

DIRECTIONAL HYDROGEN BONDING IN THE MM3 FORCE FIELD. I

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The MM3 molecular mechanics program calculates a fair representation of hydrogen bonding interactions, but to improve the MM3 hydrogen bond potential, a directional term has been added to the hydrogen bonding function. The resulting total function was reoptimized. Comparisons of the hydrogen bonding potential functions from *ab initio*, the original MM3, the current MM3(92) force field and the reoptimized MM3 force field MM3(94) for a variety of C,N,O systems are described.

INTRODUCTION

The concept of the hydrogen bond is well established, and because of its important role in chemistry and biology, a large number of experiments and quantum mechanical calculations have been carried out regarding it.¹ The strength of the hydrogen bond formed is believed to be best correlated with the acidity of the hydrogen atom and the basicity of the atom with the unshared electron pair (or the hydrogen acceptor),² although electrostatic interactions are also important. Unless the acidity of the hydrogen and the basicity of the acceptor atom are sufficient, any hydrogen bonds formed are usually too weak to be of significance. Of course, if the hydrogen atom is too acidic and the acceptor atom is too basic, the hydrogen will be transferred as a proton to form a covalent bond with the acceptor atom in a simple acid-base reaction.

In 1975, Allen³ proposed that the hydrogen bond energy is proportional to the difference between the effective first ionization potentials of the hydrogen acceptor atom Y and the noble gas atom in its row, ΔI , and also proportional to the bond moment of the X-H bond, μ_{X-H} , and inversely proportional to the distance between the hydrogen and the acceptor atom, R_{YH} , at the equilibrium distance (see Figure 1):

$$E_{HB} \propto \mu_{X-H}(\Delta I/R_{YH})$$

In the MM3 force field,^{4,5} the hydrogen bonding energy was originally described as the sum of electrostatic and

an explicit hydrogen bonding potential energies, where the latter was of the van der Waals form (E_{vdw-HB}),

$$E_{HB} = E_{ele} + E_{vdw-HB}$$

where E_{ele} is usually a dipole-dipole interaction.

With the original force field MM3(89), the calculation of hydrogen bonding was reasonably satisfactory for most but not all cases. According to the model of the hydrogen bond introduced by Coulson⁶ in 1957, the strength of the hydrogen bond is also proportional to the overlap integral (S_{YH}) between the HOMO of the electron donor atom Y and the LUMO of the electron acceptor atom H. More precisely, the HOMO is taken to be a hybridized lone pair orbital of the electron donor atom Y and the LUMO a σ^* antibonding orbital of the electron-pair acceptor X-H bond.⁷ Therefore, we believed that the lack of directionality in the original MM3 hydrogen bonding potential, which amounts to a neglect of this overlap, was responsible for these inadequate results. A directional term was therefore added to the hydrogen bonding function. This function was included in MM3(92). More recently the parameters in the latter function have been reoptimized, and now are included in MM3(94). A comparison of MM3(92) and MM3(94) with the original MM3 is described in the following.

HYDROGEN BONDING POTENTIAL FUNCTIONS

In MM3, the hydrogen bonding energy was described as the sum of dipole-dipole interaction and an explicit

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hydrogen bond potential of the van der Waals form. The dipole-dipole parts of the potentials for MM3 and MM3(92) are identical. The explicit van der Waals-type hydrogen bonding potentials are given below for both MM3 and MM3(92). Equation (2) differs from equation (1) by the addition of the term $F(\beta, R_{X-H})$. Otherwise the two equations are the same. The equations used for MM3(94) are the same as those for MM3(92); only the parameters have been reoptimized.

Explicit MM3 hydrogen bonding potential function (original):

$$E_{HB} = \epsilon_{HB} \times \{184\,000 \exp[-12 \cdot 0(R_{YH}/r)] - 2 \cdot 25(r/R_{YH})^6\} / D \quad (1)$$

Explicit MM3(92) hydrogen bonding potential function:

$$E_{HB} = \epsilon_{HB} \{184\,000 \exp[-12 \cdot 0(R_{YH}/r)] - F(\beta, R_{X-H}) \times 2 \cdot 25(r/R_{YH})^6\} / D \quad (2)$$

where

$$F(\beta, R_{X-H}) = \cos \beta (R_{X-H} / R_{X-H}^0)$$

ϵ_{HB} is hydrogen bonding energy parameter, r is equilibrium hydrogen bonding distance, R_{YH} is hydrogen bonding distance $Y \cdots H$, $\cos \beta$ is the cosine of angle $H-X \cdots Y$, R_{X-H} is the bond length of bond $X-H$, R_{X-H}^0 is the natural bond length of bond $X-H$ and D is the dielectric constant. These relationships are summarized in Figure 1. In our hydrogen bonding formulation, the magnitude of ϵ_{HB} is proportional to the difference of the first ionization potential between the hydrogen acceptor Y and the donor X , and also the bond moment of bond $X-H$. The $\cos \beta$ term is introduced to account for the overlap between the HOMO of the electron donor Y and the LUMO of the electron acceptor bond $X-H$. The linearity of the hydrogen bond is believed to be due mainly to the cylindrical (or nearly cylindrical) symmetry of the LUMO. As we know, the bond moment is defined as the product of charge separation Δq_{X-H} and the bond length R_{X-H} :

$$\mu_{X-H} = K \Delta q_{X-H} R_{X-H}$$

If the charge separation in the bond were approximately constant:

$$\Delta q_{X-H} = \mu_{X-H} / (K R_{X-H}^0)$$

we could then assume the bond moment is proportional to the ratio R_{X-H} / R_{X-H}^0 , and thus we have reason to

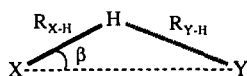


Figure 1. Hydrogen bonding parameters

believe that the hydrogen bonding potential is also proportional to the ratio R_{X-H} / R_{X-H}^0 .

Energy contours for the explicit hydrogen bonding of water to water are shown. The original MM3(89) function is shown in Figure 2(a) and the directionally dependent MM3(94) function is shown in Figure 2(b). The hydrogen-bonded $O \cdots H$ distance shown in Figure 2 is optimal at 1.82 Å. If the O—H bond is kept fixed and the other oxygen is moved elsewhere, the energy of the system is as given by the contour diagrams in Figure 2.

In Figure 3 is shown a perspective view of the potential surface from Figure 2(b). The energy is lowest when the oxygen is in the trough at the lower right.

CALCULATIONS

We have carried out a number of calculations, including for the water complex, methanol dimer, ethylene glycol, propane-1,3-diol, 2-methoxyethanol, ammonia dimer, ethylenediamine, ammonia-water complex, 2-aminoethanol, ethylene-water complex and pent-4-ene-1-ol. In each case except the last, restricted Hartree-Fock calculations (either 6-31G** or 6-31G**MP2) were carried out to give us 'experimental' results to fit to with the molecular mechanics calculation. The 6-31G* results of hydrogen-bonded complexes have been demonstrated to be internally consistent and of reasonable accuracy by Dill *et al.*⁸ We believe that the polarization functions on hydrogen may be important for the hydrogen bonding geometry in some cases. Therefore, we chose 6-31G** as our standard basis set, and did the calculations at the Hartree-Fock level, except for those systems containing double bonds, where the corresponding MP2 level was used instead. (Double bonds have bond lengths calculated much too short at the Hartree-Fock level.) In dimer cases, the basis set superposition errors (BSSE) that arise from the compensation of inadequacies of the basis set by diffuse functions of neighboring centers are corrected for by the counterpoise method of Boys and Bernardi.⁹ The overall results calculated with reoptimized parameters (shown in Table 1) compared with the experimental and *ab initio* results are better now [MM3(94)] than they were with MM3 and MM3(92). These results are shown in Tables 2-14. The details regarding each system will be discussed in turn. Additional studies on the formamide dimer, formamide-water complex, formate-water complex, ammonium ion-water complex, guanidinium-water complex and 4-chlorobutanol will be discussed in a forthcoming paper.

