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A Molecular Mechanics Force Field (MM3) for Alcohols and Ethers

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Abstract: The MM3 force field has been extended to the title class of compounds. Structures may be generally well calculated for a variety of rather simple alcohols and ethers. A number of conformational properties of molecules of this class were examined. Hydrogen bonding and anomeric effects were also studied. The vibrational spectra of four simple molecules have been fit with an rms of 35 cm^{-1}, and the effects of hydrogen bonding on vibrational spectra have been examined.

Introduction

Some ten years ago we published a paper on the study of the structures and energies of alcohols and ethers using the MM2 force field.[2] Since those studies were carried out, additional structural and thermodynamic information on these compounds has become available. In addition, the MM3 force field has been developed[3,4] and is sufficiently good to do a reasonable job with vibrational spectra, which was beyond the abilities of MM2.[5] Accordingly, it seemed now worthwhile to update our studies on compounds of this class and to find a parameter set for MM3 that would reproduce the available data as well as possible. Additionally, since the early work was carried out, the so-called "electronegativity effect", which tends to shorten bond lengths when an electronegative atom is attached to the bond, has been studied in some detail for alcohols and ethers,[6] so that bond lengths here can be better calculated than previously. With the original MM2 force field,[7] ethers in general had longer bond lengths than the corresponding alcohols, which is the reverse of the experimental facts. This was a result of the steric effect being larger between two alkyl groups than between an alkyl group and a hydrogen. The electronegativity effect is the explanation here. Actually, it is an electropositivity effect here, because the electropositive hydrogen replacing the carbon causes the C–O bond to stretch in an alcohol relative to an ether. This correction was put into recent versions of MM2[8] and has been taken into account at the outset in MM3.[3]

A major difference between MM2 and MM3 is that the former explicitly included lone pairs in the structure. This was disadvantageous for both practical and conceptual reasons. The theoretical disadvantage of including lone pairs here is that they are often not included in other classes of compounds, so the treatment is not totally consistent. Also, treating them as though they were atoms of very small mass leads to very high vibrational frequencies for them, which are artifactual. At the practical level, the lone pairs require parameters, and they take computing time. Not having them dispenses with these problems. The lone pairs were included in MM2, because we were not at the time able to adequately deal with the van der Waals and especially the torsional potentials about C–O bonds unless they were included. One of those problems still remains to a minor amount. Namely, to take methyl alcohol as an example, the methyl group is not symmetrical either by calculation or by experiment. But the experimental methyl group geometry has the two equivalent hydrogens bent toward the hydrogen on oxygen more than given by molecular mechanics, in such a way that this bending can be reproduced by the steric effects of two appropriate lone pairs. Without the lone pairs, we cannot reproduce this bending with our present model. It could be reproduced by using a more complicated force field with torsion–bend interactions, but we have decided to ignore this problem at present. The result is the methyl group is more symmetrical than it should be, but the error is fairly small, the tilt axis of the methyl group being approximately 2° different from the experimental one. The remaining torsional and van der Waals properties are dealt with adequately with the present force field, without utilizing lone pairs.

We examined the structures of several simple molecules which were experimentally known, and the results will be summarized below one molecule at a time. We wanted to fit bond lengths (r_g values), bond angles, torsion angles, torsional barriers, conformational equilibria where these were possible, and vibrational spectra. Sometimes the available structures are from microwave spectra, in which case we are not able to convert our r_g bond lengths to the experimental bond lengths in a simple way. Accordingly, we have compared moments of inertia, which we know from previous experience that we calculate about 1% too high, relative to the r_α values reported by the microwave spectroscopists.

Vibrational spectra were fit with an rms error of about 35 cm^{-1} for alkanes,[3] and we anticipated a similar fit here for simple alcohols and ethers. Most of the spectra were taken from experimental work, although ab initio spectra are now becoming available.

After the simple molecules were reasonably in hand, we examined a number of conformational equilibria in more complicated molecules, where these are known. For these molecules, structures are generally not available, and we will discuss only equilibrium constants between conformations.

Hydrogen bonding is a major topic with alcohols, and this will also be discussed below.

Heats of formation may be calculated by a bond energy scheme with MM3, as with MM2. With the original MM2 work, we had only 34 experimental heats of formation to fit, and we were able to fit them with an rms error of 0.50 kcal/mol. Our data base is somewhat expanded now, and a few experimental values have been replaced with newer values which are believed to be better. At the time the MM2 calculations were carried out, methyl *tert*-butyl ether and isopropyl *tert*-butyl ether had their heats of formation calculated with deviations from experiment of +1.36 and +1.33 kcal/mol, respectively, while that of di-*tert*-butyl ether was −0.55 kcal/mol. We utilized all of these values, as we were

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(4) The details of the MM3 program are described in ref 3. The program is available from the Technical Utilization Corporation, Inc., 235 Glen Village Court, Powell, OH 43065, and from Molecular Design Limited (ref 1).

(5) The MM2 force field for hydrocarbons was described in ref 7. Extensions to functionalized molecules have been described in subsequent papers and summarized in ref 8. The original program (MM2(77)) is available from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405, Program 395. The latest version of MM2, referred to as MM2(87), is available to academic users from QCPE and to commercial users from Molecular Design Limited (ref 1).

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Table I. Structure of Methanol

parameter	Millimeter wave spectrum[10]	ED data[9] at 0 °C[b]	MM3
C–H	1.0936 ± 0.0032	1.095 ± 0.010	1.111
O–H	0.9451 ± 0.0034	0.960 ± 0.015	0.948
C–O	1.4246 ± 0.0024	1.428 ± 0.003	1.431
<HCH	108°38′ ± 42′	(109°28′)[a]	108.9 (av)
<COH	108°32′ ± 29′	109° ± 3°	108.3
torsional barrier	1.07		0.78
dipole moment	1.71		1.712
I_a	3.963		4.033 (1.8%)
I_b	20.483		20.696 (0.7%)
I_c	21.268		21.422 (0.7%)

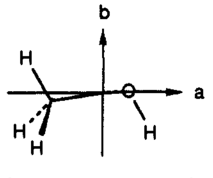
[a] This was assumed. [b] Probably r_a values.

Table II. Vibrational Spectrum of Methanol (C_s) (cm^{-1})

no.	sym	obs[11]	MM3	assignment
1	A′	3682	3679	O–H str
2	A′	2977	2976	CH_3 asym str
3	A″		2970	
4	A′	2844	2873	CH_3 sym str
5	A′	1477	1484	CH_3 def
6	A″	1455	1446	
7	A′	1430	1430	
8	A′	1340	1287	COH bend
9	A″		1106	CH_3 rock
10	A′		1086	CH_3 wag
11	A′	1034	1052	CO str
12	A″	270	263	CH_3–O tor
		rms 22		

not able to decide for sure which ones were better. More recently, two of the three compounds have had their heats of formation redetermined, and both of them have new values which changed in the direction toward the MM2 calculated values. The remaining value (isopropyl *tert*-butyl ether) has not been redetermined, and we conclude that this value is in error, and we have weighted it zero in our present study. The other two values are now well fit, when the newer experimental values are used. Our present heat of formation data set has been expanded to 40 compounds, and the rms error is only 0.38 kcal/mol.

Methanol. The geometry of methanol is known from an electron diffraction study[9] and from a millimeter wave spectrum (Table I).[10] The dipole moment and the torsional barrier are also known. The O–H stretching constant and the C–O–H bending constant were picked to fit as well as possible the frequencies reported in the IR spectra of methanol[11] (Table II) and ethanol.[24,25] The C–O–H bending frequency was calculated to be too low in methanol and too high in ethanol, so the error was averaged out as well as possible. The constant V_3 for a dihedral angle of type 5-1-6-21 (H-C-O-H) was picked to give the best possible fit to the reported torsional frequencies of methanol and ethanol.



Jorgensen[12] reported a molecular mechanics treatment of alcohols, including liquid state properties, which is largely complimentary to the present study. The reader is referred to that paper for background and references to the earlier literature.

By using a natural bond length of 1.413 Å for the C–O bond and an electronegativity correction of +0.015 Å for the alcoholic hydrogen, we are now able to fit the reported C–O bond lengths in both dimethyl ether and methanol. The bond moments for the C–O and O–H bonds were adjusted to fit the reported dipole moments for dimethyl ether and methanol.

Table III. Structure of Dimethyl Ether

parameter[a] θ_{av}	ED[16]/microwave[15]	MM3
C–O	1.415 ± 0.001	1.418
C–H	1.118 ± 0.002	1.110
<COC	111.8 ± 0.2°	111.9
<HCH	109.2 ± 0.2°	108.7 (av)
ϕ^b	3.6 ± 1.7°	1.6°
τ^c	2 ± 11°	0°
dipole moment[d]	1.30	1.309
energy barrier[d]	2.72	2.45
I_a	13.128	13.079 (−0.4%)
I_b	50.412	51.042 (1.2%)
I_c	56.959	57.495 (0.9%)

[a] Bond lengths r_g (Å) and bond angles θ_{av} (deg). [b] ϕ is the tilt angle of the methyl groups, defined as an angle between the C–O bond and a line perpendicular to the H_3 plane. [c] τ is the methyl torsion angle. [d] These quantities from the microwave work.[15]

Table IV. Dimethyl Ether (C_{2v})

no.	sym	obs[17-19]	MM3	assignment
1	A1	2991	2978	CH_3 asym str
2	B1	2991	2976	
3	B2		2975	
4	A2		2974	
5	A1	2820	2876	CH_3 sym str
6	B1	2820	2876	
7	B1	1462	1497	CH_3 def
8	A1	1470	1488	
9	B2	1462	1476	
10	A2		1454	
11	B1	1462	1434	
12	A1	1454	1431	
13	A1	1250	1174	CH_3 wag.
14	B1	1165	1173	CO asym str
15	B2	1181	1140	CH_3 asym twist
16	A2	1150	1084	CH_3 sym twist
17	B1	1092	1044	CH_3 rock
18	A1	918	924	CO sym str
19	A1	424	400	COC bend
20	B2	242	273	CH_3–O asym tor
21	A2	198	188	CH_3–O sym tor
		rms 38		

Since the lone pairs have been removed from the oxygen atom, the latter is treated as a sphere and is assigned the same van der Waals parameters as a carbonyl oxygen (type 7) and other types of oxygen. We initially started out with an alcoholic hydrogen which was much smaller (r = 0.95) and a little softer (ϵ = 0.016) than a type 5 hydrogen for which r = 1.62 and ϵ = 0.020. These van der Waals parameters for the alcoholic hydrogen were based on some data on carboxylic acids (which contain type 24 hydrogen) and on some work on hydrogen bonding.[13] However, in the course of this work we found that if we used such a small value for r, it was impossible to fit the literature data on the methanol dimer. According to the literature, the linear methanol dimer is more stable than the cyclic dimer by 1.7–3.3 kcal/mol depending on the type of study.[14] However, a value of 0.95 for r and the best possible hydrogen bonding parameters in the MM3 calculations gave a linear dimer which was less stable than the cyclic dimer by about 0.7 kcal/mol. When r was increased to 1.60 keeping ϵ at 0.016 and the hydrogen bonding parameters were optimized, the repulsion between the alcoholic hydrogens in the cyclic form increased considerably, so that the linear dimer became more stable than the cyclic dimer by about 0.8 kcal/mol. All the other data that are affected by this change (that we are aware of) fit about as well as before.

