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Peeter BURK and Mati KARELSON**

CRITICAL TEST OF THE VALIDITY OF ZDO SEMIEMPIRICAL METHODS FOR HYDROGEN-BONDED SYSTEMS

Hydrogen bond energies, geometries and dipole moments were calculated using different semiempirical molecular orbital methods (MINDO/3, MNDO, AM1, PM3) for several hydrogen-bonded complexes. A relatively good description of the energy and geometry of these systems was obtained by AM1 method, while PM3 fails to predict the correct energies as compared to the respective experimental data. Both MINDO/3 and MNDO proved to be unsatisfactory for the description of the geometry and energy of hydrogen-bonded complexes.

1. Introduction

Numerous articles have been published in recent years where different semiempirical quantum chemical methods have been used to find the properties of hydrogen-bonded complexes. In many cases authors report good agreement with experimental data [1–4]. However, in general the predictive ability of various semiempirical methods is questionable [5–7] and often special modifications of the parametrization are needed in order to get meaningful results [8–12].

In the present work various ZDO quality semiempirical quantum-chemical calculation methods (MINDO/3 [13], MNDO [14], AM1 [15], PM3 [16]) were critically tested for the decription of hydrogen-bonded complexes as compared between themselves and the *ab initio* calculations.

2. Method

The energy of the intermolecular hydrogen bond X—H··B was calculated according to the formula

$$B = H_c - (H_{XH} + H_Y), \tag{1}$$

where H_c is the calculated heat of formation of the hydrogen-bonded complex and H_{HX} and H_Y are the heats of formation for individual molecules XH and Y. In the case of intramolecular hydrogen bond the bond energy was calculated as

$$B = H_b - H_a, \tag{2}$$

where H_b is the heat of formation for the hydrogen-bonded conformation and H_a is the heat of formation of the conformation where hydrogen bond is nonexistent (bridge hydrogen atom is turned out of the plane formed by the free electron pair of the hydrogen bond acceptor and the nucleus of the hydrogen bond donor).

The MOPAC program package [17] was used in a modified form to account for the reaction field effects in dense media [18]. Calculations were carried out by using four different semiempirical parametrizations: MINDO/3 [13], MNDO [14], AM1 [15] and PM3 [16]. In all cases the

* Tartu Ülikooli füüsika-keemia teaduskonna keemia osakond (Department of Chemistry, Tartu University). 202400 Tartu, Jakobi 2, Estonia.

geometry of molecules and complexes was fully optimized. In order to avoid premature completion of calculations in local minimum, the calculations were carried out starting off from several different initial geometries.

3. Results

3.1. Gas phase calculations

The following complexes with an intermolecular hydrogen bond were calculated: the dimers of water, ammonia, methanol, formamide, formic acid and acetic acid, and complexes methanol—water, ammonia—water, formaldehyde—water, formiate—water, formamide—water, formamide—methanol. Malonaldehyde and 2,4-pentanedione (acetylacetone) were calculated as examples of systems with an intramolecular hydrogen bond. The following charged complexes were also calculated: $H_2O\cdot\cdot OH^-$, $H_2O\cdot\cdot OH^-\cdot H_2O$, $H_2O\cdot\cdot OH^-\cdot 2H_2O$, $H_3O^+\cdot\cdot H_2O$, $H_3O^+\cdot H_2O\cdot\cdot H_2O$, $NH_4^+\cdot\cdot H_2O$ and $NH_4^+\cdot\cdot NH_3$.

Results of calculations are presented in Tables 1—15, where *B* denotes the energy of hydrogen bond as defined by formulae (1) or (2), μ denotes the dipole moment of the complex, *IP* — its ionization potential and *R* — the distance between atoms X and Y in the hydrogen bond X—H··Y.

In the case of water dimer different conformations were predicted to be the most stable by different methods: cyclic by MINDO/3, bifurcational by MNDO and AM1, and linear by PM3 (Fig. 1). The dimer of ammonia was predicted to be linear (Fig. 2) by all methods in accordance with the experimental observation [9, 19].

Two possible mixed ammonia—water complexes were calculated. In the complex where ammonia acts as the hydrogen-bond donor, all methods predict the linear structure to be the most stable. If ammonia is the hydrogen-bond acceptor, MINDO/3 and PM3 predicted the linear, the two other methods the bifurcational conformation as the most stable (Fig. 3).

In the case of methanol—water complexes there are two possible conformations, too. For a complex, where methanol is the donor of the hydrogen-bond, all the four methods used predict the most stable complex to be linear. If the water molecule was the hydrogen-bond donor, the most stable complex was predicted to be cyclic by MINDO/3, bifurcational by MNDO and AM1, and linear by PM3 (Fig. 4).