DISCUSSION

Water complexes

There are three water dimers, three water trimers and an ice-like pentamer included in this study. An *ab initio*

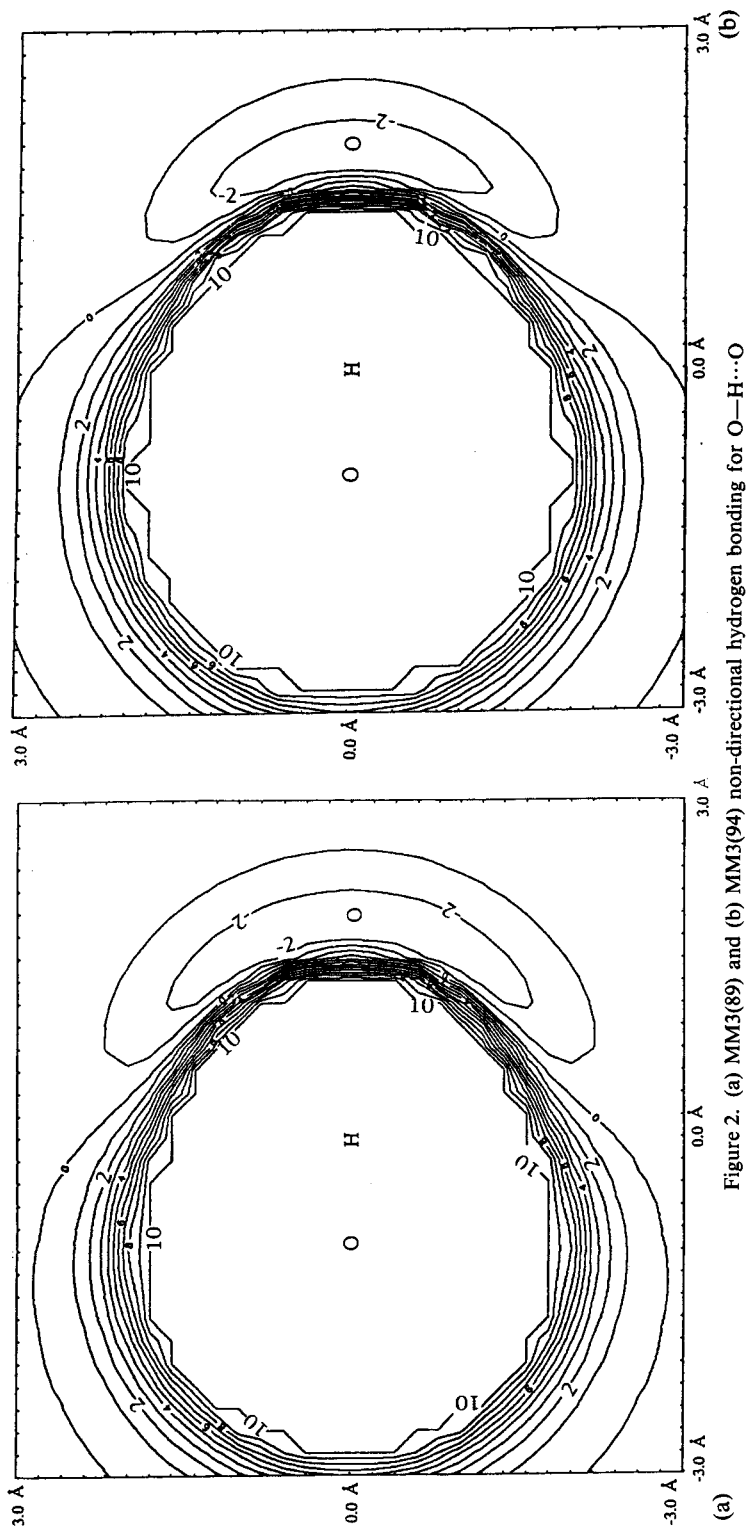


Figure 2. (a) MM3(89) and (b) MM3(94) non-directional hydrogen bonding for O—H...O

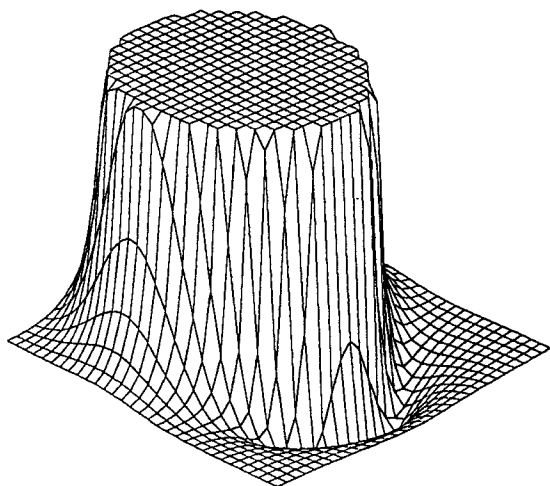


Figure 3. MM3(94) directional hydrogen bonding for O—H...O [see Figure 2(b)]

Table 1. MM3(94) force field for directional hydrogen bonding^a

(a) Hydrogen bonding parameters			
Hydrogen bond type	ϵ_{HB}	r	
=C...H(O) (2...21)	0.550	2.65	
O...H(O) (6...21)	3.000	2.11	
O...H(N) (6...23)	1.300	2.38	
N...H(O) (8...21)	4.700	2.15	
N...H(N) (8...23)	2.280	2.40	

(b) Torsional parameters			
Angle type	V_1	V_2	V_3
O—C—C—O (6-1-1-6)	0.50	-2.00	1.90
O—C—C—N (6-1-1-8)	0.00	-1.05	1.85
O—C—C—N (8-1-1-8)	0.00	-0.90	1.70

^a ϵ_{HB} is the well depth parameter in the Van der Waals equation⁴ in kcal mol⁻¹ and r is the distance between the atoms at the energy minimum in Å. V_1 , V_2 and V_3 are in kcal mol⁻¹.

study of the three water dimers using a 6-31G** basis set plus a BSSE correction and full geometry optimization was carried out, and our results are comparable to those reported by others.¹⁰ The MM3 directional hydrogen bonding potential for type 6-21...6 (O—H...O) was then reoptimized to fit to the *ab initio* structures and dimerization energies. Table 2 clearly shows that MM3(94) with the directional hydrogen bonding gives more reasonable results. Unlike

MM3(89), which predicted the bifurcated dimer (3) to be more stable, MM3(94) now calculates the linear dimer (1) as the most stable, with no negative eigenvalues for the force constant matrix. Compared with the *ab initio* results, MM3(94) still somewhat overestimates the hydrogen bonding interaction for the bifurcated water dimer, although the structure and energy have been much improved. Further studies of the water trimers and the pentamer with MM3(94) also show reasonable results as shown in Table 3.