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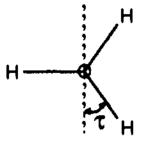
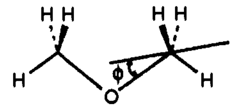
Table V. Structure of Ethanol[a]

parameter	microwave (r_s) structure[20]	microwave (r_0) structure[21]	MM3
C–C	1.5115 (50)	1.5297 ± 0.0020	1.525
C–O	1.4310 (50)	1.4247 ± 0.0025	1.433
O–H	0.9710 (70)	0.9451 ± 0.0024[b]	0.948
C–H(CH_2)	1.098 (10)	1.0936 ± 0.0050	1.112
C–H(CH_3)	1.088 (10) (s)	1.0936 ± 0.0032[b]	1.113
	1.091 (10) (a)		1.113
<HCH(CH_3)	108.79 (100) (s,a)	108°38′ ± 42′[b]	107.3
	108.45 (100) (a,a′)		107.5
<CCO	107.77 (30)	107°20′ ± 14′	109.0
<COH	105.43 (100)	108°32′ ± 29′[b]	108.3
<CCH(CH_2)	110.72 (100)	110°18′ ± 42′	110.3
<HCH(CH_2)	107.97 (100)	109°5′ ± 33′	107.8
<CCH(CH_3)	110.49 (100) (s)		111.4
	110.13 (100) (a)		111.6
I_A		14.489	14.433 (–0.4%)
I_B		54.065	55.449 (2.6%)
I_C		62.141	63.377 (2.0%)

[a] Bond lengths Å, angles deg. All values are for the trans conformation. [b] The values of methanol were assumed.

Dimethyl Ether. For dimethyl ether, the geometry is known from both microwave[15] and electron diffraction[16] experiments, and the dipole moment and the torsional barrier are also known.[15] The natural bond lengths, natural bond angles, torsional parameters, and bond moments were adjusted as needed so that the MM3 results were in satisfactory agreement with experiment (Table III). The vibrational spectrum of dimethyl ether was calculated, and the C–O stretching parameter and the C–O–C bending parameter were adjusted to give the best possible fit to the frequencies reported in an IR study[17] and in a vibrational force field calculation.[18] The C-O-C force parameter was later reduced somewhat so as to give a better calculated geometry for ditrityl ether. The vibrational spectra of dimethyl ether obtained by the different methods are shown in Table IV. The torsional parameter V_3 for the dihedral angle 5-1-6-1 was picked in order to obtain a good fit to the torsional frequencies reported for dimethyl ether,[17,18] rather than the reported torsional barrier, since the frequencies are known more accurately than the torsional barrier. That is why the calculated barrier shown in Table III appears to be a little low. The bending parameter for the angle H–C–O (5-1-6) is actually a reasonable guess, because the value of this parameter is not known experimentally. Synder and Zerbi, in their paper on the vibrational spectra of ethers,[18] did not assign a value to this type of a vibration, because this frequency falls somewhere in the range of 1500–1430 cm^{-1}, which also includes many other types of frequencies. With the available data, an interpretation of this region was not possible.





Ethanol. The geometry of the trans form of ethanol is known from microwave studies.[20,21] The results are shown in Table V and compared with the corresponding MM3 values. Here again the difference between the calculated and observed moments of inertia is greater than 1%. Again, we believe that this is due to the fact that, for this molecule, the difference between the r_s and r_g structures is greater than normal. The values reported in the literature for the C–C–O angles in ethanol and ethyl methyl ether are widely scattered. The values reported in the microwave studies on both compounds are much smaller than the value reported in the electron diffraction study on methyl ethyl ether. The values obtained from the MM3 calculations are close to the ED values. This discrepancy could be due to the fact that there is an electronegativity effect on the bond angles as well as on the bond lengths. We have decided to leave this the way it is at present.

Table VI. Vibrational Spectrum of Ethanol (C_s) (cm^{-1})

no.	sym	obs[24,25]	MM3	assignment
1	A′	3676	3679	OH str
2	A″	2989	2965	CH_3 asym str
3	A′	2989	2964	
4	A″		2949	CH_2 asym str
5	A′	2900	2898	CH_2 sym str
6	A′		2870	CH_3 sym str
7	A′		1537	CH_2 wag. + CO str + CC str
8	A″	1452	1457	CH_3 def
9	A′	1452	1452	
10	A′		1434	
11	A′	1393	1370	CH_2 wag. + CH_3 def
12	A″		1299	CH_2 twist
13	A′	1241	1290	COH bend + CO str
14	A′	1062	1106	CO str + CCO bend
15	A″	1033	1041	CH_3 rock + CH_2 rock
16	A′		993	CC str + CH_3 wag. + CCO bend
17	A′	885	896	CC str + CO str + CCO bend
18	A″	801	856	CH_2 rock + CH_3 rock
19	A′	419	409	CCO bend + OH str
20	A″	243	237	CH_3–CH_2 tor
21	A″	201	227	C_2H_5–O tor
			rms 26	

Table VII. Structure of Ethyl Methyl Ether[a]

parameter	gas E.D. data (r_g)[26]	microwave (r_s)[27]	MM3
C–C	1.520 (4)	1.521 (7)	1.526
(C–O) av	1.418 (2)		1.420
C(methyl)–O	1.413 (9)	1.415 (5)	1.418
C(methylene)–O	1.422 (7)	1.407 (4)	1.421
(C–H) av	1.118 (4)		1.112
<COC	111.9 (5)	111°42′ (28′)	112.1
<OCC	109.4 (3)	108°9′ (23′)	108.7
<HCH	109.0 (4)		108.0
ω_g	84 (6)		74.5
$\Delta H = \Delta H_g - \Delta H_a$	1.21 ± 0.27	1.59	1.49
I_A		18.054[28]	18.152 (0.5%)
I_B		121.500[28]	123.421 (1.6%)
I_C		129.877[28]	131.748 (1.4%)

[a] Bond lengths Å, angles deg, *I*'s in a.u.

It is reported that the trans form of ethanol is more stable than the gauche by about 0.4 kcal/mol.[22,23] We were unable to find a reliable value for the torsional barrier about the C–O bond in this molecule.[22] However, the IR spectra of ethanol in both the vapor phase[22,24] and in an argon matrix[25] are known (Table VI). These studies report the torsional frequencies of both the methyl group and the hydroxyl group. When V_3 for a dihedral angle of type 1-1-6-21 was taken to be 0.10, MM3 gave a good fit to the reported torsional frequencies. We then picked $V_1 = 0.40$ for a dihedral angle of type 1-1-6-21 so that the trans form of ethanol was calculated to be more stable than the gauche form by 0.40 kcal/mol. Since the C–O–C force constant was slightly reduced to give a better calculated geometry for ditrityl ether, the C–C–O force constant was also reduced slightly.

The best experimental value for the barrier to internal rotation about the C-C bond in ethanol is 3.08 kcal/mol.[22] By using a value of 0.30 for V_3 for a dihedral angle of the type 5-1-1-6 we

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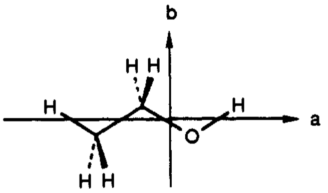
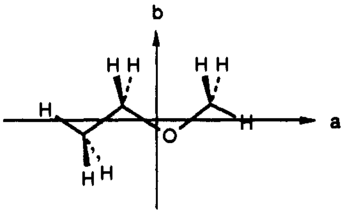
calculate a value of 2.80 kcal/mol for this barrier.



Ethyl Methyl Ether. The geometry of ethyl methyl ether is known from both electron diffraction[26] and microwave[27,28] studies. The data for the trans form are shown in the following table and compared with the corresponding MM3 values (Table VII). It is evident from Table VII that the structural parameters obtained from the MM3 calculations are in good agreement with the ED data. However, the moments of inertia calculated by the MM3 program do not agree well with the reported MW values. In the MM3 calculations we try to fit to r_g values, while the MW study gives an r_s structure. Normally, when we go from an r_s geometry to an r_g geometry the moments of inertia increase by less than 1%. However, in the case of methyl ethyl ether the difference between the r_s and r_g geometries is greater than normal, and we think that this is responsible for the greater discrepancy between the calculated and observed moments of inertia. Closing the C–O–C angle and shortening the C–C bond would lead to better agreement with both the ED work and the moments of inertia. These changes were not made because of undesirable results on other molecules.

The theoretical[18] and calculated vibrational spectra are presented in Table VIII. There are a few major discrepancies for this molecule. Bands (19) and (21), which are methyl and methylene rocking, are calculated too low at about 64 and 103 cm^{-1}, respectively. These are problems which stem from the hydrocarbon part of the force field.



Ab initio calculations of the rotational potential function for ethyl methyl ether using a 4-31G basis set have been reported.[29] Some calculations were also carried out in the present work with the GAUSSIAN 82 program by using a 6-31G* basis set. The results are shown in Table IX, and they are compared with the corresponding MM3 and MM2 energies.

The best experimental value for the energy differences between the gauche and the anti forms is believed to be 1.5 ± 0.2 kcal/mol (the gauche form being higher in energy) and was obtained from the infrared spectrum of ethyl methyl ether in the gas phase.[30] With the present set of parameters in MM3, we calculate an energy difference of 1.49 kcal/mol. Ab initio calculations at the 6-31G* level give the cis barrier in butane too high by about 1 kcal/mol,[31] and it is believed that the same is probably true here. Accordingly, we fit this barrier on the low side.

1-Propanol. Ab initio calculations of the rotational potential function for propanol using a 4-31G basis set have also been reported.[29] Some single point calculations using a 6-31G* basis set were carried out in the present work with the program GAMESS.[32] These results are shown in Table X and are compared with the corresponding MM3 and MM2 energies. The 4-31G* value at 0° is probably about 1.5 kcal/mol too high as with the ether.[31]

Table VIII. Vibrational Spectrum of Methyl Ethyl Ether (C_s) (cm^{-1})

no.	sym	obs[18]	MM3	assignment
1	A′		2977	CH_3 (CH_3–O) asym str
2	A″		2975	
3	A″		2964	CH_3 (CH_3–C) asym str
4	A′		2964	
5	A″		2953	CH_2 asym str
6	A′		2900	CH_2 sym str
7	A′		2876	CH_3 (CH_3–O) sym str
8	A′		2870	CH_3 (CH_3–C) sym str
9	A′		1548	CH_2 wag. + CO str + CC str
10	A′		1485	CH_3 def + CO str
11	A″		1468	CH_3 def
12	A″		1457	
13	A′		1452	
14	A′		1435	
15	A′	1394	1431	CH_3 def + CC str
16	A′	1367	1373	CH_2 wag. + CH_3 def
17	A″	1275	1311	CH_2 twist
18	A′	1219	1186	CO str (ethyl-O)
19	A″	1175	1111	CH_3 rock + CH_2 rock
20	A′	1118	1089	CO str (methyl-O)
21	A″	1149	1046	CH_2 rock + CH_3 rock
22	A′	1094	1044	CH_3 wag. + CO str + CC str
23	A′	1019	1000	CC str + CO str
24	A′	855	897	CO str + CH_3 wag. + CC str
25	A″	820	870	CH_3 rock + CH_2 rock + CH_2 twist
26	A′	472	420	CCO bend + COC bend
27	A′	308	296	COC bend + CCO bend
28	A″	238	257	CH_3–O tor + CH_3–C tor
29	A″		216	CH_3–C tor + CH_3–O tor
30	A″		114	C_2H_5–O tor
				rms 46

Table IX. The Rotational Energies for Ethyl Methyl Ether (kcal/mol)

C–C–O–C torsion angle	ab initio 4-31G	ab initio 6-31G*[b]	MM2	MM3
180°	0.0	0.0	0.0	0.00
120°	3.31	2.67	3.46	2.61
gauche	2.21 (71.2°)	1.92 (70.0°)	1.77	1.49 (74.5°)
0°	8.35	7.55[a]	4.49	6.02

[a] Electron correlation should lower this ~1 kcal (ref 31). [b] Single point calculations by Dr. P. Bowen using MM2 optimized geometries.