In the case of formaldehyde—water complex MINDO/3 and PM3 gave in optimum the linear geometry, whereas MNDO and AM1 lead to the bifurcational configuration (Fig. 5). Formiate—water complex was predicted to be symmetric and cyclic by all the methods used (Fig. 6).

Dimers of formamide, formic and acetic acids were predicted to be cyclic by all methods, but using MINDO/3 and MNDO methods nonplanar cyclic conformations (Fig. 7*a*) were found to be the most stable, while AM1 and PM3 predict the most stable conformations to be planar in agreement with experiments (Fig. 7*b*) [32, 34, 36].

For the formamide—water complex there is again a disagreement between the results obtained by different methods. MINDO/3 and MNDO predict the linear, but AM1 and PM3 the cyclic conformation (Fig. 8) to be the most stable. The latter conformation is experimentally observed [36, 37]. All the methods used predict the most stable complex of formamide and methanol to be cyclic (Fig. 9).

For the dimer of methanol MINDO/3 gives the cyclic and the other three methods the linear complex to be the most stable (Fig. 10).

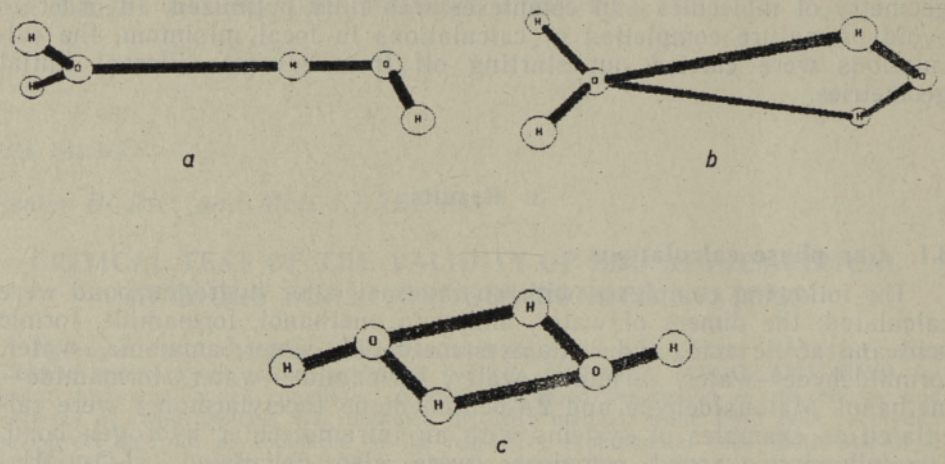

Fig. 1. Different conformations of the water dimer: *a* — linear, *b* — bifurcational, and *c* — cyclic.

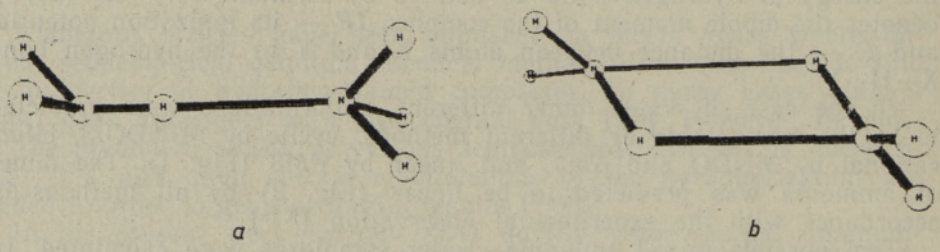

Fig. 2. Different conformations of the ammonia dimer: *a* — linear, *b* — cyclic.