Methanol dimers

Again, *ab initio* calculations with a 6-31G** basis set, full geometry optimization and a BSSE correction have been carried out for the linear and cyclic methanol dimers. Our results appear similar to those reported earlier.¹¹ The results (Table 4) indicate that the linear complex (8) is the most stable with no negative eigenvalues, while the cyclic complex (9) (C_{2h} symmetry) has three negative eigenvalues. Compared with the water dimers, the MM3 potential surface for the methanol dimers is more simple. All MM3 calculations predict that the linear dimer is the most stable. It appears that steric effects help to hold the linear dimer in the local minimum. As shown in Table 4, the energy difference between the two complexes has been greatly improved with the directional hydrogen bonding potential [from 0.9 to 1.5 kcal mol⁻¹ (1 kcal = 4.184 kJ)] In the MM3(94) calculation, the O...O distances are calculated to be 2.957 Å, (*ab initio* 2.957 Å) and 2.791 Å (*ab initio* 2.804 Å) for linear and cyclic dimers, respectively.

Ethylene glycol

To see how the directional hydrogen bonding will affect a molecule with the internal hydrogen bonding, we chose ethylene glycol as our first target. Four stable conformations and two rotamers (with dihedral angles O—C—C—O of 0° and 120°, respectively) of ethylene glycol were investigated. *Ab initio* calculations with a 6-31G** basis set were carried out. Compared with the 4-21G results,¹² our relative energies among the conformations are about 0.2–1.6 kcal mol⁻¹ smaller. The original O—C—C—O (6-1-1-6) torsional parameter was modified to improve the calculated energy difference among the ethylene glycol conformations. For the most stable conformation tGg' (10), the geometries are basically the same from MM3(94) as they were with MM3(89), except that the O—C—C—O dihedral angle increased (from 59.6° to 61.6°) owing to the directional hydrogen bonding. The moments of inertia of the two isotopic species are, however, significantly improved (see Table 5). A study of Table 5 also shows that the dipole moments and energy differences among conformations (10–13) as calculated by MM3(94) are in reasonable agreement with the 6-31G** results.

Table 2. Dimerization energies and geometries for water dimer

(I) (H ₂ O) ₂ linear, C _s (1)					
	6-31G**	Exp.	MM3	MM3(92)	MM3(94)
<i>E</i> (dimerization)	-5.54				
BSSE	-0.96				
<i>E</i> (corrected)	-4.58	-5.2(1.5) ¹⁶	-5.97	-5.44	-4.77
Dipole moment	2.667	2.6 ¹⁷	3.691	3.532	3.508
Imaginary frequency	0	0	N/A	0	0
O...O distance	2.981	2.976 ¹⁸	2.671	2.689	2.942
O...H distance	2.038		1.723	1.747	2.007
O—H bond length	0.948		0.950	0.953	0.952
∠ H—O...O	5.0	6(20) ¹⁸	0.0	7.0	8.9
∠ O...O...X	117.9	123(10) ¹⁸	180.0	163.2	160.3
(II) (H ₂ O) ₂ cyclic, S ₂ (2)					
	6-31G**		MM3	MM3(92)	MM3(94)
<i>E</i> (dimerization)	-5.09				
BSSE	-1.82				
<i>E</i> (corrected)	-3.27		-5.46	-3.13	-3.47
Dipole moment	0.025		0.000	0.001	0.000
Imaginary frequency	1		1	1	1
O...O distance	2.887		2.395	2.633	2.832
O...H distance	2.334		1.956	2.144	2.300
O—H bond length	0.945		0.950	0.950	0.950
∠ H—O...O	45.8		51.1	49.6	47.5
(III) (H ₂ O) ₂ bifurcated, C _{2v} (3)					
	6-31G**		MM3	MM3(92)	MM3(94)
<i>E</i> (dimerization)	-4.08				
BSSE	-0.83				
<i>E</i> (corrected)	-3.25		-7.20	-4.43	-4.36
Dipole moment	4.634		4.195	4.186	4.163
Imaginary frequency	1		0	1	1
O...O distance	3.012		2.360	2.532	2.746
O...H distance	2.535		1.895	2.057	2.266
O—H bond length	0.944		0.947	0.948	0.948
∠ H—O...O	51.5		50.0	50.1	50.6

Table 3. Binding energies and geometries for water trimers and pentamer

	E (kcal mol ⁻¹)		
	6-31G** (with BSSE correction)	PM3 ¹⁹	MM3(94)
Trimer 4	-13.71	-10.14	-12.25
Trimer 5	-7.36	-6.06	-8.73
Trimer 6 ^a	-7.73	-6.76	-8.71
Pentamer 7 ^a	-21.09	-17.93	-19.30

	O...O distance (Å)	
	6-31G**	MM3(94)
Trimer 4	2.865/2.869/2.888	2.934/2.936/2.936
Trimer 5	2.936/2.974	2.959/2.963
Trimer 6 ^a	3.010/3.010	2.959/2.959
Pentamer 7 ^a	2.890/2.890/2.932/2.932	2.942/2.942/2.944/2.944

^a Trimer 6 and pentamer 7 have been restricted to C_{2v} symmetry.

Table 4. Dimerization energies and geometries for methanol dimer

(I) (CH₃OH)₂ linear, C_1 (8)

	6-31G**	MM3	MM3(92)	MM3(94)
E (dimerization)	-5.42			
BSSE	-0.89			
E (corrected)	-4.52	-5.54	-5.34	-4.87
Dipole moment	3.151	3.040	3.063	3.112
Imaginary frequency	0	0	0	0
O...O distance	2.957	2.697	2.707	2.957
O...H distance	2.011	1.748	1.753	2.004
O—H bond length	0.947	0.947	0.955	0.953

(II) (CH₃OH)₂ cyclic, C_{2h} (9)

	6-31G**	MM3	MM3(92)	MM3(94)
E (dimerization)	-4.29			
BSSE	-1.02			
E (corrected)	-3.28	-4.65	-2.97	-3.41
Dipole moment	0.003	0.000	0.000	0.000
Imaginary frequency	3	3	3	3
O...O distance	2.804	2.419	2.612	2.791
O...H distance	2.311	1.933	2.164	2.306
O—H bond length	0.944	0.951	0.951	0.951