Table X. The Rotational Energies for Propanol (kcal/mol)

C–C–C–O torsion angle (deg)	ab initio 6-31G*	ab initio 4-31G	MM2	MM3
180	0.0	0.0	0.0	0.00
120	3.85	4.02	3.09	3.09
60	–0.12	0.0	0.20	0.36
0		5.55	3.57	4.08

Diethyl Ether. The MM3 calculations show that the TT conformer is more stable than the TG conformer by 1.51 kcal/mol. The dihedral angles C–C–O–C have values of 176.7° and 74.8°, respectively, in the TG form. High-resolution infrared and Raman spectra of diethyl ether[33] show that in the vapor phase, the pure liquid, and in CCl_4 and CS_2 solutions the TT conformer predominates and is more stable than the TG conformer by about 1.1 kcal/mol (ΔH). This value for ΔH was arrived at by measuring the temperature dependence of some bands in the infrared spectra (in CCl_4 solution). There is room for quite a lot of error in this method, so 1.1 kcal/mol is probably only an

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Table XI. The Structure of Methyl Isopropyl Ether[a]

parameter	microwave (r_s)[34]	MM3
C–O (Me)	1.416	1.419
C–O(iPr)	1.422	1.425
$C–C_t$	1.528	1.530
$C–C_g$	1.519	1.531
COC	112.5	113.9
OCC_g	113.7	109.8
OCC_t	107.7	106.5
CCC	112.7	110.5
COCH	47.0	45.7
$COCC_g$	71.9	76.3
$COCC_t$	162.6	164.0
I_a	66.437	66.426 (–0.0%)
I_b	132.917	134.775 (1.4%)
I_c	179.416	179.795 (0.2%)

[a] Bond lengths are in Å, angles in deg, and moments of inertia in au.

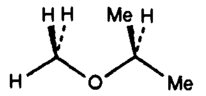
Table XII. The Structure of the Most Stable Conformer of Diisopropyl Ether

	gas ED[35] (r_g bond lengths, r_α angles)			
parameter	model I[a]	model II[b]	MM3	MM2
C–O	1.431 (3)	1.431 (3)	1.426	1.422
C–C	1.526 (3)	1.526 (3)	1.531	1.531
C–H	1.119 (3)	1.119 (3)	1.113	1.114
<COC	117.9 (19)	118.5 (16)	115.0	114.4
$<OCC_3$	111.5 (7)	110.3 (9)	109.0	110.5
$<OCC_4$	106.9 (5)	106.5 (6)	106.6	107.8
<CCC	113.4 (9)	113.5 (11)	110.5	110.1
$<CCH_{me}$	111.8 (14)	111.1 (16)	111.6	111.3
ϕ_1(COCH)		39 (4)	39.0	37.7
$\phi(C_5OC_2C_3)$	82	80	82.8	84.1
$\phi(C_5OC_2C_4)$	153	156	157.8	155.5

[a] ED results assumed that only the C_2 conformer exists in the gas phase. [b] ED results for the conformational composition of 80% C_2 ($\phi_1 = \phi_2$) + 20% C_1 ($\phi_1 = 0'$, $\phi_2 = 180'$). The parameters listed in this column are regarded as the final results of this ED study.

approximate value for ΔH. The MM1 and MM2(85) values for ΔH were 0.84 and 1.78 kcal/mol, respectively.

Methyl Isopropyl Ether. It would have been desirable at the outset of this work to have available structures for isopropyl alcohol and for methyl isopropyl ether, as these would have helped to better define the structure of the isopropyl group attached to an oxygen. Neither of these structures was available when this work was commenced, although a microwave structure of methyl isopropyl ether[34] did become available after completion of this part of the work. Our calculated structure does not agree very well with the experimental structure. However, the moments of inertia themselves do agree marginally, and we believe our structure is in fact satisfactory. The results are summarized in Table XI.



Diisopropyl Ether and Di-*tert*-butyl Ether. Calculations were carried out on diisopropyl ether and di-*tert*-butyl ether with both the MM2 and MM3 force fields. No experimental information was available on the structure of di-*tert*-butyl ether until after the present work was completed. A gas-phase electron diffraction study has been carried out on diisopropyl ether at 19 °C.[35] This study[35] indicated that the most stable conformer has C_2 symmetry. The bond lengths (r_g) and angles (r_a) with the estimated limits of error have been reported. With the help of MM2 calculations, the relative abundance of the next most stable conformer was determined to be 20 ± 20%, and the dihedral angles ϕ_1 (COCH) and ϕ_2 (COCH) of this conformer were reported to be 0 ± 30° and 180 ± 20°, respectively.[35] The results of this ED study, together with the corresponding values obtained from MM3 and MM2 calculations are shown in Table XII.

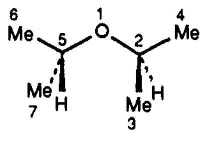
Table XIII. Partial Structure for Di-*tert*-butyl Ether

parameter	ED[36]	MM3	MM2
C–O	1.436 (5)	1.427	1.427
$C–C_{av}$	1.532 (3)	1.534	
<COC	130.8 (22)	129.5	123.2
τ	20.0 (50)	14.5	

Table XIV. Structure of Oxetane

parameter	micro-wave[37]	X-ray (90 K)[39]	MM3	MM2 (1985)
C–O	1.448 (5)	1.460 (1)	1.451	1.418
C–C	1.546 (5)	1.534 (2)	1.548	1.533
<COC	91.9 (10)	90.18 (8)	91.6	92.9
<CCO	91.8 (10)	91.99 (7)	91.5	91.3
<CCC	84.6 (10)	84.79 (9)	84.4	84.2
CCCO		7.56 (9)	7.1	
CCOC		7.9 (1)	7.6	
I_A	6.974		7.045 (1.0%)[a]	6.849
I_B	7.149		7.202 (0.7%)[a]	7.012
I_C	12.535		12.537 (+0.0%)[a]	12.088

[a] These are the moments of inertia calculated for the (r_g) planar form (vibrationally averaged).



From Table XII it is evident that for diisopropyl ether the C–O bond length needs to be longer and the COC angle needs to be bigger in the MM3 calculations, although the MM3 values are reasonable. At present we are using a stretch–bend parameter of 0.10 for the C–O–C angle in open chain compounds. A smaller stretch–bend parameter should cause the COC angle to open out and the C–O bond lengths to stretch out. We tried using a negative stretch–bend parameter of –0.10 and optimized all the necessary parameters so that the structure of dimethyl ether was the same as before (although some of the vibrational frequencies changed, especially two of the C–O stretching frequencies). The results of this calculation were that the C–O bond lengthened by 0.002 Å and the C–O–C angle opened by 0.1°. So, the improvement is not significant. However, the MM3 results are definitely better than the MM2 results.

In the case of di-*tert*-butyl ether the MM3 value for the COC angle is 6° larger than the MM2 value and in agreement with experiment (Table XIII).[36] The use of a negative stretch–bend parameter caused the C–O bond to stretch a great deal (by 0.012 Å), but the C–O–C angle actually closed by 0.2°.

Oxetane. Oxetane has been given special parameters, as was justified for hydrocarbons with four-membered rings.[3] The energy calculated with the present set of parameters decreases only 0.014 kcal/mol as the dihedral angle for ring bending changes from 0 to 7.3°. Because the first vibrational level lies above the barrier, this indicates a planar ring with a large out-of-plane vibrational amplitude. This kind of potential is also found experimentally.[37] Experimentally,[37,38] the height of the barrier is found to be 15 cm^{-1} (0.043 kcal/mol), and the C–C bond length is relatively long (1.549), as in cyclobutane (1.554). The C–O bond length is well calculated. In order to obtain a good fit between the MM3 data and the reported microwave data, the torsion–stretch parameter for a dihedral angle of type 1–1–6–1 (or 56–6–56–56) was increased to 0.14 (based on ab initio calculations on dimethyl ether), the stretch-bend parameter for a four-membered ring having an angle of the type X–O–Y was increased to 0.26 (from 0.10 in the

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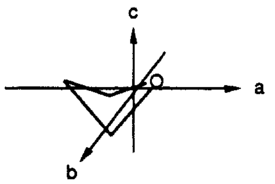
Table XV. Structure of 2-Methyloxetane

parameter	gas ED (r_a)[40]	MM3		
C–O	1.448 (5)	C_4–O_1	1.452	
				C–O_{av} = 1.453
		C_2–O_1	1.453	
		C_3–C_4	1.548	
C–C	1.534 (4)	C_2–C_3	1.549	C–C_{av} = 1.542
		C_2–C_5	1.530	
C–H	1.118 (3)		1.113	
<CCO	91.2 (15)	$C_3C_2O_1$	91.5	
		$C_5C_2O_1$	110.8	
		$C_1C_4O_3$	91.6	
<CCC	85.5 (18)	$C_2C_3C_4$	84.3	
		$C_3C_2C_5$	117.4	
<COC	92° (assumed)	$C_1O_5C_3$	91.4	
$\omega_{4-1-2-5}$	120.4 (40)		128.5	

open chain). The other parameters are as in Table XXXIII. An X-ray structure[39] of oxetane has also been reported, and the microwave and X-ray structures are quite different. According to the X-ray study, in the crystal, the four-membered ring has exact C_s symmetry, and the ring is found to be nonplanar. The angle of pucker at 90 K was found to be 10.7 (1)°. The results of these two experiments are shown in Table XIV and compared with the corresponding MM3 values.



2-Methyloxetane. The structure of 2-methyloxetane is known from an electron diffraction study[40] at room temperature. The four-membered ring is planar. The mean r_a values for the C–O, C–C, and C–H bonds have been reported. According to MM3 the ring is a little puckered (8.1°). The MM3 calculations give an average C–O bond length which is longer than the electron diffraction bond length by 0.001 Å if we convert the ED bond lengths to r_g values by adding 0.002 Å. The results of this study are shown in Table XV and compared with the corresponding MM3 values.