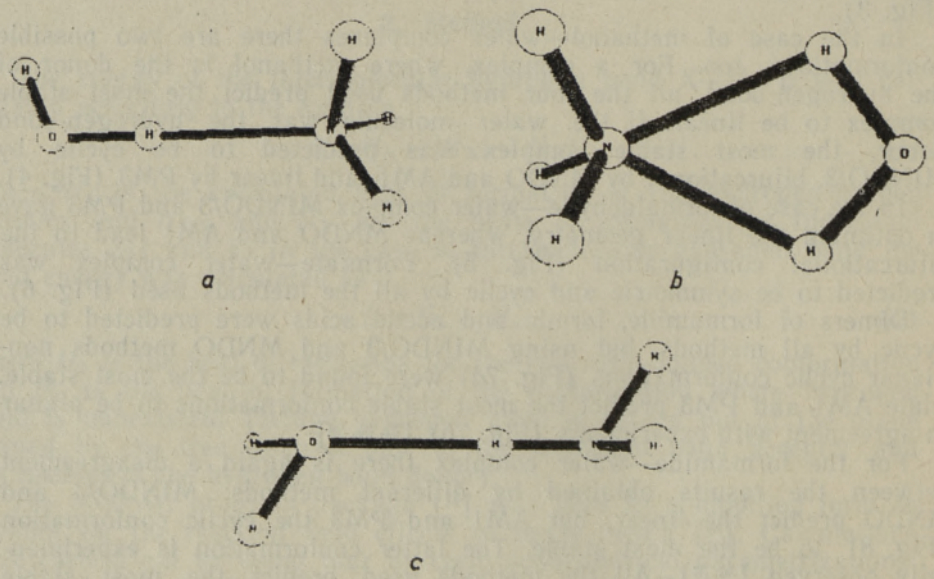

Fig. 3. Different conformations of the water—ammonia complex (the donor of the hydrogen bond is water): *a* — linear, *b* — cyclic; the donor of the hydrogen bond is ammonia — *c*.

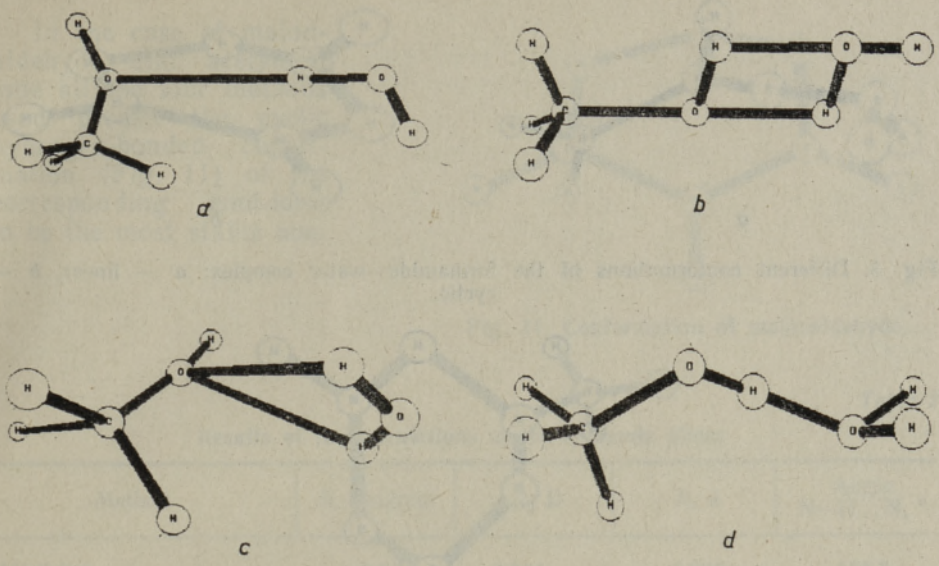

Fig. 4. Different conformations of the methanol—water complex (the donor of the hydrogen bond is water): *a* — linear, *b* — cyclic, *c* — bifurcational; the donor of the hydrogen bond is methanol — *d*.

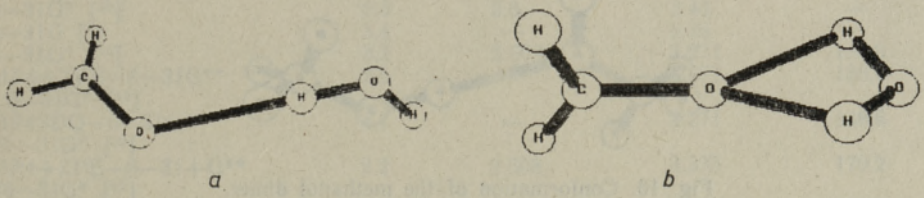

Fig. 5. Different conformations of the formaldehyde—water complex: *a* — linear, *b* — bifurcational.

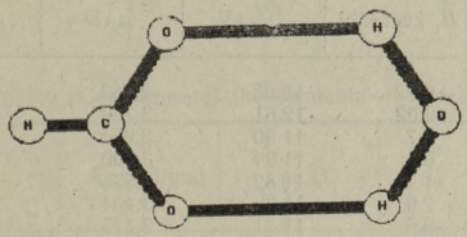

Fig. 6. Conformation of the formiate—water complex.