Table 5. Energetic and geometric quantities for ethylene glycol (tGg')^a

	6-31G**	E.D. ²⁰	MM3	MM3(92)	MM3(94)
$E(tTt) - E(tGg')$	2.02		1.90	1.41	2.04
C1—C2	1.513		1.522	1.524	1.524
C2—O3	1.406		1.433	1.434	1.434
C1—O4	1.396		1.431	1.432	1.432
O3—H5	0.942		0.948	0.948	0.948
O4—H6	0.945		0.950	0.950	0.950
Av. C—C/C—O	1.438	1.455	1.462	1.463	1.463
Av. C—H/O—H	1.040	1.066	1.058	1.058	1.058
C1—C2—O3	106.9		107.4	108.0	108.1
C2—C1—O4	111.4		108.5	109.7	109.2
Av. C—C—O	109.2	110.0	108.0	108.9	108.7
C2—O3—H5	110.5		108.2	108.2	108.2
C1—O4—H6	107.9		106.3	106.5	106.2
Av. C—O—H	109.2	99.2	107.3	107.9	107.2
H5—O3—C2—C1	-169.9		-179.7	-179.7	179.5
O3—C2—C1—O4	60.8	57.9	59.6	62.6	61.6
C2—C1—O4—H6	-53.9		-50.5	-52.5	-50.5
Ia			5.611	5.509	5.526
Ib			14.671	15.138	15.121
Ic			17.996	18.275	18.304

Moments of inertia of OH'/OD^b

	MW ²¹	MM3	MM3(92)	MM3(94)
Ia	5.548	5.664 (2.1%)	5.555 (0.1%)	5.575 (0.5%)
Ib	15.801	15.493 (-1.9%)	15.996 (1.2%)	15.959 (1.0%)
Ic	19.020	18.860 (-0.8%)	19.162 (0.7%)	19.180 (0.8%)

Moments of inertia of OD'/OH^c

	MW	MM3	MM3(92)	MM3(94)
Ia	5.740	5.877 (2.4%)	5.774 (0.6%)	5.793 (0.9%)
Ib	15.125	14.783 (-2.3%)	15.285 (1.1%)	15.243 (0.8%)
Ic	18.575	18.374 (-1.1%)	18.683 (0.6%)	18.693 (0.6%)

 E_{rel} (kcal mol⁻¹)/dipole moment (D)

	6-31G**	MM3	MM3(92)	MM3(94)
tGg' (10) ^d	0.000/2.65	0.000/2.69	0.000/2.62	0.000/2.66
tTt (11)	2.024/0.00	1.896/0.00	1.406/0.00	2.039/0.00
gGg' (12)	0.644/2.60	0.975/2.66	1.022/2.64	0.980/2.62
tGt (13)	3.659/1.61	2.337/1.34	2.005/1.37	2.618/1.45
TS1 ^e	6.907/3.61	3.690/3.28	4.161/3.28	6.967/3.19
TS2 ^f	5.794/1.96	4.141/1.89	3.720/1.88	5.807/1.91

^a g and G mean *gauche*(+); g' and G' mean *gauche*(-); t and T mean *trans*; s means *syn*. We use different case letters here, such as g and G, only to improve readability.

^b OH' is the hydrogen-bonded OH group.

^c OD' is the hydrogen-bonded OD group.

^d The three dihedral angles are H1—O1—C—C, O1—C—C—O2 and C—C—O2—H2, respectively.

^e TS1: O1—C—C—O2 = 0.0° (three dihedral angles are *trans*-0°-0°).

^f TS2: O1—C—C—O2 = 120.0° (three dihedral angles are *trans*-120°-*gauche*(-)).

Table 6. Energetic and geometric quantities for propane-1,3-diol^a

	G'gG't (14)			
	E.D. ²²	MM3	MM3(92)	MM3(94)
Av. C—C	1·514(8)	1·530	1·531	1·530
Av. C—O	1·410(6)	1·434	1·435	1·434
Av. C—H	1·140(2)	1·113	1·113	1·113
O1—H6	1·04 (7)	0·950	0·953	0·952
O5—H7	0·98 (7)	0·948	0·948	0·948
C2—C3—C4	112(1·5)	112·8	113·0	114·0
C3—C2—O1	108(1·5)	110·4	110·4	111·1
C3—C4—O5	112(1·5)	109·0	109·2	110·0
C2—O1—H6	109(3·0)	107·6	107·1	107·3
C4—O5—H7	97(3·0)	108·2	108·2	108·2
Av. C—C—H	109	109·8	109·8	109·8
H6—O1—C2—C3	-46 (5)	-43·1	-40·4	-44·6
O1—C2—C3—C4	68 (3)	65·4	65·2	71·4
C2—C3—C4—O5	-61 (5)	-55·2	-56·4	-61·4
C3—C4—O5—H7	180	-175·0	-174·9	-175·2

	E_{rel} (kcal mol ⁻¹)/dipole(D)			
	6-31G**	MM3	MM3(92)	MM3(94)
G'gG't (14) ^b	0·000/3·73	0·000/3·43	0·000/3·44	0·000/3·42
GgG'g (15)	-0·029/2·67	0·477/2·53	0·678/2·78	0·493/2·49
TgGg' (16)	1·362/2·50	3·349/2·57	3·000/2·47	2·205/2·72

^aSee footnote a in Table 5.^bThe four dihedral angles are H1—O1—C—C, O1—C—C—C, C—C—C—O2 and C—C—O2—H2 respectively.

Propane-1,3-diol

Our *ab initio* 6-31G** calculations showed that the most stable conformer of propane-1,3-diol is an internally hydrogen-bonded form, which is chair-like with a non-bonded O—H group in an axial-like position, GgG'g (15). The next most stable conformer is also an internally hydrogen-bonded form, but with the non-bonded O—H group in an equatorial-like position, G'gG't (14). The second conformer is higher in energy than the first one by only 0·03 kcal mol⁻¹. The third stable conformation (16) is a boat-like form, and it is higher in energy than the second one by 1·36 kcal mol⁻¹. In contrast, all MM3 calculations predict the second conformer as most stable one, and lower in energy than the first one by about 0·5 kcal mol⁻¹. Table 6 shows that the MM3 results agree with those of the gas-phase ED study. The directional hydrogen bonding term in this case mainly reduces the energy difference between chair-like and boat-like conformers to nearer the *ab initio* value.

2-Methoxyethanol

Compared with ethylene glycol and other diols, the

intramolecular hydrogen bond in this 2-substituted ethanol is thought to be weaker, but it appears to be the key factor determining the relative stability of the molecular conformations observed in both the microwave and in the *ab initio* studies. Our 6-31G** and MM3 calculations show that the *gauche* conformer, tGg' (17), with an internal hydrogen bond is the most stable conformation. Generally, the MM3 structure of the tGg' conformation is in agreement with both the MW and *ab initio* results. The discrepancy between the MM3(94) moments of inertia and experiment suggests that the dihedral angle of O—C—C—O is calculated to be slightly too large in this case. The C—C—O angle at the alcohol end of the molecule which does not open up enough may be a factor in the discrepancy. A further study of the C—C—O angle opening due to the torsion-bend interaction will be discussed elsewhere. Table 7 shows that the MM3(94) calculations agree fairly well with the *ab initio* results in both conformational energies and dipole moments.

