

MNDO calculations on hydrogen bonds. Modified function for core-core repulsion

Konstantin Ya. Burstein and Alexander N. Isaev

N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of USSR,
Leninsky Prospect 47, 117913 Moscow, USSR

The MNDO method has been modified to calculate the properties of the structures involving hydrogen bonds $X \cdots H - Y$, $X, Y = N, O$ and F . A new method (referred to as MNDO/H) has been tested by calculation of a wide range of molecular systems with weak and strong (ionic) hydrogen bonds. The results obtained are in good agreement with the experimental data. In the cases where direct comparisons are possible, the MNDO/H method seems to give more accurate values of hydrogen bond energy than the *ab initio* method using STO-4-31G basis set.

Key words: MNDO—Hydrogen bonds.

As hydrogen bonding is known to play a significant role in chemistry and molecular biology, both theoretical and experimental methods are extensively used in studying hydrogen bonded structures. As to the theoretical approach in recent years, a large number of semiempirical and *ab initio* molecular orbital calculations have been carried out. It should be emphasised that semiempirical CNDO/2 and *ab initio* STO-3G treatments are used most frequently. Both treatments, however, greatly overestimate heats of formation of strong (ionic) hydrogen bonds and fail to describe most interesting chemical properties, such as ground state potential surfaces, activation energies and heats of formation, giving large errors. For these reasons the CNDO/2 and STO-3G methods can hardly be used to account and predict for "chemical" behavior of molecular systems. *Ab initio* calculations with extended basis have been applied more successfully to calculate chemical properties of some small structures with hydrogen bonds. But they cannot be practically used for relatively complex chemical and biochemical systems because it takes too much computer time to calculate them.

In recent years potential surfaces and thermochemistry values for large molecular systems have been most frequently calculated by MINDO/2, MINDO/3 and MNDO semiempirical methods. These methods developed by Dewar's group can be used to study properties of molecular systems large enough to be interesting to the organic chemist and often to the biochemist. However, the MINDO/2, MINDO/3 and MNDO methods in their present form cannot predict correct interatomic distances and energies for systems with hydrogen bonds [1-3]. This is the main shortcoming of Dewar's methods. The present paper reports a new empirical function for core-core repulsion to overcome this shortcoming in MNDO method.

Dewar and Thiel used the following function for core-core repulsion between the cores of atoms A and B [4]

$$E_{AB}^{\text{core}} = Z_A Z_B (s^A s^A, s^B s^B) (1 + f(R_{AB})) \quad (1)$$

where Z_A and Z_B are core electric charges, $(s^A s^A, s^B s^B)$ two-center two-electron repulsion integral, R_{AB} = interatomic distance, $f(R_{AB})$ = an empirical function. The following expression has been proposed by Dewar and Thiel

$$f(R_{AB}) = \exp(-\alpha_A R_{AB}) + \exp(-\alpha_B R_{AB}) \quad (2)$$

where α_A and α_B are the atomic parameters. For the pairs N-H and O-H it has been found advantageous to use a slightly modified expression

$$f(R_{XH}) = R_{XH} \exp(-\alpha_X R_{XH}) + \exp(-\alpha_H R_{XH}) \quad X = \text{N or O}. \quad (3)$$

Eqs. (2) and (3) are purely empirical, but they show the correct behavior in the limit $R_{AB} \rightarrow \infty$ where $f(R_{AB})$ vanishes.

The MNDO method tends to overestimate the repulsion between the molecules in the case of hydrogen bonded systems. The repulsion depends on the expression used for the function $f(R_{AB})$. Therefore heats and geometries of hydrogen bonded systems may be reproduced by appropriate choice of this function.

We tried to find a new expression $f(R_{XH})$ for atomic pairs $X \cdots H$ taking part in formation of hydrogen bonds $X \cdots H - Y$ ($X, Y = \text{N, O, F}$). Dewar's expressions (2) and (3) were used for other atomic pairs. Exponential terms of the form $\exp(-\alpha R_{XH})$ and $\exp(-\alpha R_{AB}^2)$ were tested for atomic pairs $X \cdots H$. The suitable expression was found to be

$$f(R_{XH}) = \exp(-\alpha R_{XH}^2)$$

where α is the atomic parameter. α was determined empirically by a fit to the experimental heats of formation of hydrogen bonds. The value proposed is equal to 2.0 (\AA^{-2}) for all pairs $X \cdots H$, $X = \text{N, O}$ and F .

We modified the standard MNDO program to use the new expression $f(R_{XH})$ for pairs $X \cdots H$ taking part in formation of hydrogen bonds. In our program the user has to determine in advance which atoms are H-bonded to one another. We dwelt on this variant of modification as only small changes are needed in the standard MNDO program to adapt it to the new core-core repulsion function.

We tested the new method (referred to as MNDO/H) by calculation of a wide range of systems with weak and strong (ionic) hydrogen bonds. MNDO/H results together with the corresponding CNDO/2 and *ab initio* STO-4-31G are presented in the Tables. Table 1 shows that MNDO/H results are in good agreement with the experimental data. In some cases the MNDO/H energies of hydrogen bond seem more preferable than those from *ab initio* STO-4-31G calculations. The CNDO/2 method gives the worst results.

Energies of linear, cyclic and bifurcated structures were compared for complexes $\text{H}_2\text{O}\cdot\text{H}_2\text{O}$, $\text{H}_2\text{O}\cdot\text{NH}_3$, $\text{HF}\cdot\text{H}_2\text{O}$, $\text{HF}\cdot\text{NH}_3$, $\text{HF}\cdot\text{HF}$ and $\text{H}_2\text{O}\cdot\text{F}^-$. The MNDO/H method predicts the linear structures to be most stable. This result is in good agreement with the data of the best *ab initio* calculations.