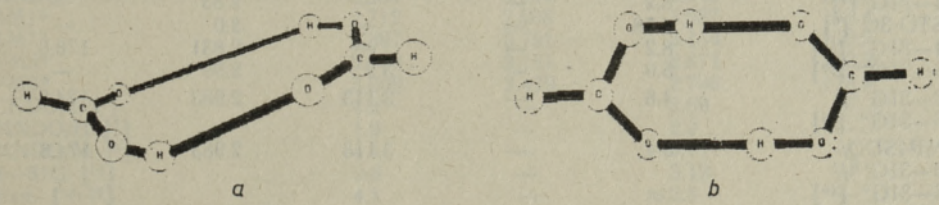

Fig. 7. Different conformations of the dimer of formic acid: *a* — nonplanar, *b* — planar.

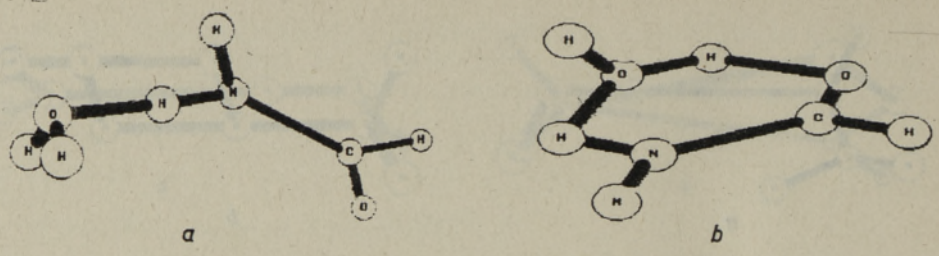

Fig. 8. Different conformations of the formamide—water complex: *a* — linear, *b* — cyclic.

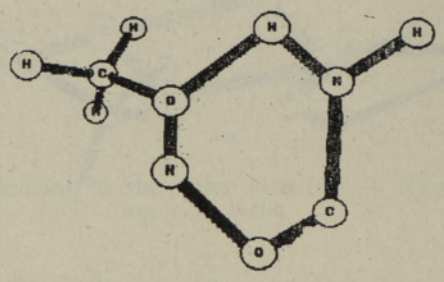

Fig. 9. Conformation of the formamide—methanol complex.

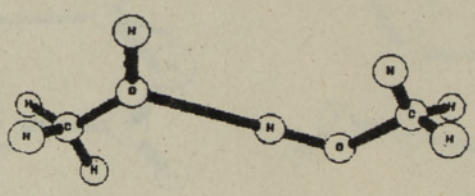

Fig. 10. Conformation of the methanol dimer.

Table 1

Results of gas phase calculations for water dimer

Method	*B*, kcal/mol	*IP*, eV	μ, D	*R*, Å	Angle O—H . . O, °
MINDO/3	—0.82	12.65	2.162	3.920	94.4
MINDO/3[a]	—0.02	12.61	3.769	4.878	180.0
MNDO	0.7	11.90	2.951	4.153	147.1
MNDO[a]	0.4	11.94	3.200	4.349	180.0
AM1	4.7	11.82	3.538	2.621	48.5
AM1[a]	2.9	11.93	3.404	3.102	180.0
PM3	3.5	11.71	2.475	2.769	179.4
CNDO/2 [7]	8.7	—	—	2.54	—
I-MNDO [6]	5.6	11.86	2.6	2.98	—
MNDO/H [7]	4.4	—	—	2.62	—
MNDO/M [22]	5.5	—	—	2.9	—
4—31G [7]	8.2	—	—	2.83	—
STO-3G [6]	4.58	—	—	3.0	—
4—31G* [12]	8.2	—	—	2.831	178.6
6—31G [23]	5.6	—	3.2	2.99	—
6—31G *// 6—31G [19]	4.6	—	3.113	2.983	174.8
MP4SDQ/ 6—31G *// 6—31G* [19]	5.4	—	3.113	2.983	174.8
Exp. [12, 22, 24, 25]	5.4	11.86	2.601	2.976	180.0

[a] — angle O—H··O is fixed at 180°.

In the case of malonaldehyde and acetylacetone all the four methods used predict the cyclic hydrogen-bonded conformation (Fig. 11) of the corresponding enol-form to be the most stable one.

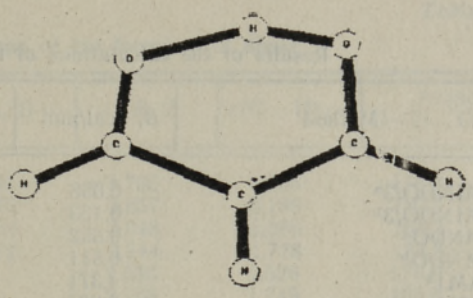

Fig. 11. Conformation of malonaldehyde.