Hydrogen bonding O—H frequency

It has been found in infrared studies that a hydrogen-bonded hydroxyl absorbs at a lower frequency than

Table 7. Conformational energies, dipole moments and moments of inertia for 2-methoxyethanol^a

	E_{rel} (kcal mol ⁻¹)/dipole moment(D)			
	6-31G**	MM3	MM3(92)	MM3(94)
tGg' (17) ^b	0.000/2.55	0.000/2.15	0.000/2.10	0.000/2.16
tTt	2.019/0.33	1.617/0.51	1.258/0.51	1.934/0.51
tGt	3.536/1.64	1.854/1.64	1.577/1.65	2.141/1.72
tTg	2.304/2.17	2.472/2.01	2.119/2.01	2.803/2.01
g'Gt	3.691/1.77	2.900/1.91	2.597/1.91	3.470/1.93
g'Tt	3.866/1.92	3.377/2.14	3.022/2.14	3.740/2.09
gGt	5.449/3.21	3.866/2.87	3.591/2.87	4.066/2.90

	tGg' (17)				
	6-31G**	M.W. ²³	MM3	MM3(92)	MM3(94)
C—C	1.514	1.52	1.523	1.524	1.525
Av. C—O	1.396	1.41	1.424	1.424	1.424
Av. C—H	1.088	1.09	1.113	1.113	1.113
O—H	0.944	1.01	0.949	0.949	0.950
C—O—C	114.7	111.7	112.0	112.0	112.0
C—O—O(—C)	107.3	109.6	107.4	107.9	108.0
C—C—O(—H)	111.5	112	108.7	109.2	109.2
C—O—H	107.9	105	106.8	107.0	106.7
O—C—H(t)	107.7	107.2	109.3	109.3	109.3
O—C—H(g)	111.4	110.8	110.7	110.7	110.7
H(g)—C—H(t)	108.9	109.6	108.3	108.3	108.3
H(g)—C—H(g)	108.5	108.7	109.5	109.5	109.5
Av. C—C—H	109.8	111.4	110.5	110.5	110.5
C—O—C—C	-175.9	172(3)	-179.8	-179.8	-179.8
O—C—C—O	60.6	45(5)	61.4	63.9	62.1
H—O—C—C	-53.8	-57(3)	-52.7	-54.5	-51.7
Dipole moment	2.55	2.36	2.15	2.10	2.16

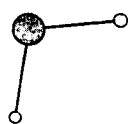
Moments of inertia of CH₃OCH₂CH₂OH (tGg', 17)

	M.W.	MM3	MM3(92)	MM3(94)
Ia	6.4642	6.4845(0.3%)	6.4176(-0.7%)	6.4481(-0.2%)
Ib	30.6004	30.5710(-0.1%)	31.0510(1.5%)	30.9178(1.0%)
Ic	34.0023	33.9924(-0.0%)	34.3188(0.9%)	34.2754(0.8%)

Moments of Inertia of CH₃OCH₂CH₂OD (tGg', 17)

	M.W.	MM3	MM3(92)	MM3(94)
Ia	6.7756	6.7838(0.1%)	6.7201(-0.8%)	6.7466(-0.4%)
Ib	30.7996	30.8076(0.0%)	31.3094(1.6%)	31.1617(1.2%)
Ic	34.5152	34.5259(0.0%)	34.8769(1.0%)	34.8160(0.9%)

^a See footnote in Table 5.^b The three dihedral angles are C—O—C—C, O—C—C—O and C—C—O—H, respectively.



1



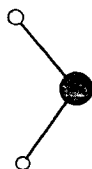
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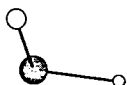
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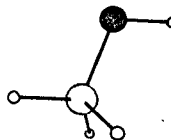
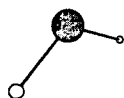
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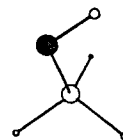
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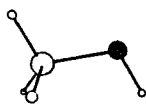


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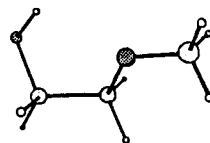
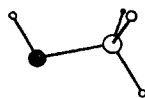


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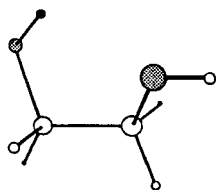




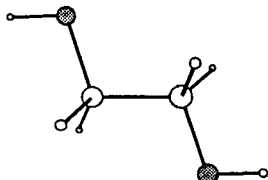
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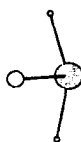
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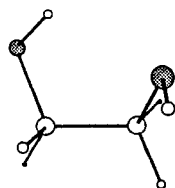
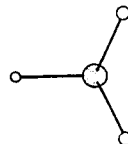
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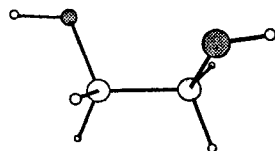
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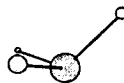
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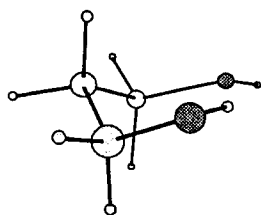
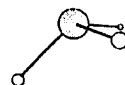
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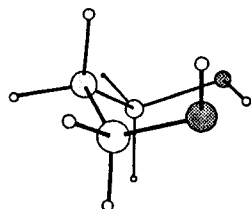
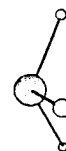
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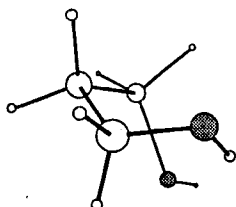
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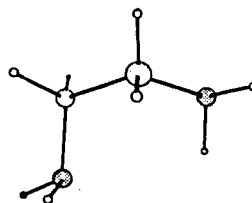
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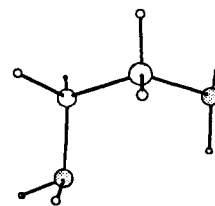
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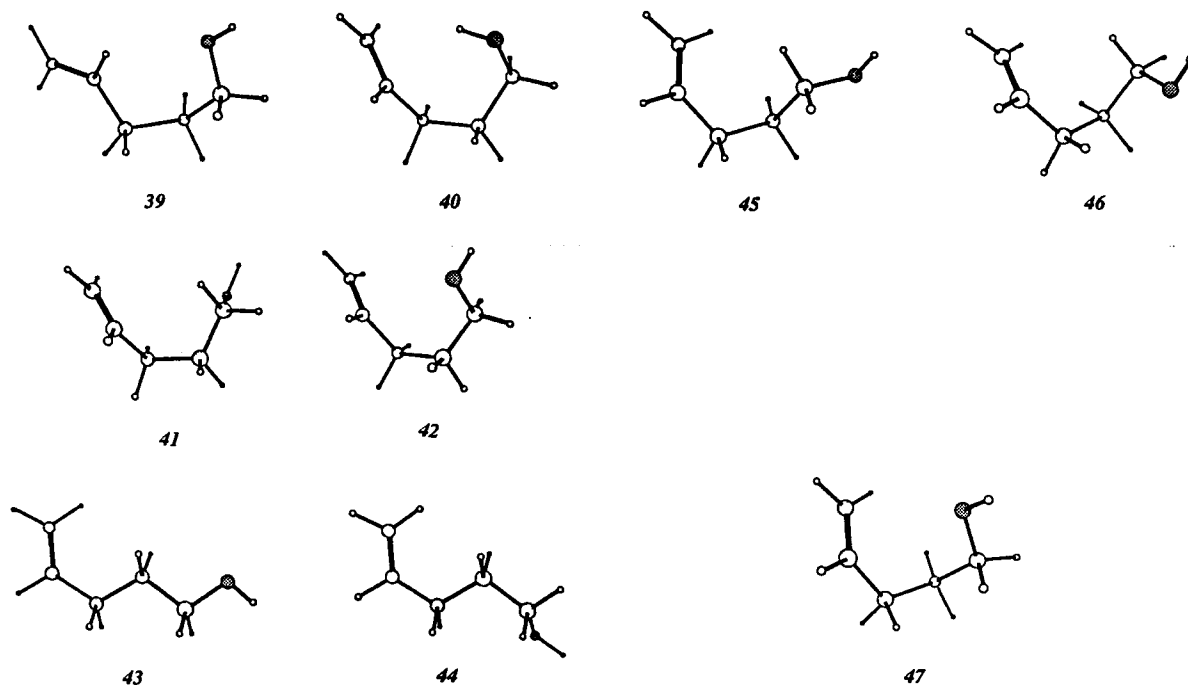
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21



