energy are reproduced well by this scheme. Among 28 complexes with strong hydrogen bonds there is only one system with binding energy error greater than 3 kcal/mol. Therefore, the modified MNDO values for hydrogen bond energy are, in general better than those from 4-31G *ab initio* model which errors are ca. 5 kcal/mol.

Unfortunately, there are no available experimental data for hydrogen bond lengths in most systems, so the calculated distances in complexes are compared with *ab initio* 4-31G data. Table 3 shows, that the modified MNDO allows one to obtain reasonable values of hydrogen bond lengths.

Table 2. Calculated and experimental energies of hydrogen bonds (kcal/mol)

Hydrogen bond X′-H-X″ X′-H	X″	MNDO	Experiment [7, 8, 15-17]
H_2O	H_2O	5.5	5.4
H_3O^+	H_2O	30.6	31.6
$H_3O^+{\cdot}H_2O$	H_2O	19.9	19.5
$H_3O^+{\cdot}2H_2O$	H_2O	17.9	17.5
H_2O	OH^-	31.8	34.5
H_2O	$OH^-{\cdot}H_2O$	18.4	23.0
H_2O	$OH-{\cdot}2H_2O$	15.1	18.0
$(CH_3)_2COH^+$	H_2O	21.4	21.0
$(CH_3)_2OH^+$	H_2O	23.6	22.6
$HCOOH_2^+$	H_2O	21.4	24.1
H_3O^+	H_2CO	28.9	28.9
H_3O^+	CH_3OH	29.3	27.3
CO_2H^+	CO_2	20.9	20.1
$NH_4{}^+$	H_2O	20.7	23.1
$NH_4^+{\cdot}H_2O$	H_2O	17.1	14.7
$NH_4^+{\cdot}2H_2O$	H_2O	15.1	13.4
$NH_4^+{\cdot}3H_2O$	H_2O	13.4	12.2
$CH_3{\cdot}NH_3^+$	H_2O	17.8	18.4
$CH_3{\cdot}NH_3^+$	CH_3OH	16.3	19.0
$HCNH^+$	H_2O	28.1	29.8
CH_3CNH^+	H_2O	25.9	24.8
NH_3	H_2O	4.1	
H_2O	NH_3	5.1	
NH_3	NH_3	4.0	4.0
NH_4^+	NH_3	26.2	24.8
$NH_4^+{\cdot}NH_3$	NH_3	15.8	17.5
$NH_4^+{\cdot}2NH_3$	NH_3	14.4	13.8
$NH_4^+{\cdot}3NH_3$	NH_3	12.7	12.5
PyH^+	NH_3	18.2	17.3
$HCNH^+$	HCN	27.2	30.0
$CH_3{\cdot}NH_3^+$	CH_3NH_2	22.2	21.7
$CH_3{\cdot}NH_3^+$	NH_3	22.0	21.4

Table 3. X′-X″ distances in the systems with hydrogen bonds X′-H-X″ (Å)

Hydrogen bond X′-H-X″ X′-H	X″	MNDO	4-31G [8]
H_2O	H_2O	2.90	2.83
H_2O	OH^-	2.48	2.45
H_2O	$OH^- \cdot H_2O$	2.54	2.53
H_2O	$OH^- \cdot 2H_2O$	2.59	2.61
H_3O^+	H_2O	2.51	2.36
$H_3O^+ \cdot H_2O$	H_2O	2.57	2.46
$H_3O^+ \cdot 2H_2O$	H_2O	2.62	2.54
NH_3	H_2O	3.11	3.19
H_2O	NH_3	3.06	2.98
NH_4^+	H_2O	2.67	2.65
NH_3	NH_3	3.35	3.36
NH_4^+	NH_3	2.65	2.75

Table 4. Energy barriers to proton transfer for $NH_4^+ \cdot NH_3$ (kcal/mol)