Table 2

Results of the calculations of the ammonia dimer

Method	*B*, kcal/mol	μ, D	*R*, Å	Angle N—H . . N, °
MINDO/3	—0.03	2.344	6.307	178.7
MNDO	0.72	3.288	4.251	129.6
AM1	1.3	2.392	3.693	167.5
PM3	0.12	2.964	2.918	176.4
CNDO/2 [7]	5.8	—	2.74	—
MNDO/H [7]	1.0	—	3.4	—
MNDO/M [7]	4.0	—	3.35	—
6—31G* [23]	2.9	3.6	3.44	—
4—31G [7]	3.4	—	3.36	—
6—31G* [19]	3.2	2.608	3.271	138.6
MP4+ZPE—6—31G** //6—31G* [19]	2.5	—	3.271	138.6
MP4SDQ—6—31G** //6—31G* [19]	4.1	—	3.271	138.6
MP4+ZPE—6—31+G** //6—31G* [19]	2.2	2.608	3.375	170.2
MP4SDQ—6—31+G** //6—31+G* [19]	3.7	2.608	3.375	170.2
6—31+G* [19]	2.8	—	3.271	170.2
6—31G** //6—31+G* [19]	3.1	—	3.271	170.2
Exp. [19, 9]	4.5	0.9	≈3.10	180

Table 3

Results of the calculations of the ammonia—water complex

Method	*B*, kcal/mol	μ, D	R, Å	Angle O—H . . N or N—H . . O, °
MINDO/3[a]	—0.043	3.298	5.714	173.0
MINDO/3[b]	—0.005	3.585	6.404	168.3
MNDO[a]	0.430	2.062	4.490	176.2
MNDO[b]	0.960	3.544	4.048	122.5
AM1[a]	2.712	2.508	3.037	150.4
AM1[b]	2.897	3.791	3.134	110.9
PM3[a]	0.852	2.181	2.871	172.2
PM3[b]	3.009	3.479	2.796	178.9
CNDO/2 [7]	4.5	—	2.69	—
MNDO/H [7]	1.9	—	2.9	—
MNDO/M [9]	4.1	—	3.11	—
4—31G [16]	3.6	—	3.19	—
Exp. [26, 27]	4.1	—	≈2.8	—

[a] — the donor of hydrogen is ammoniac,
[b] — the donor of hydrogen is water.

Table 4

Results of the calculations of the methanol—water complex

Method	*B*, kcal/mol	μ, D	*R*, Å	Angle O—H . . O, °
MINDO/3[a]	0.058	0.922	5.696	106.4
MINDO/3[b]	0.133	3.133	5.617	178.1
MNDO[a]	0.652	2.838	4.156	135.6
MNDO[b]	0.511	3.076	4.188	173.5
AM1[a]	4.371	3.418	2.655	110.8
AM1[b]	2.831	2.274	3.043	160.2
PM3[a]	2.437	3.131	2.775	175.1
PM3[b]	2.652	2.872	2.762	169.4
6—31G [28]	6.74	—	2.82	173.1
Exp. [26]	4.5	—	≈2.74	—

[a] — the donor of hydrogen is methanol,
[b] — the donor of hydrogen is water.

Table 5

Results of the calculations of the formaldehyde—water complex

Method	*B*, kcal/mol	μ, D	*R*, Å	Angle C=O . . H, °	Angle O—H . . O, °
MINDO/3	0.22	3.584	5.354	159.4	171.7
MNDO	0.90	3.775	4.082	158.3	146.7
AM1	3.97	4.456	2.706	157.7	109.2
PM3	2.73	2.768	2.777	119.4	178.7
6—31G* [29]	—	—	2.02	116.0	178.1

Table 6

Results of the calculations of the formiate—water complex

Method	*B*, kcal/mol	*R*, Å	*r*(O . . H), Å
MINDO/3	3.259	4.129	3.389
MNDO	6.846	3.569	2.874
AM1	16.139	2.838	2.043
PM3	15.567	2.814	2.051
MP2// 4—31+G* [30]	20.5	2.924	—
MNDO/H [31]	12.1	2.89	—
MNDO/M [31]	16.6	2.67	—
Exp. [31]	16.0	—	—

Table 7

Results of the calculations of the formamide dimer

Method	*B*, kcal/mol	μ, D	*R*, Å	Angle N—H · · N, °
MINDO/3	0.602	4.189	4.180	95.8
MNDO	1.826	3.290	3.626	102.3
AM1	8.072	0.312	3.049	165.0
PM3	4.708	1.368	2.831	169.2
STO—3G [32]	13.24	—	2.639	171.2
4—31G [32]	17.20	—	2.896	168.4
6—31G** [29]	13.18	—	2.988	168.1
Exp. [32]	14.0	3.71	2.948	—