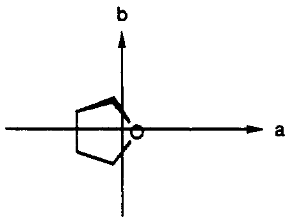
Tetrahydrofuran. Most of the parameters for five-membered rings have been taken to be the same as those for open chain compounds. The only parameters that are different are the constants V_3 for dihedral angles of type 1–1–1–6, 1–1–6–1, 1–6–1–6, and 6–1–1–6. The value of V_3 for 1–1–1–6 for open chain compounds is 0.30 and was picked to give a reasonable fit to the rotational barriers in propanol obtained from ab initio calculations and at the same time to make the differences between the calculated and observed heats of formation for 3,3-dimethyloxetane and 3-oxabicyclo[3.2.2]nonane as small as possible. The value of V_3 for a dihedral angle of type 1–1–6–1 for open chain compounds is 0.757. However, for five-membered rings the value of V_3 for a dihedral angle of type 1–1–1–6 is 1.80 and V_3 for a dihedral angle of type 1–1–6–1 is 0.657, and these were picked to give the best possible fit to the data available on alcohols and ethers containing five-membered rings. The value of V_3 for five-membered rings for a dihedral angle of type 6–1–1–6 was increased to 3.80 (from 0.30) and V_3 for 1–6–1–6 was increased to 1.72 (from 0.20) in order to fit the equilibrium data and heat of formation of 1,3-dioxolane. The other parameter which is different for five-membered rings is the stretch–bend parameter for an angle of the type X–O–Y, and this was picked to fit the C–O bond lengths in both tetrahydrofuran and 7-oxanorbornane.

The half-chair conformation of tetrahydrofuran is reported to be more stable than the envelope form by 0 ± 0.3 kcal/mol.[41] With the present set of parameters, MM3 calculates the half-chair (C_2) form to be more stable than the envelope (C_s) form by 0.04 kcal/mol. A microwave study[42] reports that the planar configuration of tetrahydrofuran lies 1220 cm^{-1} (or 3.49 kcal/mol) higher in energy than the C_2 form. The barrier to invert the ring-puckering configuration would be 1220 cm^{-1} for direct inversion through the planar configuration. This is in contrast to a barrier of only 57 cm^{-1} (or 0.16 kcal/mol) for inversion along the pseudorotation track. According to the MM3 calculations, the barrier for inversion along the pseudorotation track is 0.04 kcal/mol, and the planar form is 4.41 kcal/mol higher in energy than the half-chair. The geometry of tetrahydrofuran has been investigated by electron diffraction experiments,[43] and the rotational constants have been reported in the microwave study.[42] The results are shown in Table XVI and compared with the corresponding MM3 values.

Table XVI. Structure of Tetrahydrofuran

parameter	gas ED (r_g) at 0 °C (conformation av)	MM3 calculations half-chair (C_2)	envelope (C_s)	av
C–H	1.115	1.112	1.112	1.112
C–C	1.536	1.527 (av)	1.537 (av)	1.532
C–O	1.428	1.434 (av)	1.431	1.433
<CCC	101.5–104.4	101.1 (av)	103.6	
<CCO	104.0–107.5	106.7 (av)	105.0	
<COC	106.4–110.6	108.7	104.6	
$\omega_{C-O-C-C}$	1.0–40.5	11.4, 14.1	42.0	
$\omega_{O-C-C-C}$	0.9–37.5	31.8, 33.4	24.9, 24.9	
$\omega_{C-C-C-C}$	0.0–35.4	38.4	0.0	
I_A	11.825[a]	11.782 (–0.4%)	11.847	11.815 (–0.1%)
I_B	12.030[a]	12.099 (0.6%)	12.103	12.101 (0.6%)
I_C	20.938[a]	20.900 (–0.2%)	20.974	20.937 (–0.0%)

[a] These values have been calculated from the rotational constants reported in the microwave study.[42]



7-Oxanorbornane. The geometry of 7-oxanorbornane is known from a microwave study[44] and also from an electron diffraction study.[45] The use of a much bigger stretch–bend parameter (0.50) for five-membered rings for an angle of the type X–O–Y now gives a much better geometry for this compound. The C–O bond length

Table XVII. Structure of 7-Oxanorbornane

parameter	microwave[44]	ED/MW[45] (r_g)	MM3	MM2 (1985)
C_1–C_2	1.537 (5)	1.533 (14)	1.536	1.529
C_2–C_3	1.551 (5)	1.571 (15)	1.547	1.540
C_1–O_7	1.452 (10)	1.442 (10)	1.449	1.410
<$C_1O_7C_4$	95.3 (10)	94.5 (22)	96.6	97.4
<$C_1C_2C_3$	101.2 (5)	100.3 (6)	101.6	100.9
<$C_2C_1C_6$	109.9 (5)	110.7 (4)	110.4	111.0
<$C_2C_1O_7$		103.6 (13)	101.9	
$(C–H)_{av}$		1.116	1.113	
$(C–C)_{av}$		1.546	1.540	
I_A	21.377		21.319 (–0.3%)	20.785
I_B	25.389		25.374 (–0.1%)	25.075
I_C	29.471		29.582 (0.4%)	29.250

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Table XVIII

(a) Structures for the Conformations of Dimethoxymethane

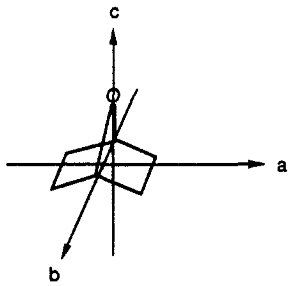
	gauche–gauche		anti–gauche		anti–anti	
parameter	MM2(82)	MM3	MM2(82)	MM3	MM2(82)	MM3
E_{rel} (kcal/mol)	0.0	0.0	1.98	2.00	4.03	4.04
CH_3–O	1.422	1.418	1.421, 1.422	1.418, 1.419	1.422	1.419
O–CH_2	1.413	1.416	1.425, 1.398	1.425, 1.403	1.410	1.412
O–C–O	111.7	112.3	109.3	110.4	106.4	108.4
C–O–C	112.8	112.4	111.9, 112.8	112.1, 112.6	111.9	112.2
C–O–C–O	72.9	72.6	175.0, 73.0	176.6, 73.6	180.0	179.6

(b) Structures for the Different Conformations of Dimethoxymethane

	gauche–gauche		anti–Gauche		anti–anti	
parameter	ab initio[a,47]	MM3	ab initio[a,47]	MM3	ab initio[a,47]	MM3
CH_3–O	1.426	1.418	1.419, 1.425	1.418, 1.419	1.421	1.419
O–CH_2	1.400	1.416	1.410, 1.386	1.425, 1.403	1.397	1.412
O–C–O	112.4	112.3	109.5	110.4	105.9	108.4
C–O–C	144.5	112.4	114.9, 114.3	112.1, 112.6	114.0	112.2
C–O–C–O	62.4	72.8	179.4, 57.4	177.6, 73.6	180.0	179.6

[a] The 4-21G ab initio values are corrected by adding –0.023 Å to give the r_g values [an average of the recommended (ref 48) corrections –0.019 (3) to –0.027 (4)].

is calculated to be 1.449 Å compared to a value of 1.452 (10) Å by microwave and 1.442 (10) Å by ED experiments. The results obtained for this compound are shown in Table XVII.

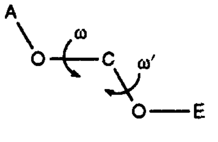


Compounds Which Involve the Anomeric Effect. In the course of this work, we have studied dimethoxymethane, 1,3-dioxane, 2-methoxytetrahydropyran, 1,3-dioxacycloheptane, and 1,3-dioxolane. All these compounds involve the anomeric effect[46] as they contain the C–O–C–O–C functionality. Originally, the program was written so that it calculated the change in the C–O bond lengths as a function of the torsional angles involving the lone pairs on oxygen.[46] Since the lone pairs have been removed now, the program has been modified so that the change in the C–O bond lengths is a function of the torsional angles involving other atoms. The equations involved in the anomeric effect are

$$l_0' = l_0 - \Delta l$$

$$\Delta l = \frac{k}{2}(1 - \cos 2\omega) - \frac{1}{2}kc(1 - \cos 2\omega') + d$$

When the anomeric effect was first incorporated into the MM2 program,[46] the best values for the constants *k*, *c*, and *d* were determined based on the information available on dimethoxymethane. Unfortunately a good ab initio study of this effect appeared after this work was completed. In the present work, the constants *k* and *c* have not been changed; only the constant *d* has been modified to get the best fit to the structure of dimethoxymethane. Table XVIII gives a comparison of the results obtained with the MM2 (1982) and MM3 force fields.



Experimentally only the gauche–gauche form of dimethoxymethane is detected.[49,50] With the MM2(82) program, the anti–gauche form was calculated to be 1.98 kcal/mol higher in energy than the gauche–gauche form, while with the present MM3 force field the anti–gauche form is found to be higher in energy than the gauche–gauche form by 2.00 kcal/mol at a dielectric constant of 1.5. We would like the energy difference between these two forms of dimethoxymethane to be larger than what we calculate, but we also want to fit the equilibrium data for 1,3-dioxolane and 2-methoxytetrahydropyran. This seems to be the best we can do at present. From Table XVIIIb it is evident that the MM3 values for the C–O bond lengths involving the methyl groups are too small. Aped et al.[51] have worked out a method to correct for these bond lengths. According to them, an inspection of the experimental data reveals a secondary effect to the anomeric effect; an outer C–O bond gets longer when its adjacent inner C–O bond gets shorter and vice versa (perhaps a hybridization effect). This effect has not yet been incorporated in MM3.

It is known from a temperature-dependent study of the NMR spectrum of 2-methoxytetrahydropyran in tetralin solvent[52] that the axial form is more stable than the equatorial form by 1.05 kcal/mol (ΔH). The MM3 calculations give an enthalpy difference of 0.88 kcal/mol for this equilibrium.

According to Greenhouse and Strauss,[53] the far-infrared spectrum of 1,3-dioxolane shows that it pseudorotates and the barrier to pseudorotation is about 50 cm^{-1} (0.14 kcal/mol). According to a microwave study,[54] the molecule undergoes pseudorotation and the maximum in the potential energy is at the C_2 configuration with the C_s configuration being 10.2 cm^{-1} (~0.03 kcal/mol) lower in energy. A far-infrared and Raman study[55,56] also reports that 1,3-dioxolane undergoes pseudorotation, and the barrier to pseudorotation is estimated to be 0.12 kcal/mol. An electron diffraction study by Hilderbrandt et al.[57] finds a pseudorotational model with a 2-fold barrier of about 0.3 kcal/mol. According to this report, the stable conformer is probably the twist form. The electron diffraction study[57] reports the structures

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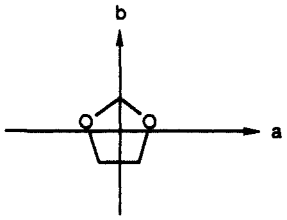
Table XIX. Structure of 1,3-Dioxolane

	ED				MM3 (D = 1.5)	
parameter	envelope[57]	twist[57]	twist[54] ED/MW	dynamic	envelope	distorted twist
r(C–H)	1.122 (8)	1.107 (7)	1.105 (6)	1.106 (6)	1.111	1.111
r(C–C)	1.546 (9)	1.538 (9)	1.559 (6)	1.542 (6)	1.535	1.518
r(C–O) av	1.422 (2)	1.422 (2)		1.423 (1)	1.425	1.427
r(C_2–O)			1.411 (7)		1.421	1.423, 1.432
r(C_5–O)			1.439 (5)		14.29	1.423, 1.429
<CCO	105.1 (6)	102.0 (9)	101.0 (3)	101.0 (4)	104.1	100.3, 103.8
<HCH	115.0 (fix)	120 (7)	109.1 (23)	118 (5)	109.0 (av)	108.9 (av)
ω_{1543}	0.0	36 (7)	39.0 (10)	41.8 (31)	0.0	37.8
I_A			10.722		10.754	10.706 (−0.1%)
I_B			11.138		11.164	11.175 (0.3%)
I_C			19.542		19.361	19.254 (−1.4%)

[a] Distances are r_g, and angles are r_a, at room temperature.