The hydrogen bond length calculations by the MNDO/H, CNDO/2 and STO-4-31G methods are listed in Table 2. Though the MNDO/H method tends to

Table 1. Calculated energies of hydrogen bonds (kcal/mole)

H-bonds Y—H···X		CNDO/2	MNDO/H	STO-4-31G	Experimental
Y—H	X	[5-7]		[8-10]	data [11-16]
H_2O	$\text{H}_2\text{O}^{\text{a}}$	8.7	4.4	8.2	5
H_2O	OH^-	72	32	41	34
H_2O	$\text{OH}^- \cdot \text{H}_2\text{O}$	37	21	30	23
H_2O	$\text{OH}^- \cdot 2\text{H}_2\text{O}$	25	15	23	18
H_3O^+	H_2O	60	31	44	33 and 37
$\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$	H_2O	35	23	31	22 and 23
$\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$	H_2O	25	19	26	17
NH_3	H_2O	4.5	1.9	3.6	—
H_2O	NH_3	11.2	2.9	7.9	—
NH_3	NH_3	5.8	1.0	3.4	4.5
NH_4^+	H_2O	—	20	28	17
$\text{NH}_4^+ \cdot \text{H}_2\text{O}$	H_2O	—	17	—	15
$\text{NH}_4^+ \cdot 2\text{H}_2\text{O}$	H_2O	—	15	—	13
$\text{NH}_4^+ \cdot 3\text{H}_2\text{O}$	H_2O	—	11	—	12
NH_4^+	NH_3	—	37	31	25
$\text{NH}_4^+ \cdot \text{NH}_3$	NH_3	—	23	—	18
$\text{NH}_4^+ \cdot 2\text{NH}_3$	NH_3	—	17	—	14
$\text{NH}_4^+ \cdot 3\text{NH}_3$	NH_3	—	14	—	12
FH	H_2O	15	9	14	7
H_2O	FH	3	5	5	—
FH	NH_3	20	12	15	—
NH_3	FH	1.5	2.2	3.2	—
HF	FH^{a}	9.4	8.9	8.0	5-7
HF	F^-	102	47	—	40-60
H_2O	$\text{F}^{-\text{a}}$	82	31	—	23
H_2O	$\text{F}^- \cdot \text{H}_2\text{O}^{\text{a}}$	—	23	—	17
H_2O	$\text{F}^- \cdot 2\text{H}_2\text{O}^{\text{a}}$	—	18	—	14
H_2O	$\text{F}^- \cdot 3\text{H}_2\text{O}^{\text{a}}$	—	12	—	13

^a The most stable linear structure

Table 2. Y...X distances in structures with hydrogen bonds, Å

H-bonds Y...X		CNDO/2	MNDO/H	STO-4-31G
Y—H	X	[5-7]		[8-10]
H ₂ O	H ₂ O	2.54	2.62	2.83
H ₂ O	OH ⁻	2.34	2.42	2.45
H ₃ O ⁺	H ₂ O	2.34	2.44	2.36
NH ₃	H ₂ O	2.69	2.90	3.19
H ₂ O	NH ₃	2.58	3.00	2.98
NH ₃	NH ₃	2.74	3.40	3.36
NH ₄ ⁺	H ₂ O	—	2.73	2.65
NH ₄ ⁺	NH ₃	—	2.54	2.75
HF	H ₂ O	2.42	2.54	2.60
H ₂ O	HF	2.55	2.68	2.92
HF	NH ₃	2.46	2.53	2.72
NH ₃	HF	2.75	2.86	3.19
HF	HF	2.44	2.56	2.70

slightly underestimate the lengths, the errors are fewer than in the case of the corresponding CNDO/2.

Finally, we calculated the charge transfer values (Δq) for some complexes with hydrogen bonds

$$\Delta q = q(\text{X in complexe}) - q(\text{isolated X})$$

where $q(\text{X in complexe})$ is the electric charge of X in complexe X...H—Y and $q(\text{isolated X})$ is the electric charge of isolated X. The results from Table 3 show good agreement in the charge transfer values for the methods discussed.

In general, for hydrogen bonds the MNDO/H method appears to give comparable or slightly better results than *ab initio* STO-4-31G. However, the computation

Table 3. Charge transfer

H-bonds Y—H...X		CNDO/2	MNDO/H	STO-4-31G
Y—H	X	[5-7]		[8, 9]
H ₂ O	H ₂ O	0.036	0.007	0.028
H ₂ O	NH ₃	0.059	0.007	0.037
H ₂ O	HF	—	0.014	0.028
HF	H ₂ O	0.064	0.036	0.036
HF	NH ₃	0.097	0.064	0.057
H ₂ O	OH ⁻	0.365	0.207	0.210
H ₂ O	OH ⁻ ·H ₂ O	—	0.132	0.130
H ₂ O	OH ⁻ ·2H ₂ O	—	0.109	0.100
H ₃ O ⁺	H ₂ O	0.289	0.139	0.140
H ₃ O ⁺ ·H ₂ O	H ₂ O	—	0.086	0.080
H ₃ O ⁺ ·2H ₂ O	H ₂ O	—	0.073	0.070

time required is shorter by three or four orders of magnitude and so we believe that the MNDO/H method may have wide applications. In particular, it may be used to treat large chemical systems with intramolecular hydrogen bonds, biochemical complexes, and the solvent effect in supermolecular approach.

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