Table 8

Results of the calculations of the formic acid dimer

Method	B, kcal/mo	μ, D	R, Å	r(O..H), Å	Angle O—H..O, °
MINDO/3	0.309	1.341	4.766	4.266	116.4
MNDO	1.169	1.028	3.857	3.189	129.1
AM1	6.440	0.154	3.048	2.086	168.3
PM3	8.498	0.072	2.744	1.778	174.8
STO—3G [33]	15.13	—	2.536	1.526	178.9
4—31G [33]	20.02	—	2.708	1.749	165.6
6—31G** [32]	15.19	—	2.789	—	173.9
Exp. [34]	16.1	1.41	2.703	1.667	180.0

Table 9

Results of the calculations of the acetic acid dimer

Method	B, kcal/mol	μ, D	R, Å	Angle O—H..O, °
MINDO/3	0.015	2.195	4.573	114.6
MNDO	1.291	0.821	3.654	135.0
AM1	6.278	0.102	3.048	166.3
PM3	8.738	0.213	2.745	176.2
Exp. [26, 35]	14.2	0.94	2.76	—

Table 10

Results of the calculations of the formamide—water complex

Method	B, kcal/mol	μ, D	r(O..HN), Å	r(O..HO), Å	Angle O—H..O, °
MINDO/3	0.168	3.079	4.489	—	—
MNDO	0.645	1.465	3.387	4.559	—
AM1	6.197	2.517	2.172	3.346	134.8
PM3	3.904	2.766	2.669	3.287	161.6
Exp. [36, 37]	—	2.379	2.006	2.02	107.5

Table 11

Results of the calculations of the formamide—methanol dimer

Method	B, kcal/mol	μ, D	r(O..HN), Å	r(O..HO), Å	Angle O—H..O, °
MINDO/3	0.096	3.000	4.491	5.944	107.6
MNDO	0.738	1.773	3.321	3.812	112.7
AM1	5.559	2.769	2.168	2.130	133.9
PM3	3.429	2.983	2.712	1.810	160.1
Exp. [36, 37]	—	2.347	1.974	2.005	144.3

Table 12

Results of the calculations of methanol dimers

Method	B, kcal/mol	μ, D	R, Å	Angle O—H..O, °
MINDO/3	—0.845	2.100	6.952	102.1
MNDO	—0.346	2.980	4.255	179.7
AM1	1.386	2.839	3.131	171.4
PM3	1.430	3.143	2.776	177.8
Exp. [26, 38]	3.51	—	—	—

Table 13

Results of the calculations of malonaldehyde

Method	B, kcal/mol	μ, D	r(O . . O), Å	r(O . . H), Å	Angle O—H . . O, °
MINDO/3	0.949	2.549	3.392	2.833	118.6
MNDO	2.537	2.142	3.166	2.540	123.7
AM1	9.338	2.499	2.848	2.078	134.5
PM3	8.804	2.250	2.643	1.825	140.3
6—31G** [39]	—	—	2.085	1.880	139.7
6—31G** [39]	—	—	1.884	1.897	138.5
DZ+P [39]	—	—	2.133	1.880	139.9
MP2// 6—31G** [39]	—	—	2.204	1.694	147.6
Exp. [39, 40]	—	2.58	2.574	1.68	146.9

Table 14

Results of the calculations of acetylacetone

Method	B, kcal/mol	μ, D	r(O . . O), Å	Angle O—H . . O, °
MINDO/3	2.390	3.089	3.247	121.6
MNDO	1.486	2.374	3.125	125.2
AM1	8.231	2.914	2.819	135.9
PM3	8.525	2.693	2.631	141.9
Exp. [4, 41]	—	3.07	2.519	137.0

Table 15

Hydrogen bond *Y*—H . . X energy in charged systems

Y—H	*X*	MINDO/3	MNDO	AM1	PM3	MNDO/H [7]	MNDO/M [9]	Exp. [7, 9]
H_2O	OH^-	18.3	20.8	30.3	31.2	32.0	31.8	34.5
H_2O	$H_3O_2^-$	6.0	8.4	19.5	6.9	12.0	18.4	23.0
H_2O	$H_5O_3^-$	3.2	6.9	17.8	31.6	15.0	15.1	18.0
H_3O^+	H_2O	4.2	10.2	25.6	19.1	31.0	30.6	31.6
$H_5O_2^+$	H_2O	3.3	7.8	19.3	23.7	23.0	19.9	19.5
NH_4^+	H_2O	3.4	7.6	14.6	13.1	21.5	20.4	20.6
NH_4^+	NH_3	10.2	4.3	18.6	17.1	37.0	26.2	24.8