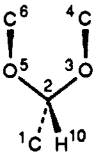
obtained with rigid models, and only the twist form and the envelope form were tested, a combined electron diffraction and microwave study (using rotational constants reported in ref 54) was carried out, and a pseudorotational model was tested. An NMR study on substituted dioxolanes indicates that the parent molecule has a very low barrier to pseudorotation.[58] According to the MM3 calculations, the most stable form is a distorted twist form, which is more stable than the envelope form by 0.93 kcal/mol at a dielectric constant of 1.5. It is also more stable than the C_2 twist by 0.27 kcal/mol. Both the symmetrical twist (half-chair) and the envelope forms correspond to saddle points on the potential energy surface. The results of the ED study and the MM3 calculations are shown in Table XIX.



The microwave study by Baron and Harris[54] reports the rotational constants. The moments of inertia have been calculated from these constants, and those obtained from the MM3 calculations have been collected in Table XIX.

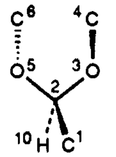
1,1-Dimethoxyethane. One might expect that the gauche–gauche form would be the most stable conformer, followed by one of the two possible anti–gauche forms, analogous to dimethoxymethane. The gauche–gauche form having the two methoxy groups on opposite sides of the O–C–O plane is found to be more stable than the anti–gauche conformer by 0.60 kcal/mol at a dielectric constant of 1.5. The structure of these two conformers together with the important torsion angles involved are shown below.

Conformer I (E_{rel} = 0.60 kcal/mol)



$\omega_{1-2-3-4}$ = −168.9
$\omega_{1-2-5-6}$ = 100.6
$\omega_{3-2-5-6}$ = −143.2
$\omega_{4-3-2-5}$ = 74.5
$\omega_{6-5-2-10}$ = −20.4
$\omega_{4-3-2-10}$ = −49.3

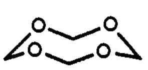
Conformer II (E_{rel} = 0.00 kcal/mol)

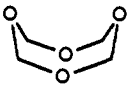


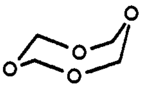
$\omega_{1-2-3-4}$ = −164.9
$\omega_{1-2-5-6}$ = −55.7
$\omega_{3-2-5-6}$ = 65.0
$\omega_{4-3-2-5}$ = 72.6
$\omega_{4-3-2-10}$ = −47.7
$\omega_{6-5-2-10}$ = −174.1

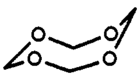
We then looked at a series of 1,3-dioxanes and tried to fit the conformational energies of these compounds, together with data for a few other ethers and alcohols, by adjusting the torsional parameters of the dihedral angles of type 1–1–6–1, 1–1–1–6, 1–6–1–6, and 6–1–1–6. The results are shown in Table XX and compared with the corresponding MM2 values. This table indicates that most of the results are better with the MM3 force field. This is probably mainly due to the fact that the hydrocarbon part of the force field is better in MM3 than it was in MM2.

1,3,5,7-Tetraoxacane. 1,3,5,7-Tetraoxacane is a fairly well studied polyether containing an eight-membered ring. Experimentally, the C_{2h} conformation was found[55] in the crystal of tetraoxacane, apparently deformed from the symmetrical (C_{4v}) solution conformation. It was concluded[59,60] that one of the chair–boat conformations is the next dominant conformer in solution. The chair–chair form was found to be more stable than the more stable chair–boat by values ranging from about 1 to more than 2 kcal/mol, depending on the solvent, and possibly concentration and temperature. It was stated that the energy differences increased with increasing solvent polarity.


chair–chair
(crown)
C_{4v}


boat–boat
D_{2d}


boat–chair (1)
C_s


boat–chair (2)
C_s

MM3 calculations were carried out for four conformations, at a dielectric constant of 1.5 (chosen to represent the gas phase). One of the boat–chair conformations (1) was calculated to be the most stable, followed in turn by the chair–chair, the boat–boat, and finally the other boat–chair (2). When the calculations were repeated at a dielectric constant of 5.0, it was found that the crown conformation had become more stable than the boat–chair (1), followed by the boat–boat, and the boat–chair (2) was still much higher in energy. When the calculations were carried out at a dielectric constant of 30.0, the crown conformation was found to be more stable than boat–chair (1) by 2.30 kcal/mol. These results are shown in Table XXI together with the corresponding experimental and MM2 results.

In a more recent paper[61] Astrup has reported the results of an electron diffraction study on 1,3,5,7-tetraoxacane in the gas phase. According to this report, satisfactory agreement between experimental and theoretical data is obtained for an equilibrium mixture of 32 (6)% symmetric crown (C_{4v}) and 68 (6)% boat–chair (C_s) conformers at 100 °C. So ΔG for this equilibrium is 0.56 ± 0.20 at 100 °C. The MM3 calculations also show that the boat–chair (1) is the most stable conformer, followed by the crown. However, ΔG for the equilibrium between the crown and the more stable boat–chair is found to be 0.59 kcal/mol at 25 °C at a dielectric constant of 1.5. The calculated value for ΔG is somewhat larger than the experimental value. As usual, some assumptions have been made in the electron diffraction study. It was assumed that all COC angles and OCO angles, respectively, are equal within one conformer. According to the author, a satisfactory fit between experimental and theoretical RD curves may be obtained in

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(59) Kobayashi, M.; Kawabata, S. Spectrochim. Acta 1977, 33A, 549.

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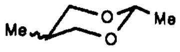
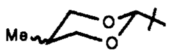
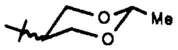
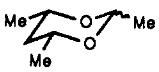
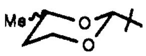
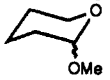
Table XX. Conformational Energies of Some Ethers and Alcohols (kcal/mol)

compound	favor	experimental values[c] ΔG	experimental values[c] ΔH	MM2 values (ΔH)	MM3 values (ΔH)
$CH_3OCH_2CH_3$	anti		1.5 (2)	1.73	1.49
$CH_3CH_2OCH_2CH_3$	anti–anti		1.1	0.84 (MM1)	1.51
	equatorial	0.60		0.33 (MM1)	0.77[a]
	equatorial		0.9	0.66	0.77
	equatorial	0.89	0.86 (9)	0.44	0.67
	equatorial	1.46		2.28	2.22
	equatorial	4.0	4.0	3.55	4.69 (2 ax)
	equatorial	2.8		2.55	2.75
	equatorial	(0.8)			0.81
$CH_3OCH_2OCH_3$	GG			1.98	2.00
	axial		1.05	1.23	0.88[a]
	C_2	0.0 (3)		0.16	0.04
	C_1				0.27
	C_s (nonpla)			0.0	0.02
	C_1 (equat)	0.52		0.58	0.74
$MeOCH_2CH_2OMe$	TTT over TGT			0.31	0.05

[a] This is the enthalpy difference between the most stable equatorial form and the most stable axial form. [b] The first torsional level is above the barrier experimentally, so the molecule is effectively planar. [c] References to the experimental work in this table: Allinger, N. L.; Chung, D. Y. *J. Am. Chem. Soc.* **1976**, *98*, 6798.

XXI. Relative Energies of Tetraoxacane Conformations (kcal/mol)

	D = 1.50 (gas)			D = 5.0			D = 30.0		
conformation	MM2	MM3[a]	experiment	MM2	MM3[a]	experiment (CS_2)	MM2	MM3[a]	experiment (CH_3CN)
C_{4v}(chair–chair)	1.93	H = −0.23 G = 0.59	minor G = 0.56 (20)[b] (Astrup)	0.0	0.0	0	0.0	0.0	major
C_s(1)(boat–chair(1))	0.0	0.0	major G = 0.0	0.17	H = 1.76 G = 0.94	H = 1.2	0.92	H = 2.30 G = 1.48	minor
D_{2d}(boat–boat)	1.20	H = 0.06 G = 0.76	not obs	1.48	H = 1.55 G = 1.55	trace	2.28	H = 2.05 G = 2.05	not obs
C_s(2)(boat–chair(2))	4.85	H = 4.15 G = 4.15	not obs	4.44	H = 6.05 G = 5.23	not obs	4.98	H = 6.65 G = 5.83	not obs

[a] All thc MM3 data is for 25 °C; the entropy differences considered in the free energy (G) calculation are only those due to symmetry and mixing.
[b] At a 100 °C.

different ways: (i) ∠COC = ∠OCO (~114.5°), (ii) ∠COC ≠ ∠OCO (one angle about 112° and the other about 116°). According to the MM3 calculations, in the crown form, all the COC angles are about the same and all the OCO angles are about the same, but the COC angles are very different from the OCO angles. In case of the boat–chair form, the COC angles range from 113.5° to 115.1° and the OCO angles range from 110.7° to 113.4°. So these assumptions in the electron diffraction study could introduce errors.

The structural parameters for the crown and the more stable boat–chair conformers obtained from the electron-diffraction study[61] and from MM3 calculations at a dielectric constant of 1.5 are shown in Table XXII.

Calculations on Some Ethers Containing the OCCO Functionality. 1,2-Dimethoxyethane has been investigated in the gas phase

Table XXII. Structure of 1,3,5,7-Tetraoxacane

	boat–chair (C_s)		crown (C_{4v})		boat–boat (D_{2d})
parameters	gas ED 100 °C[57] (r_a)	MM3	gas ED 100 °C[57] (r_a)	MM3	MM3
O–C	1.404 (1)	1.415 (av)	1.404 (1)	1.414 (av)	1.416
C–H	1.088 (3)	1.109 (av)	1.088 (3)	1.108 (av)	1.109
<COC	114.4 (2)	114.1 (av)	114.6 (20)	116.0 (av)	114.0
<OCO	114.3 (21)	112.0 (av)	114.2 (22)	113.9	112.7
<HCH	112.4	106.4 (av)	112.4	105.4	106.7
δ_1	66.5 (40)	69.6	−90.2 (36)	−89.2	57.7
δ_2	46.2 (28)	48.8	90.2 (36)	89.2	−57.7
δ_3	−106.5 (15)	−108.9	−90.2 (36)	−89.2	57.7
δ_4	66.5 (40)	66.1	90.2 (36)	89.2	−57.7
δ_5	−66.5 (40)	−69.6	−90.2 (36)	−89.2	57.7
δ_6	106.5 (15)	108.9	90.2 (36)	89.2	−57.7
δ_7	−46.2 (28)	−48.8	−90.2 (36)	−89.2	57.7
δ_8	−66.5 (40)	−66.1	90.2 (36)	89.2	−57.7

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(61) Astrup, E. E. *Acta Chem. Scand.* **1980**, *A34*, 85.