22



does an unbonded one. The separation between the bonded and unbonded frequencies is larger the stronger the hydrogen bond. Table 8 shows that the frequency separation is slightly improved in the MM3(94) calculation, but the calculated shifts are still far from the observed values, and especially so for those compounds which have eclipsed O—C—C—O geometries. As with earlier MM3 calculations, we believe that the main reason for this problem is that the C—C—O angle does not open up enough in the eclipsed O—C—C—O conformation. If the C—C—O angle opened more in the *cis*-2,3-bicyclo[2.2.1]heptane diols, the O···H distance would also increase. Such a change would cause the hydrogen bonding distance to approach the distance

[2.11 Å in MM3(94)] corresponding to the minimum in the hydrogen bond potential, and this would increase the hydrogen bonding energy and widen the calculated frequency separation. Unfortunately, this cannot be improved within the constraints of the MM3 force field.

Ammonia dimer

In this study, we carried out the *ab initio* calculations for the linear, cyclic and staggered ammonia dimers. According to these calculations, the cyclic dimer (19) is slightly more stable than the linear one (18) at the uncorrected 6-31G** level, but with the BSSE correction added, the results favor the linear dimer by

Table 8. Separation of the bonded and unbonded hydroxy stretching frequency

	$\Delta\nu$ (Cm ⁻¹)				O···H distance (Å)		
	I.R. ²⁴	MM3	MM3(92)	MM3(94)	MM3	MM3(92)	MM3(94)
Ethylene glycol	32	29	28	39	2.271	2.361	2.342
<i>trans</i> -Cyclohexane-1,2-diol	32	24	26	38	2.341	2.380	2.355
<i>cis</i> -Cyclohexane-1,2-diol	39	40	45	46	2.122	2.180	2.247
<i>cis</i> -Cyclopentane-1,2-diol	61	45	56	48	2.031	2.090	2.206
<i>trans</i> -Cyclopentane-1,2-diol	0	0	0	0	4.300	4.301	4.306
<i>cis</i> -Bicyclo[2.2.1]heptane-2,3-diol (<i>exo</i>)	100	22	73	32	1.811	1.836	2.017
<i>cis</i> -Bicyclo[2.2.1]heptane-2,3-diol (<i>endo</i>)	100	33	76	40	1.846	1.874	2.045

Table 9. Dimerization energies and geometries for ammonia dimer

(I) (NH ₃) ₂ linear, C _s (18)				
	6-31G**	MM3	MM3(92)	MM3(94)
<i>E</i> (dimerization)	-3.05			
BSSE	-0.57			
<i>E</i> (corrected)	-2.49	-2.18	-1.69	-2.54
Dipole moment	2.875	2.808	2.480	2.162
Imaginary frequency	1	0	0	0
N...N distance	3.408	3.035	3.161	3.342
N...H distance	2.411	2.113	2.156	2.324
(II) (NH ₃) ₂ cyclic (19)				
	6-31G**	MM3	MM3(92)	MM3(94)
<i>E</i> (dimerization)	-3.14			
BSSE	-1.05			
<i>E</i> (corrected)	-2.09	-1.79	-1.15	-2.19
Dipole moment	0.008	0.000	0.000	0.000
Imaginary frequency	0	2	2	2
N...N distance	3.276	2.960	3.207	3.302
N...H distance	2.607	2.400	2.587	2.593
(III) (NH ₃) ₂ bifurcated, C _{3v} ((20)				
	6-31G**	MM3	MM3(92)	MM3(94)
<i>E</i> (dimerization)	-1.10			
BSSE	-0.48			
<i>E</i> (corrected)	-0.62	-1.83	-0.96	-1.35
Dipole moment	3.915	3.099	3.067	3.091
Imaginary frequency	2	2	2	2
N...N distance	3.750	2.845	3.168	3.174
N...H distance	3.481	2.614	2.926	2.925

0.4 kcal mol⁻¹. Again, our calculations confirm the results reported by others.^{10b,c,13} The dimerization energies are calculated to be -2.49, -2.09 and -0.62 kcal mol⁻¹ for linear, cyclic, and staggered dimer respectively. In general, MM3(94) gives better results for both energies and geometries than MM3. Unlike the *ab initio* results, MM3 calculated the cyclic dimer as a hill top instead of as a minimum (see Table 9). Another significant error in the original MM3 calculation is the N...N distance in the staggered dimer (20). MM3(94) gives a value of 3.18 Å which is still far from the *ab initio* value of 3.75 Å, but better than MM3 (2.61 Å).

Ethylenediamine

Microwave studies of ethylenediamine show that there are two low-energy forms of this compound, the gGg' (21) and tGg' (22) forms. Both van Alsenoy *et al.*'s 4-21G¹⁴ and our 6-31G** studies also show that these two forms are the most stable of the ten conformers

studied. Again, here the N—C—C—N (8-1-1-8) torsional parameter was slightly modified to fit the energy differences among the ethylenediamine conformers. Table 10 shows that MM3 calculations gave a systematic error for those conformations that have close N...N contacts and lone pairs on the nitrogens that are either pointing away from hydrogens [e.g. tGt (23) and g'Gg' (24)] or toward each other [e.g. gGg (25) and tGg (26)]. MM3(94) overestimates the hydrogen bonding energy for the above cases, which suggests that the position of the lone pair (rather than just the nitrogen) plays a significant role in the hydrogen bonding potential, especially for the ethylenediamine case. The results here are not significantly improved from those obtained earlier.

Ammonia-water complex

Two ammonia-water complexes, one with an N...H—O and the other with an O...H—N bridge, were

Table 10. Conformational energies and dipole moments for ethylenediamine^a

	E_{rel} (kcal mol ⁻¹)/dipole moment (D)			
	6-31G**	MM3	MM3(92)	MM3(94)
gGg' (21) ^b	0.000/2.03	0.000/1.87	0.000/1.85	0.000/1.89
tGg' (22)	0.018/2.51	-0.294/1.88	-0.220/1.86	-0.268/1.85
tTt	1.095/0.00	1.642/0.00	1.359/0.00	1.058/0.00
gGg (25)	0.560/0.30	0.123/1.08	0.138/1.10	-0.086/1.14
tGt (23)	1.508/0.50	0.562/1.45	0.676/1.43	0.330/1.40
tTg	1.201/2.45	1.649/2.12	1.332/2.12	1.065/2.12
gTg'	1.053/0.00	1.348/0.00	0.996/0.00	0.742/0.00
tGg (26)	1.293/2.47	0.546/2.50	0.613/2.50	0.329/2.51
gTg	1.177/2.00	1.587/2.09	1.236/2.09	0.984/2.09
g'Gg' (24)	3.709/1.80	1.359/0.88	1.288/0.92	1.639/0.89
TS1 ^c	6.285/2.55	5.336/2.38	5.863/2.37	6.109/2.33
TS2 ^d	5.491/2.32	5.059/1.80	4.786/1.80	5.109/1.80

^a See footnote a in Table 5.^b The three dihedral angles are LP1-N1-C-C, N1-C-C-N2 and C-C-N2-Lp2, respectively.^c TS1: N-C-C-N = 0.0°.^d NS2: N-C-C-N = 120.0°.