3.2. Liquid state (self-consistent reaction field) calculations

Using MINDO/3, MNDO, AM1, and PM3 methods in combination with the self-consistent reaction field model [17], the following systems were calculated: dimer of water (radius of the cavity $a_0=2.025$ Å) in the polarizable medium of the macroscopic dielectric permittivity of water ($\varepsilon=78$), dimer of formic acid ($a_0=2.719$ Å) in the medium of the dielectric permittivity of formic acid ($\varepsilon=57$), dimer of methanol ($a_0=2.619$ Å) in the medium of the dielectric permittivity of methanol ($\varepsilon=31.2$) and carbon tetrachloride ($\varepsilon=2.24$), dimer of acetic acid ($a_0=3.087$ Å) in the medium of the dielectric permittivity of acetic acid ($\varepsilon=6.15$) and carbon tetrachloride ($\varepsilon=2.24$). Results of these calculations are presented in Tables 16 and 17. In all cases all the methods used predicted the cyclic conformation of the respective hydrogen-bonded complex to be the most stable.

Table 16

Results of the calculations of the water dimer in a polarizable isotropic medium (ε=78)

Method	*B*, kcal/mol	μ, D	*R*, Å	Angle O—H..O, °
MINDO/3	—5.377	4.579	4.310	89.7
MNDO	—1.844	3.794	3.929	130.8
AM1	2.847	4.208	2.599	107.5
PM3	1.935	4.127	2.678	153.7
Exp. [26, 42]	3.4	—	2.802	—

Table 17

Results of the calculations (B values) of acetic acid, formic acid and methanol in various polarizable isotropic media

Method	Acetic acid dimer		Formic acid dimer	Methanol dimer	
	ε=6.15	ε=2.24	ε=57	ε=31.2	ε=2.24
MINDO/3	—4.09	—2.19	0.83	—3.14	—3.14
MNDO	—1.69	—0.31	1.01	—0.68	—0.69
AM1	2.48	4.25	18.4	1.86	1.86
PM3	5.27	6.93	3.23	2.58	1.58
Exp. [26]	11.6	10.8	13.9	4.7	4.6

4. Discussion

4.1. Gas phase calculations

4.1.1. Energy of hydrogen bond. Dependences between calculated and experimentally found hydrogen bond energies are presented in Fig. 12. The dispersion analysis of the calculational data vs. experimental data and one-parameter regressional analysis according to the formula

$$B_{\mathrm{CALC}}=a+b\cdot B_{\mathrm{EXP}}, \tag{3}$$

where B_{CALC} is the calculated and B_{EXP} is the experimentally observed energy of the hydrogen bond, was carried out. The corresponding results are presented in Tables 18 and 19, where b is the slope, D is the average deviation, r denotes the correlation coefficient, s is the standard deviation and s_0 is normalized standard deviation, which is calculated according to the formula

$$s_0=\sqrt{s^2/\sigma^2}, \tag{4}$$

where σ^2 is the dispersion of the quantity to be correlated. It can be easily seen that MINDO/3 and MNDO fail to reproduce the energy of the hydrogen bond, which was previously observed on different systems [10, 11, 20, 21], somewhat surprisingly the same is observed for the PM3 results. In the case of AM1 the agreement with experiment is considerably better, but hardly satisfactory. There is a significant residual (—1.18 kcal/mol) and the slope is by no means unity. It should be mentioned that in case of *ab initio* calculations the agreement with the experiment of the same quality as AM1 has been obtained only using 6—31G* and higher level basis sets [19, 23]. Therefore, search for better semiempirical parametrizations for the hydrogen-bonded systems is necessary.