Table XXIII. Relative Energies of 1,2-Dimethoxypropane in the Gas Phase

conformer	gas phase NMR[60] [a] ΔG	MM2[a] ΔH	MM3 at $D = 1.50$[a] ΔH
1 (OCCO trans)	0.0	0.0	0.00
2 (OCCO gauche, CCCO trans)	–0.50	0.0	–0.35
3 (OCCO gauche, CCCO gauche)	0.80	0.2	0.35

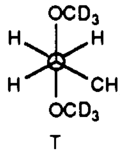
[a] Relative energies in kcal/mol.

by the electron diffraction method.[62] Satisfactory agreement between experimental and theoretical data could not be obtained for any single conformer. However, several mixtures of two conformers give acceptable correspondence to the experimental data, but a unique solution to the problem was not possible. The best fit was obtained for a mixture composed of 13% aaa, 23% aga, 53% agg, 3% gaa, 5% gag, and 3% ggg at about 0 °C. This corresponds to a ΔH of 0.07 kcal/mol favoring the aaa form over the aga form.

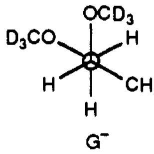
In another study, vicinal CH_2–CH_2 coupling constants were determined for 1,2-dimethoxyethane at 28 °C in solvents with dielectric constants ranging from 2 to 44 and over a wide range of temperatures.[63] The average coupling constants were analyzed in terms of a trans–gauche conformational equilibrium to obtain a ΔG for this equilibrium. Solvent interactions were taken into account by using a simple dielectric theory, considering the solvent as a continuous dielectric medium interacting with the dipoles and the quadrupoles of the solute molecule. In nonpolar solvents, the gauche form is preferred for 1,2-dimethoxyethane by –0.5 to –0.6 kcal/mol (ΔG). So ΔH for this equilibrium is –0.1 to –0.2 favoring the aga form at 28 °C.

When the MM3 calculations are carried out at a dielectric constant of 1.5, the aaa form is found to be more stable than the aga form by 0.05 kcal/mol (ΔH). (See Table XX).

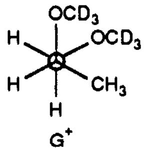
The gas-phase ^{1}H NMR spectrum of 1,2-dimethoxypropane-d_3 has been measured.[64] The conformational energies of this molecule in the gas phase were determined from the observed coupling constants with a three rotational state model. If we consider rotation about the central carbon–carbon bond in this molecule, there are three important conformers. In one conformer, the two methoxy groups are trans to one another so that the dihedral angle OCCO is anti (conformer 1). There are two possible gauche forms. In one form, one of the methoxy groups is gauche to the other methoxy group and anti to the methyl group so that OCCO is gauche and CCCO is anti (conformer 2). In the other gauche form, one of the methoxy groups is gauche to both the methyl group and the other methoxy group so that both OCCO and CCCO are gauche (conformer 3). The NMR study reports the relative energies of these three conformers when the main chain bonds other than the central C–C bond are kept in trans positions. The relative energies reported in the NMR study are shown in Table XXIII together with the corresponding MM2 values and the corresponding MM3 values. The relative energies obtained from the MM3 calculations do not agree very well with the NMR values, although they are better than the MM2 values.



T
1



G⁻
2



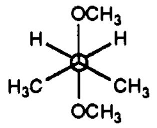
G⁺
3

The relative energies of the trans and gauche forms of 1,2-dimethoxy-2-methylpropane have been derived from the ^{13}C NMR undecoupled spectra taken in cyclohexane-d_{12}.[65] This study reports the relative energies of the two conformers in which the dihedral angle OCCO is either trans or gauche, and the main chain bonds other than the central C–C bond are kept in the trans position. The relative energies reported in the NMR study are shown in Table XXIV, together with the corresponding MM3 values.

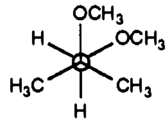
Table XXIV. Relative Energies of 1,2-Dimethoxy-2-methylpropane

conformer	^{13}C NMR in cyclohexane[61] [a] ΔG	MM3 at $D = 1.50$[a] ΔH
1 (OCCO trans)	0.0	0.00
2 (OCCO gauche)	0.5	–0.53

[a] Relative energies in kcal/mol.



T
1



G
2

It is evident from Table XXIV that the MM3 results are in very poor agreement with the NMR data. One reason for this discrepancy may be that the NMR measurements were conducted in cyclohexane-d_{12}, whereas the MM3 calculations refer to the gas phase. When the MM3 calculations were repeated with a more positive V_1 for the dihedral angle CCCO there was a small improvement.

According to the MM3 calculations, the all-trans form of 1,2-diethoxyethane is more stable than the conformer in which the dihedral angle 0.02 is gauche (having a value of 72.7°) and all the other skeletal dihedral angles are trans by 0.02 kcal/mol at a dielectric constant of 1.5.

Hydrogen Bonding. Hydrogen bonding in hydroxylic substances is conveniently measured by the infrared method, since a hydrogen-bonded group, for example, hydroxyl, absorbs at a lower frequency than does an unbound one.[66] Intramolecular hydrogen bonding has proved to be the most informative. The spectrum must be obtained in dilute solution so that intermolecular hydrogen bonding is suppressed. Under these conditions the O–H···O region gives one or the other of two general patterns. Either there is just one peak (near 3630 cm^{-1} if there is no hydrogen bonding, or near 3600 if there is), or there are two separate peaks with an intensity ratio which depends on the ratio of conformers present. Kuhn and Allerhand showed that the separation between the bonded and unbonded frequencies was larger the stronger the hydrogen bond.[67,68] *cis*-1,2-Cyclopentanediol ($\Delta\nu$ 61 cm^{-1}) has the hydroxyls closer and the hydrogen bond stronger than does *cis*-1,2-cyclohexanediol ($\Delta\nu$ 39 cm^{-1}).

The *trans*-cyclopentane-1,2-diol showed only an unbonded frequency because the hydroxyl groups are too far apart to participate in hydrogen bonding. The *trans*-cyclohexane-1,2-diol, on the other hand, showed that the bond was not so strong as in the cis isomer ($\Delta\nu$ 32 cm^{-1}). The reason for the difference between the cis and trans isomers is that the hydroxyls are closer together in the cis. In *cis*-2,3-bicyclo[2.2.1]heptanediol (both exo and endo forms) the separation of the unbonded and bonded hydroxyl stretching frequencies in the infrared is of the order of 100 cm^{-1}.[69-71] The separation here is much bigger because the hydroxyl groups are necessarily eclipsed (torsion angle 0°), close together, and the hydrogen bond is much stronger.

One good way to tell how well hydrogen bonding is accounted for in the MM3 force field is to carry out calculations on the vicinal

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(66) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; John Wiley and Sons, Inc.: 1965; pp 147 and 203 and references therein.

(67) (a) Kuhn, L. P. *J. Am. Chem. Soc.* **1954**, *76*, 4323. (b) Kuhn, L. P. *J. Am. Chem. Soc.* **1952**, *74*, 2492. (c) Kuhn, L. P. *J. Am. Chem. Soc.* **1958**, *80*, 5950.

(68) Comparisons refer to the same solvent: Allerhand, A.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1963**, *85*, 371.

Table XXV. Optimized Geometries and Dimerization Energies of the Methanol Dimer

	$R_{O\cdots O}$ (Å)	$-\Delta E$ (kcal/mol)	H···H (Å)	O···H (Å)
		Linear Dimer		
STO-3G	2.688	6.13		
12-6-1[a]	2.644	6.33		
D-12-6-1[b]	2.635	6.91		
6-31G*	2.95	5.66		
best values[c]	2.788–2.888	5.5		
MM3[d]	2.696	5.55	2.432	1.748
		Cyclic Dimer		
STO-3G	2.747	2.14		
12-6-1[a]	2.863	2.38		
D-12-6-1[b]	2.822	3.80	2.097	
MM3[d]	2.417	4.72	1.993	2.001

[a] Values obtained by using a 12-6-1 potential given by $\Delta E(12\text{-}6\text{-}1) = \sum_{i<j}^{\text{charges}} q_i q_j / r_{ij} + \sum_{\mu<\nu}^{\text{atoms}} (C_{mn}/r^{12}\mu\nu + D_{mn}/r^{12}{}_{\mu\nu})$. [b] Values obtained by using a modified potential which includes correction terms for methyl–methyl and oxygen–hydrogen dispersion interactions. [c] Jorgensen's "best" values (ref 14). [d] Values obtained from the MM3 calculations by using $\epsilon = 2.20$ and sum of $R^* = 1.82$ at a dielectric constant of 1.5.

diols mentioned in this discussion. We can then compare the separation of the unbonded and bonded hydroxyl stretching frequencies calculated by the program with that reported in the IR study. In addition to reproducing the frequency shifts in these diols, we also need to obtain a good structure and a good dimerization energy for the methanol dimer, for which an intermolecular potential function has been derived from ab initio calculations by using an STO-3G basis set.[14] The dimerization energies and the O···O distances for both the linear and cyclic methanol dimers have been reported in this study.[14] In this paper Jorgensen reports the O···O distance and the dimerization energy for both the linear dimer and the cyclic dimer obtained from ab initio calculations by using an STO-3G basis set.[14] He also reports the values obtained by using a 12-6-1 potential and also a 12-6-1 potential with a correction for methyl–methyl and oxygen–hydrogen dispersion interactions. The original potential was modified because the STO-3G calculations do not accurately describe interactions between nonpolar groups because of the importance of dispersion effects in this case. By analyzing accurate potential functions for methanol dimers it was found that a simple solution that brings the STO-3G results into general accord with the empirical potentials is to add a dispersion term, $-\Delta C r_{CC}^{-6}$. It also seemed appropriate to analyze the methyl–hydroxyl interactions, although dispersion should be less critical in this case. An analysis of accurate potential functions for water dimers shows that an O···H dispersion term is necessary whose form is $(C'/r_{OH}^{6})f(r)$ where $f(r)$ is the scaling function of Rahman and Stillinger[72] given by

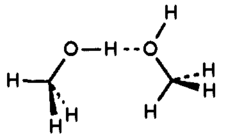
$$f(r) = (r - r_0)^2(3r_m - r_0 - 2r)/(r_m - r_0)^3$$

So, two corrections were made to the STO-3G 12-6-1 potential. The r^{-6} Me–Me coefficient was reduced by 2850, and the scaled dispersion correction was added to the O···H interactions. Jorgensen calls the resultant function a D-12-6-1 function, and the results obtained with this function for the linear methanol dimer are also shown in Table XXV. An ab initio study using a 6-31G* basis set has also been reported on the linear methanol dimer.[73] This is the best theoretical study to date of the linear dimer. According to this study, the dimerization energy for the linear methanol dimer is −5.66 kcal/mol, and the oxygen–oxygen distance is 2.95 Å. Jorgensen has also surveyed the literature and concludes that the true value for the dimerization energy for the linear methanol dimer is near −5.5 kcal/mol, and the O···O distance is 2.788–2.888 Å. MM3 calculations were carried out with different hydrogen bonding parameters for the atom pair 6···21. A reasonable fit to the O···O distance and the dimerization energy in the linear methanol dimer, and the best possible fit to the frequency shifts in the diols was obtained with $\epsilon = 2.20$ and the sum of $R^* = 1.82$ for the atom pair 6···21. With the present set of parameters, both the linear and the cyclic (nonplanar) dimers are minima on the potential energy surface, the linear dimer being more stable than the cyclic dimer by 0.83 kcal/mol. The O···O distance in the cyclic dimer is much smaller in the MM3 calculations than the values reported by Jorgensen. There is no simple way to improve this at present. The results of the different studies carried out on the methanol dimer have been collected in Table XXV.