Table 11. Energetic and geometric parameters for ammonia-water complex

NH₃-H₂O linear (N is hydrogen acceptor, 27)

	6-31G**	MM3	MM3(92)	MM3(94)
E (dimerization)	-6.37			
BSSE	-0.63			
E (corrected)	-5.75	-5.96	-5.40	-5.80
Dipole moment	3.906	3.460	3.258	3.185
Imaginary frequency	0	1	0	0
O...N distance	3.050	2.599	2.654	3.009
N...H distance	2.101	1.705	1.706	2.063
O-H bond length	0.951	0.948	0.953	0.955

NH₃-H₂O linear (O is hydrogen acceptor, 28)

	6-31G**	MM3(92)	MM3(94)
E (dimerization)	-2.86		
BSSE	-0.92		
E (corrected)	-1.94	-1.65	-1.92
Dipole moment	1.963	2.576	1.890
Imaginary frequency	1	1	1
O...N distance	3.350	2.985	3.296
O...H distance	2.347	1.885	2.279
N-H bond length	1.002	1.017	1.018

investigated. Our 6-31G** calculations with geometry optimization and BSSE correction show that the nitrogen is a good hydrogen acceptor but a poor hydrogen donor. The complex (27) with the N...H—O bridge is calculated to be the more stable by 3.81 kcal mol⁻¹. The N...O distances are calculated to be 3.05 and 3.35 Å for complexes 27 and 28, respectively. Table 11 shows that the MM3(94) results agree fairly well with the *ab initio* results, and are much better than the earlier results.

2-Aminoethanol

The conformational energies of eleven conformations and two conformational transition states (with dihedral angles O—C—C—N of 0° and 120°) of 2-aminoethanol were studied. Both the *ab initio* and MM3 calculations (Table 12) showed that conformation g'Gg' (29) with internal N...H—O hydrogen bonding is the most stable one, and is about 1 kcal mol⁻¹ more stable relative to the other conformations from our 6-31G* calculations

than was found at the 4-21G level.¹⁴ The conformations with O...H—N internal hydrogen bonding, such as gGt (30), tGt, tGg and gGg, are calculated to be higher in energy than g'Gg' (29) by 1.5–2.2 kcal mol⁻¹. The MM3(94) results are in agreement with the 6-31G** results, except for the conformation tGg' (31). On examining the tGg' structure, we found that the lone pair on nitrogen is pointing away from the hydrogen which is close to the nitrogen. Again, MM3 overestimates the hydrogen bonding energy in this conformation, which points out the importance of the lone pair position in the hydrogen bonding.

Ethylene–water complex

The ethylene–water complex (32), with one hydrogen of the water molecule pointing toward the middle of the C=C bond, and the C=C bond lying in the water molecule plane, is calculated to be most stable by *ab initio*, MM3(92) and MM3(94) (Table 13). In contrast, MM3,

Table 12. Conformational energies and dipole moments for 2-aminoethanol^a

	g'Gg' (29) ^b			
	6-31G**	MM3	MM3(92)	MM3(94)
O...N	2.819	2.880	2.908	2.851
H...N	2.324	2.386	2.426	2.305
O...H1	3.333	3.327	3.428	3.270
O...H2	3.638	3.770	3.795	3.755
CCHN1	76.9	66.5	66.3	66.1
CCNH2	-163.0	-174.2	-174.4	-174.6
OCCN	57.9	62.5	63.9	57.9
HOCC	-43.6	-44.8	-45.7	-38.3
<i>E</i> _{rel} (kcal mol ⁻¹)/dipole moment (D)				
	6-31G**	MM3	MM3(92)	MM3(94)
g'Gg' (29)	0.000/3.20	0.000/2.91	0.000/2.90	0.000/2.95
gGt (30)	1.662/1.04	0.492/0.73	0.369/0.72	1.487/0.79
tGt	1.897/2.85	0.924/2.56	0.842/2.55	1.854/2.55
tGg	2.130/1.46	1.146/0.86	1.103/0.87	2.058/0.82
gGg	2.216/2.66	1.247/2.26	1.149/2.25	2.234/2.32
gTt	2.717/1.10	3.573/1.60	3.271/1.60	2.569/1.60
tTg	2.836/1.71	3.886/1.53	3.592/1.53	2.873/1.54
tTg	3.042/1.61	4.429/1.90	4.170/1.90	3.435/1.91
tTt	3.037/2.87	4.159/2.97	3.888/2.97	3.171/2.98
tGg' (31)	3.127/1.76	1.849/2.28	1.831/2.30	2.336/2.03
gTg'	3.049/2.89	4.255/2.96	3.962/2.96	3.245/2.96
TS1 ^c	8.232/1.74	7.958/1.89	8.254/1.90	8.355/1.65
TS2 ^d	8.206/3.18	6.183/2.79	5.910/2.79	7.729/2.79

^a See footnote a in Table 5.

^b The three dihedral angles are Lp—N—C—C, N—C—C—O and C—C—O—H, respectively.

^c TS1: O—C—C—N = 0.0°.

^d TS2: O—C—C—N = 120.0°.

Table 13. Energetic and geometric parameters for ethylene-water complex, C₂H₄-H₂O, C₁ (32)

	6-31G**	MP2 6-31G**	MM3	MM3(29)	MM3(94)
<i>E</i> (dimerization)	-2.14	-2.97			
BSSE	-0.68	-1.27			
<i>E</i> (corrected)	-1.46	-1.71	—	-1.898	-1.876
Dipole moment	2.368	2.461	—	2.050	2.052
Imaginary frequency	0	0	—	0	0
C=C...O distance	3.692	3.475	—	3.770	3.438
C=C...H distance	2.766	2.542	—	2.929	2.515
O—H bond length	0.945	0.963	—	0.949	0.949