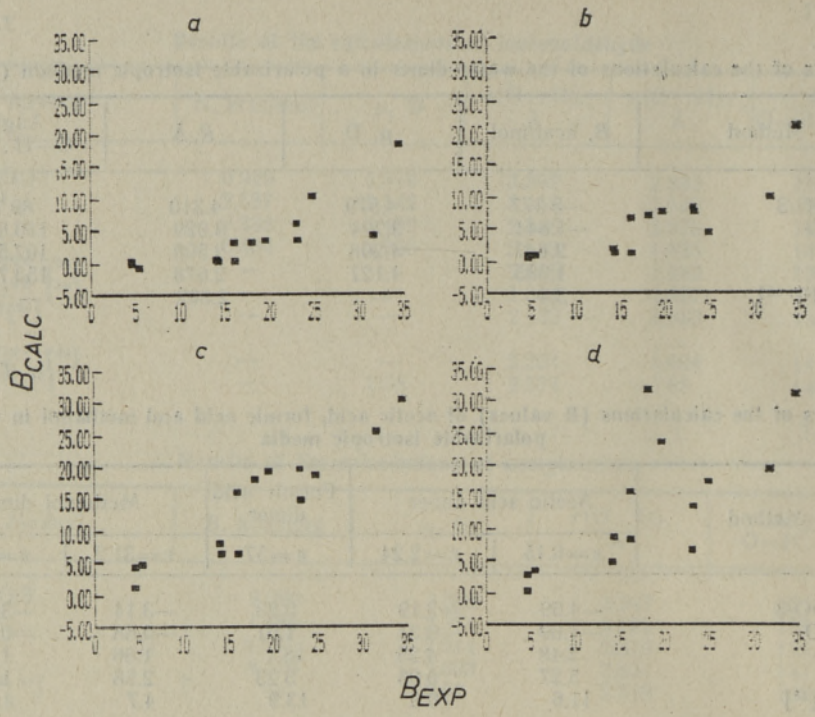

Fig. 12. Dependences between calculated and experimentally found hydrogen bond energies: *a* — for MINDO/3, *b* — MNDO, *c* — AM1, and *d* — PM3.

Table 18

Statistical parameters of the dispersion analysis of calculational data vs. experimental data

Method	*b*	*r*	*s*	*D*
MINDO/3	0.256±0.049	0.701	3.674	14.06
MNDO	0.357±0.045	0.798	3.341	12.12
AM1	0.797±0.045	0.924	3.343	4.000
PM3	0.758±0.096	0.717	7.132	7.008

Table 19

Results of the linear regression analysis of the calculational data according to Eq. (3)

Method	*b*	*a*	*r*	*s*	s_0
MINDO/3	0.440±0.098	—4.10±1.95	0.792	3.268	0.176
MNDO	0.506±0.092	—3.33±1.83	0.846	3.080	0.153
AM1	0.878±0.101	—1.81±2.01	0.930	3.367	0.107
PM3	0.793±0.222	—0.78±4.42	0.718	7.414	0.201

4.1.2. Geometry of complexes. The best agreement with experimental geometry is obtained by using the PM3 parametrization, the AM1 parametrization gives somewhat worse agreement with the experiment whereas MINDO/3 and MNDO are unable to reproduce the right configuration of hydrogen-bonded systems. In the case of *ab initio* calculations 4—31G* and higher level basis sets are needed for the correct prediction of geometry [19, 23, 39].

4.2. Liquid state (self-consistent reaction field) calculations

It should be noted that in the case of condensed systems the agreement with experimental results was generally not satisfactory. As we have studied only a relatively small number of complexes whose results had notable deviation from experimental data in the gas phase too, the problem needs more thorough experimental and theoretical investigation. Nevertheless, it can be concluded that a new parametrization for the hydrogen bond in liquid media is necessary. The corresponding effort has been undertaken by the present authors and will be discussed elsewhere.

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Peeter BURK, Mati KARELSON

POOLEMPIIRILISTE KVANTKEEMILISTE ARVUTUSMEETODITE VÕIMEST KIRJELDADA VESINIKSIDEMEGA SÜSTEEME

Erinevaid poolempiirilisi kvantkeemilisi arvutusmeetodeid (MINDO/3, MNDO, AM1, PM3) kasutades on arvutatud mõnede vesiniksidemega komplekside struktuur, dipoolmomendid ja vesiniksideme energia. Suhteliselt hea kokkulangevus eksperimendiga saavutati ainult AM1-meetodi puhul, samal ajal kui PM3-meetod ei suutnud reprodutseerida vesiniksideme energiat. On leitud, et MINDO/3- ning MNDO-meetod ei ole võimelised kirjeldama vesiniksidemega süsteemide struktuuri ja energiat.

Пеетер БУРК, Мати КАРЕЛСОН

О ПРИМЕНИМОСТИ НЕКОТОРЫХ ПОЛУЭМПИРИЧЕСКИХ КВАНТОВО-ХИМИЧЕСКИХ РАСЧЕТНЫХ МЕТОДОВ ДЛЯ ОПИСАНИЯ КОМПЛЕКСОВ С ВОДОРОДНЫМИ СВЯЗЯМИ

Разными полуэмпирическими квантовохимическими расчетными методами (MINDO/3, MNDO, AM1, PM3) вычислены энергии и оптимальная структура ряда комплексов с водородными связями. Относительно хорошее совпадение с экспериментом получено только методом AM1, а метод PM3 не в силах репродуцировать энергии водородной связи. Найдено, что методы MINDO/3 и MNDO негодны для описания геометрии и энергии комплексов с водородными связями.