Table XXVI. Separation of the Bonded and Unbonded Hydroxyl Stretching Frequencies for Diols (cm^{-1})

conformer	IR CCl_4[66]	MM3 D = 1.50	O···H[a] MM3 (Å)
ethylene glycol (tGg′)	32	29	2.271
trans-1,2-cyclohexanediol	32	24	2.341
cis-1,2-cyclohexanediol	39	40	2.122
cis-1,2-cyclopentanediol	61	45	2.031
trans-1,2-cyclopentanediol	0	0	4.300
cis-2,3-bicyclo[2.2.1]heptanediol(exo)	100	22	1.811
cis-2,3-bicyclo[2.2.1]heptanediol(endo)	100	33	1.846

[a] This is the actual distance between the two atoms involved in the hydrogen bonding.



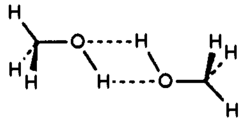
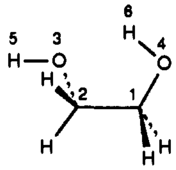


Table XXVI shows the results of the MM3 calculations on some vicinal diols, together with the corresponding experimental values.



A study of Table XXVI shows that the frequency shifts calculated by MM3 are in good agreement with the IR data for *trans*- and *cis*-1,2-cyclohexanediol. For *cis*-1,2-cyclopentanediol, the calculated $\Delta\nu$ is acceptable, and for *trans*-1,2-cyclopentanediol, MM3 correctly calculates almost the same frequency for both the OH groups, since they are too far apart to be involved in hydrogen bonding. However, for the other three compounds in this table, the calculated values for $\Delta\nu$ are much lower than the experimental numbers. The MM3 calculations give one of the poorest fits for *cis*-2,3-bicyclo[2.2.1]heptanediol (exo), and we notice that here (according to the MM3 calculations) the two atoms involved in the hydrogen bonding are very close together; in fact the distance between them is greater than the sum of R^* by only 0.010 Å. It seems that due to a defect in our model, when the two atoms involved in the hydrogen bonding get very close together, the frequency of the hydrogen-bonded O–H group increases instead of decreasing, thereby causing the calculated $\Delta\nu$ to decrease. It would seem that the van der Waals' function we use for the specific hydrogen bond potential increases in energy too steeply at short distances.

Ethylene Glycol. The structure and conformational properties of ethylene glycol have been the subject of many experimental and theoretical investigations. Schafer et al. have recently published an ab initio study of this molecule by using a 4-21G basis set with geometry optimization.[74] They studied ten conformations

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(69) Kwart, H.; Vosburgh, W. G. *J. Am. Chem. Soc.* **1954**, *76*, 5400.
(70) Kwart, H.; Gatos, G. C. *J. Am. Chem. Soc.* **1958**, *80*, 881.
(71) Angyal, S. J.; Young, R. J. *J. Am. Chem. Soc.* **1959**, *81*, 5467.
(72) Stillinger, F. H.; Rahman, A. *J. Chem. Phys.* **1972**, *57*, 1281.
(73) Tse, Y.-C.; Newton, M. D.; Allen, L. C. *Chem. Phys. Lett.* **1980**, *75*, 350.

(74) van Alsenoy, C.; Enden, L. van den; Schafer, L. *J. Mol. Struct.* **1984**, *108*, 121.

Table XXVII. Structure of Ethylene Glycol

parameter	ab initio (4-21G)[74 b]	ED[75] 376 K	MM3 $D = 1.5^b$
$E_{tTt}-E_tG_{g'}$[a]	2.55		2.90
C_1-C_2	1.5231		1.522
C_2-O_3	1.4548		1.433
C_1-O_4	1.4423		1.431
O_3-H_5	0.9620		0.948
O_4-H_6	0.9655		0.950
av C–C/C–O	1.473	1.455 (3)	1.462
av C–H/O–H	1.042	1.066 (7)	1.058
$C_1-C_2-O_3$	104.08		107.4
$C_2-C_1-O_4$	109.19		108.5
$(<CCO)_{av}$	106.64	110.0 (4)	108.0
$C_2-O_3-H_5$	111.69		108.2
$C_1-O_4-H_6$	107.13		106.3
$(<COH)_{av}$	109.41	99.2 (29)	107.3
$O_3-C_2-C_1-O_4$	57.29	57.9 (12)	59.6
$H_5-O_3-C_2-C_1$	172.33		179.7
$H_6-O_4-C_1-C_2$	49.51		50.5
I_a			5.611
I_b			14.671
I_c			17.996

[a] Energies in kcal/mol. [b] All data are for the most stable form (tGg′).

Table XXVIII. Moments of Inertia[a] for Two Isotopic Species of Ethylene Glycol[b,c]

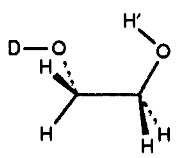
moments of inertia	OH′/OD		OD′/OH	
	MW[76]	MM3	MW	MM3
I_A	5.548	5.664	5.740	5.877
I_B	15.801	15.493	15.125	14.783
I_C	19.020	18.860	18.575	18.374

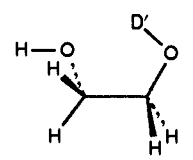
[a] Moments of inertia in gm-cm² × 10^{39}. [b] Primed hydrogen participates in the hydrogen bond. [c] MM3 calculations at D = 1.50.

of ethylene glycol and have found the two most stable forms to be tGg′ and gGg′, both of which are stabilized by internal hydrogen bonding. This is in agreement with the MM3 calculations. Hedberg has recently concluded an electron diffraction study of ethylene glycol at 376 and 733 K.[75] According to the ED data, the forms which have the dihedral angle OCCO anti are present in very small amounts. According to the MM3 calculations the enthalpy difference (ΔH) between the most stable gauche form (tGg′) and the most stable anti form (tTt) is 2.90 kcal/mol favoring the gauche form at a dielectric constant of 1.5. If we consider only the most stable gauche and anti forms, ΔG for this equilibrium is 3.31 kcal/mol at 25 °C by MM3 calculations. This corresponds to 99.6% of the gauche form and is therefore in good agreement with the ED data. The data reported in the ED and ab initio studies are shown in Table XXVII, together with the corresponding MM3 values.

It is difficult to interpret Table XXVII, because the ab initio calculations give r_e values, whereas the MM3 calculations give r_g values, and the ED data in this table are approximate because they are an average over all the conformations present. However, a few points are worth noting. The value for the dihedral angle OCCO obtained from the MM3 calculations is in good agreement with the values reported in the ab initio and ED studies. The values for the two CCO angles in the ab initio calculations are very different.

The microwave spectra of the two possible O-monodeuterated forms of ethylene glycol have been measured in a mixture containing roughly 25% of each of the four possible OH/OH, OH/OD, OD/OH, and OD/OD isotopic species.[76] Only one conformer has been detected: one oxygen is gauche with respect to the other; one hydroxyl hydrogen participates in the hydrogen bond, while the second one is trans with respect to the C–C bond, consistent with the electron diffraction work and with MM3. The rotational constants have been reported in this paper for the two different deuterated forms. The rotational constants have been converted to moments of inertia which are shown in Table XXVIII, together with the corresponding MM3 values. A study





of Table XXVIII shows that the moments of inertia calculated by MM3 are in reasonable agreement with the MW values. The calculated I_B values are a bit too small, which suggests that the C–C–O angles should be opened slightly. This is opposite of what is required for a better fit to the structures of ethanol and propanol, and the present results are a compromise.

1,3-Propanediol. With the present set of parameters the MM3 calculations show the most stable conformer of 1,3-propanediol to be an internally hydrogen-bonded form, which is chair-like and in which one CCOH angle is trans and the other is gauche. The next most stable conformer is also an internally hydrogen-bonded chair-like form, but this conformer has both CCOH angles gauche. The third most stable conformer is a boat-like form which is higher in energy than the most stable conformer by 3.35 kcal/mol and is very weakly hydrogen bonded. Here one CCOH angle is gauche and the other is trans. Table XXIX gives a summary of the results of the MM3 calculations.

Table XXIX. MM3 Calculations on 1,3-Propanediol

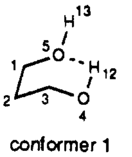
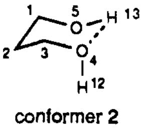
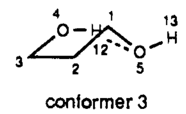
	 conformer 1	 conformer 2	 conformer 3
E_{rel} (kcal/mol)	0.0	0.48	3.35
$\omega_{1-2-3-4}$	65.4	57.1	53.7
$\omega_{3-2-1-5}$	−55.2	−62.3	50.6
$\omega_{2-3-4-12}$	−43.1	83.4	−84.4
$\omega_{2-1-5-13}$	−175.0	52.4	173.6

Table XXX. The Structure of 1,3-Propanediol

parameter	gas ED (r_a)[77]	MM3 (stable conformer)
C–C	1.514 (8)	1.530
C–O	1.410 (6)	1.434
C–H	1.140 (2)	1.113
O_1–H	1.04 (7)	0.950
O_2–H	0.98 (6)	0.948
O_1–C–C–C	68 (3)	65.4
O_2–C–C–C	61 (5)	55.2
C–C–O_1–H	46 (5)	43.1
C–C–O_2–H	180[a]	175.0
<CCC	112 (1.5)	112.8
$<CCO_1$	108 (1.5)	110.4
$<CCO_2$	112 (1.5)	109.0
$<CO_1H$	109 (3)	107.6
$<CO_2H$	97 (3)	108.2
<CCH	109[a]	109.8

[a] These quantities were assumed in this study.

A gas-phase ED study of this molecule at 460 K has been reported,[77] and it concluded that the most stable conformer has an intramolecular hydrogen bond. According to the ED study, four possible, all-staggered conformations can be characterized by the orientations of the C–O bonds relative to the C–C–C plane: (a,a), (a,g), (g,g), and (+g,−g). It is mainly the O···O distance that produces the characteristic differences in the radial distribution function. Only in the +g, −g, form are the oxygen atoms close enough to engage in internal hydrogen bonding. From the experimental data it was obvious that the (+g,−g) conformer was predominant. So the data were analyzed in terms of this form only. The experimental data could be fit by two models differing in the position of the bridging hydrogen atom. Depending on the

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(75) Hedberg, K. Personal communication.