Table 14. Conformational energies and dipole moments for pent-4-en-1-ol^{a,b}

	<i>E</i> _{rel} (kcal mol ⁻¹)/population (%)				
	6-31G**	E.D. ¹⁵	MM3	MM3(92)	MM3(94)
gTtt (33)	0.491/ 8.9		-1.906/15.9	-0.885/15.2	0.202/12.5
gTgt (34)	0.169/15.4		-1.905/15.8	-0.705/11.2	0.358/ 9.6
gTg't (35)	0.082/17.8		-1.986/18.2	-0.802/13.2	0.266/11.2
gGtt (36)	1.535/ 1.5		-0.151/ 0.8	-0.526/ 8.3	0.545/ 7.0
gGgt (37)	0.885/ 4.6		-1.676/10.8	-0.422/ 7.0	0.601/ 6.4
gGg't (38)	1.573/ 1.4		-0.530/ 1.6	0.923/ 0.7	1.815/ 0.8
gG'tt (39)	0.567/ 7.9		0.359/ 0.3	-1.038/19.7	0.039/16.5
gG'gg' (40)	0.000/20.4	-/50(± 20)	0.000/ 0.6	0.000/ 3.4	0.000/17.6
gG'gt (41)	2.201/ —		0.284/ —	0.993/ —	1.779/ —
gG'g't (42)	0.195/14.7		-1.833/14.1	-0.707/11.3	0.309/10.4
sTtt (43)	1.286/ 2.3		-1.303/ 5.8	-0.127/ 4.2	1.005/ 3.2
sTgt (44)	0.984/ 3.9		-1.132/ 4.3	0.070/ 3.0	1.187/ 2.4
sGtt (45)	2.309/ 0.4		0.029/ 0.6	0.383/ 1.8	1.496/ 1.4
sGgt (46)	2.024/ 0.7		-1.641/10.2	0.726/ 1.0	1.806/ 0.8
sGg't (47)	4.388/ 0.0		-0.213/ 0.9	2.847/ 0.0	3.687/ 0.0

	Dipole moment (D)			
	6-31G**	MM3	MM3(92)	MM3(94)
gTtt (33)	1.711	1.917	1.922	1.922
gTgt (34)	1.943	1.945	1.944	1.945
gTg't (35)	1.816	1.922	1.919	1.920
gGtt (36)	1.584	1.594	1.591	1.591
gGgt (37)	1.678	1.618	1.616	1.617
gGg't (38)	2.172	1.895	1.906	1.904
gG'tt (39)	1.383	1.587	1.548	1.548
gG'gg' (40)	1.967	1.744	1.692	1.738
gG'gt (41)	1.660	1.804	1.836	1.837
gG'g't (42)	1.560	1.578	1.580	1.585
sTtt (43)	1.917	1.939	1.939	1.939
sTgt (44)	1.847	1.906	1.905	1.906
sGtt (45)	1.606	1.578	1.591	1.593
sGgt (46)	1.281	1.617	1.550	1.553
sGg't (47)	1.979	1.875	1.873	1.871

^a See footnote a in Table 5.^b The four dihedral angles are C=C—C—C, =C—C—C—C, C—C—C—O and C—C—O—H, respectively.

without directional hydrogen bonding, gave the most stable complex with C_{2v} symmetry (two hydrogens of the water molecule pointing toward the two carbons of ethylene). This is a good example of the importance of directional hydrogen bonding in a molecular mechanics calculation.

By studying ethylene glycol and the ethylene-water complex in detail, we concluded that the energy difference among the conformers and the geometries at the 6-31G** and 6-31G** MP2 levels are about the same, except for the system with the double bond. Accordingly, the studies in this paper are at the MP2 6-31G** level for the one example that involves a double bond (ethylene-water complex) and at the corresponding Hartree-Fock level for all other systems.

Pent-4-en-1-ol

The electron diffraction study of pent-4-en-1-ol showed that conformation $gG'gg'$ (**40**), which has the O-H group pointing toward the C=C bond, contributes strongly (50 ± 20%) to the conformational mixture, and our *ab initio* result (20%) shows fair agreement with the experiment.¹⁵ Table 14 shows that MM3 and MM3(92) give poor agreement (1% and 3%, respectively) with the *ab initio* calculated conformational populations. The overestimation of hydrogen bonding energy for conformation $sGgt$ (**46**) in MM3 was reduced significantly in MM3(92) and MM3(94) by the directional hydrogen bonding. In MM3(94), the hydrogen bonding distance to the alkene carbon was reduced from 3.00 to 2.65 Å on the basis of our ethylene-water study, and the results greatly improved in terms of conformational populations. The contribution from conformation $gG'gg'$ (**40**) is now increased from 3% to 18%.

The strength of the dipole interaction can also be measured by distance of the hydrogen from the atom to which it is hydrogen bonded. One cannot compare the distance directly when the hydrogen is bonded to different atoms, because the distance also depends on the sum of the van der Waals' radii. However, what one can compare is the sum of the van der Waals' radii of the hydrogen and the atom to which it is hydrogen bonded (Σ_{vdw}), with the minimum energy distance for the hydrogen bond (HB-Dist.). If there were no hydrogen bond, then those distances would be equal, and their difference would be zero. As the hydrogen bond becomes stronger, the distance of approach becomes shorter, and the difference between those numbers ($\Delta Dist.$) becomes larger in absolute value. This information is summarized in Table 15. Thus we see that the nitrogen bonded to the alcoholic hydrogen is a stronger interaction than the oxygen bound to a similar hydrogen. Hence the hydrogen bond strength can be measured by either the distance of approach, or

Table 15. MM3(94) hydrogen-bonding data

H-acceptor	H(X)	Atom types	ϵ_{HB}	Σ_{vdw}	HB-Dist.	$\Delta Dist.$
N	H(O)	8...21	4.70	3.53	2.15	1.38
O	H(O)	6...21	3.00	3.42	2.11	1.31
N	H(N)	8...23	2.28	3.53	2.40	1.13
O	H(N)	6...23	1.30	3.42	2.38	1.04
=C	H(O)	2...21	0.55	3.56	2.65	0.91

by the depth of the potential well. It is of interest that weak hydrogen bonds (in terms of energy) still yield quite close approaches of the atoms involved.

CONCLUSIONS

Earlier versions of MM3 gave a fair account of hydrogen bonding between ether/alcohol oxygen and amino nitrogen. By adding a directional characteristic to the previous MM3 function, a better, but still not perfect, description of hydrogen bonding was obtained. A better model would include the orientation of the lone pair that is hydrogen bonded. The present model is judged to be fairly good, however (Tables 2-14), so we have decided to accept this hydrogen bonding potential for MM3, and have extended it to many other classes of compounds. Those results will be described in a later paper.

At this point we might ask if what we have learned about hydrogen bonding in this work is consistent with what we already know, and how we can use it to understand hydrogen bonding in other not yet studied molecules. Indeed, much of what is found is expected. An alcohol forms a hydrogen bond to an amine which is stronger than that which it forms to another alcohol, which in turn is stronger than that which it forms to ethylene. The hydrogen bond strength should probably be defined, in general, as the dimerization energy in the case where a hydrogen bond is formed, relative to what the dimerization energy would have been in the absence of a hydrogen bond. The hydrogen bond contains, in our formulation, two parts: the dipole-dipole interaction and the electron transfer interaction. The latter is the major part of the interaction as can be seen by comparing the values for ϵ in the potential with the dimerization energy for two molecules involving that interaction. The dipole-dipole interaction is relatively small, accounting typically for about 20-50% of the energy.

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- The MM3 program is available to all users from the Technical Utilization Corporation, 235 Glen Village Court, Powell, OH 43065, or from Tripos Associates, 1699 South Hanley Road, St Louis, MO 63144, and to academic users only from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405. The current version is available to run on most types of computers, and interested parties should contact one of the distributors directly. The calculations described herein may be carried out with the MM3(94) and later versions of the program.
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