R_{NN}, Å	4-31G	POL-CI	MNDO
2.73	3.8	1.7	0.0
2.95	11.4	7.3	4.5
3.15	20.6	14.7	14.9

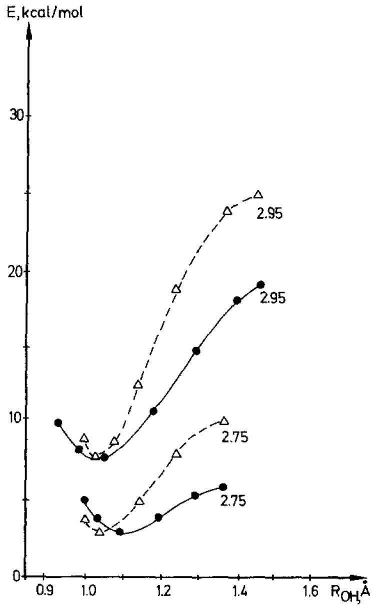
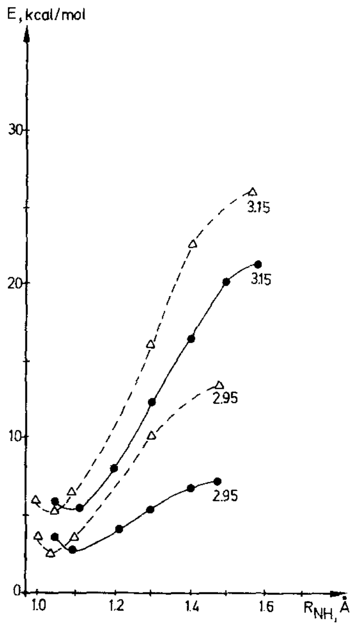


Fig. 1. Potential energy curves for proton transfer in $H_3O^+ \cdot H_2O$. MNDO data - solid curves, 4-31G results - dotted curves. The numerical label on each curve corresponds to the O-O distance (in Å)



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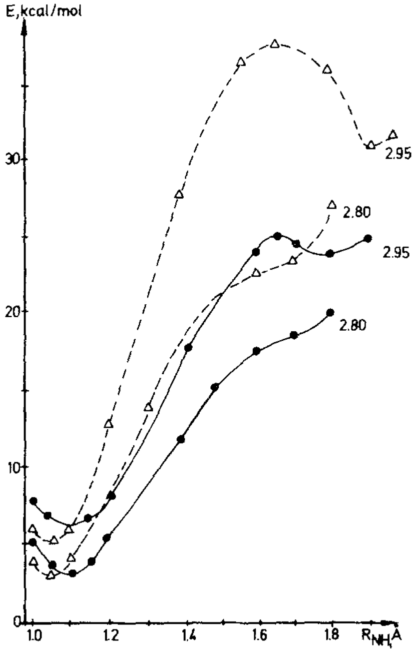

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Fig. 2. Potential energy curves for proton transfer in $NH_4^+ \cdot NH_3$
Fig. 3. Potential energy curves for proton transfer in $NH_4^+ \cdot H_2O$

In Table 4 the *ab initio* 4-31G, POL-CI [14] and the modified MNDO results for the energy of proton transfer in $NH_4^+ \cdot NH_3$ are compared. Table 4 shows that the modified MNDO values are better than those of 4-31G. In general, allowing for configuration interaction greatly decreases barrier heights [14]. Potential energy curves for proton transfer in $(H_3O \cdot H_2O)^+$, $(NH_4 \cdot NH_3)^+$ and $(NH_4 \cdot H_2O)^+$ are compared with the *ab initio* 4-31G results [11–13] on Figs. 1, 2 and 3 respectively. Figures show, that the modified MNDO barriers are less than the 4-31G ones. Taking into account the data in Table 4 and the results [14], we conclude that the modified MNDO values of the barrier heights seem to be more reasonable than those of 4-31G.

4. Conclusions

The results reported here indicate that the modified MNDO method reproduces hydrogen bonds better than *ab initio* methods. Since the computing time required for MNDO calculation for a molecule is one thousand times less than for a 4-31G calculation, it is possible to use the modified MNDO method in the studies on environmental effects in chemistry and biochemistry within the supermolecular approach.

Appendix

The main difference between the modified and original methods lies in the treatment of the core-core repulsion. The function for the interaction between H and X′ and H and X″ in the hydrogen bond X′-H-X″ has been modified according to (2). To calculate a system, it is necessary to determine in advance which atoms participate in hydrogen bond. Dewar's expression (1) is used for other atomic pairs. The standard parametrisation is used. Therefore the modified method has several advantages over the original one in calculating the interatomic distances and energies for systems with hydrogen bonds and allows to obtain comparable results in calculating other properties, e.g. bond lengths and bond angles between atoms, which are not included in hydrogen bond, dipole moments, ionisation potentials, charge distribution etc. Obviously, the modified version is equivalent to the original MNDO model in calculating molecules without hydrogen bond.

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