(76) Caminati, W.; Corbelli, G. *J. Mol. Spectrosc.* **1981**, *90*, 572.

Table XXXI. Heats of Formation for Alcohols and Ethers[a,b]

compound	eq	wt	sumh	steric	pop	tors	T/R	C–O	O–H	O–Me	O–SE	O–TE	OCCO	OCO	OC1O	OC2O	$H_f°$ calc	$H_f°$ exp	difference (calc − exp)
methanol	1	7	−13.77	1.00	0.00	−0.42	2.40	1	1	1	0	0	0	0	0	0	−48.25	−48.07	−0.18
ethanol	2	10	−19.46	2.08	0.15	0.00	2.40	1	1	0	0	0	0	0	0	0	−56.05	−56.24	0.19
1-propanol	3	7	−26.20	3.16	0.43	0.42	2.40	1	1	0	0	0	0	0	0	0	−61.01	−61.17	0.16
2-propanol	4	9	−25.15	3.66	0.09	0.00	2.40	1	1	0	1	0	0	0	0	0	−65.25	−65.12	−0.13
isobutanol	5	7	−34.51	4.77	0.56	0.42	2.40	1	1	0	0	0	0	0	0	0	−67.58	−67.84	0.26
1-butanol	6	7	−32.93	4.22	0.78	0.84	2.40	1	1	0	0	0	0	0	0	0	−65.91	−65.79	−0.12
2-butanol	7	6	−31.88	5.14	0.25	0.42	2.40	1	1	0	1	0	0	0	0	0	−69.92	−69.98	0.06
t-butanol	8	8	−30.84	5.38	0.00	0.00	2.40	1	1	0	0	1	0	0	0	0	−74.86	−74.72	−0.14
1-pentanol	9	5	−39.66	5.27	1.13	1.26	2.40	1	1	0	0	0	0	0	0	0	−70.82	−70.66	−0.16
2-pentanol	10	5	−38.61	6.20	0.60	0.84	2.40	1	1	0	1	0	0	0	0	0	−74.82	−75.00	0.18
2-methyl-2-butanol	11	5	−37.57	7.96	0.09	0.42	2.40	1	1	0	0	1	0	0	0	0	−78.50	−79.06	0.56
1-hexanol	12	6	−46.39	6.32	1.48	1.68	2.40	1	1	0	0	0	0	0	0	0	−75.73	−75.65	−0.08
1-heptanol	13	0	−53.13	7.37	1.83	2.10	2.40	1	1	0	0	0	0	0	0	0	−80.65	−79.09	−1.56
1-octanol	14	6	−59.86	8.41	2.18	2.52	2.40	1	1	0	0	0	0	0	0	0	−85.57	−85.30	−0.27
cyclopentanol	15	4	−34.58	19.34	0.30	0.42	2.40	1	1	0	1	0	0	0	0	0	−58.37	−57.97	−0.40
cyclohexanol	16	6	−35.81	9.70	0.26	0.00	2.40	1	1	0	1	0	0	0	0	0	−69.70	−69.31	−0.39
ethylene glycol	17	6	−15.91	0.80	0.40	0.42	2.40	2	2	0	0	0	1	0	0	0	−92.49	−92.64	0.15
1,2-propanediol	18	0	−21.61	1.85	0.40	0.42	2.40	2	2	0	1	0	1	0	0	0	−102.17	−102.70	0.53
1,3-propanediol	19	0	−22.65	1.36	0.20	0.84	2.40	2	2	0	0	0	0	0	0	0	−100.29	−93.71	−6.58
dimethyl ether	20	6	−27.54	2.32	0.00	0.00	2.40	2	0	2	0	0	0	0	0	0	−43.94	−43.99	0.05
methyl ethyl ether	21	8	−33.23	3.42	0.16	0.42	2.40	2	0	1	0	0	0	0	0	0	−51.71	−51.72	0.01
diethyl ether	22	6	−38.92	4.49	0.30	0.84	2.40	2	0	0	0	0	0	0	0	0	−59.53	−60.26	0.73
methyl propyl ether	23	6	−39.97	4.47	0.39	0.84	2.40	2	0	1	0	0	0	0	0	0	−56.75	−56.88	0.13
methyl isopropyl ether	24	6	−38.92	6.22	0.04	0.42	2.40	2	0	1	1	0	0	0	0	0	−59.75	−60.24	0.49
methyl *tert*-butyl ether	25	2	−44.61	9.42	0.00	0.42	2.40	2	0	1	0	1	0	0	0	0	−67.83	−67.68	−0.15
1-ethoxypropane	26	5	−45.65	5.53	0.59	1.26	2.40	2	0	0	0	0	0	0	0	0	−64.51	−65.06	0.55
dipropyl ether	27	4	−52.38	6.57	1.00	1.68	2.40	2	0	0	0	0	0	0	0	0	−69.37	−69.85	0.48
diisopropyl ether	28	3	−50.29	9.92	0.00	0.84	2.40	2	0	0	2	0	0	0	0	0	−75.83	−76.20	0.37
isopropyl *tert*-butyl ether	29	0	−55.98	13.94	0.00	0.84	2.40	2	0	0	1	1	0	0	0	0	−83.05	−85.50	2.45
dibutyl ether	30	3	−65.85	8.67	1.70	2.52	2.40	2	0	0	0	0	0	0	0	0	−79.20	−79.82	0.62
di-*tert*-butyl ether	31	6	−61.67	21.07	0.00	0.84	2.40	2	0	0	0	2	0	0	0	0	−87.16	−87.10	−0.06
oxetane	32	3	−24.42	30.91	0.00	0.42	2.40	2	0	0	0	0	0	0	0	0	−19.33	−19.25	−0.08
3,3-dimethyloxetane	33	2	−42.43	32.83	0.00	0.42	2.40	2	0	0	0	0	0	0	0	0	−35.42	−35.42	0.00
tetrahydrofuran	34	8	−34.89	16.11	0.00	0.42	2.40	2	0	0	0	0	0	0	0	0	−44.60	−44.02	−0.58
tetrahydropyran	35	10	−36.11	8.44	0.00	0.00	2.40	2	0	0	0	0	0	0	0	0	−53.91	−53.39	−0.52
3-oxabicyclo[3.2.2]nonane	36	0	−49.93	26.79	0.00	0.00	2.40	2	0	0	0	0	0	0	0	0	−49.38	−53.18	3.80
dimethoxymethane	37	8	−36.72	−1.19	0.00	0.84	2.40	4	0	2	0	0	0	1	0	0	−83.48	−83.27	−0.21
1,1-dimethoxyethane	38	5	−42.41	2.65	0.03	0.84	2.40	4	0	2	0	0	0	0	1	0	−92.86	−93.26	0.40
1,2-diethoxyethane	39	5	−54.83	7.99	0.60	2.10	2.40	4	0	0	0	0	1	0	0	0	−97.17	−97.56	0.39
1,3-dioxolan	40	7	−30.60	10.06	0.00	0.42	2.40	4	0	0	0	0	1	1	0	0	−72.21	−72.10	−0.11
1,3-dioxane	41	7	−31.83	2.23	0.00	0.00	2.40	4	0	0	0	0	0	1	0	0	−83.53	−83.71	0.18
1,4-dioxane	42	5	−31.83	7.32	0.00	0.00	2.40	4	0	0	0	0	2	0	0	0	−75.70	−75.51	−0.19
2-methoxy THP	43	4	−45.29	6.18	0.30	0.42	2.40	4	0	1	0	0	0	0	1	0	−96.12	−95.50	−0.62
1,3-dioxacycloheptane	44	3	−38.56	10.32	0.10	0.42	2.40	4	0	0	0	0	0	1	0	0	−81.65	−82.80	1.15
2,2-dimethoxypropane	45	3	−48.10	6.22	0.08	0.84	2.40	4	0	2	0	0	0	0	0	1	−102.15	−102.15	0.00

[a] Best values: C–O = −14.318, O–H = −26.901, O–Me = 3.758, O–SE = −5.031, O–TE = −10.582, OCCO = 1.839, OCO = 0.941, OC1O = −6.618, OC2O = −13.835. [b] The standard deviation = 0.38. Based on 39 equations—optimization and analysis ignores all equations whose weight is zero.

Table XXXII. Strainless Heats of Formation for Alcohols and Ethers—Input[a,b]

compound	eq	wt	sumh	steric	pop	tors	T/R	C–O	O–H	O–Me	O–SE	O–TE	OCCO	OCO	OC1O	OC2O	$H_f°$ strnls	$H_f°$ MM3	difference (strnls – MM3)
methanol	1	5	−13.77	0.00	0.00	−0.42	2.40	1	1	1	0	0	0	0	0	0	−48.25	−48.25	0.00
ethanol	2	5	−18.44	0.00	0.15	0.00	2.40	1	1	0	0	0	0	0	0	0	−56.05	−56.05	0.00
2-propanol	3	5	−23.12	0.00	0.09	0.00	2.40	1	1	0	1	0	0	0	0	0	−65.25	−65.25	0.00
tert-butyl alcohol	4	5	−27.80	0.00	0.00	0.00	2.40	1	1	0	0	1	0	0	0	0	−74.86	−74.86	0.00
dimethyl ether	5	5	−27.54	0.00	0.00	0.00	2.40	2	0	2	0	0	0	0	0	0	−43.94	−43.94	0.00
dimethoxymethane	6	5	−36.72	0.00	0.00	0.84	2.40	4	0	2	0	0	0	1	0	0	−83.48	−83.48	0.00
1,1-dimethoxyethane	7	5	−41.39	0.00	0.03	0.84	2.40	4	0	2	0	0	0	0	1	0	−92.86	−92.86	0.00
1,2-diethoxyethane	8	5	−51.74	0.00	0.60	2.10	2.40	4	0	0	0	0	1	0	0	0	−97.17	−97.17	0.00
2,2-dimethoxypropane	9	5	−46.07	0.00	0.08	0.84	2.40	4	0	2	0	0	0	0	0	1	−102.15	−102.15	0.00

[a] Best values: C–O = −13.100, O–H = −27.060, O–Me = 3.700, O–SE = −4.460, O–TE = −9.300, OCCO = 1.870, OCO = −5.000, OC1O = −9.740, OC2O = −14.400. [b] The standard deviation = 0.00.

Table XXXIII. MM3 Structural Parameters for Alcohols and Ethers[a]

torsional					V_1	V_2	V_3
	1	1	1	6	0.200	0.000	0.300
	1	1	6	1	0.450	0.050	0.757
	5	1	6	1	0.000	0.000	0.680
	6	1	6	1	1.250	−3.000	0.850
	56	6	56	1	0.000	0.000	0.400
	1	56	56	6	0.000	0.000	0.150
4	56	6	56	56	0.000	0.000	1.830
4	6	56	56	56	0.000	0.000	1.830
5	1	1	1	6	0.300	0.000	1.800
5	1	1	6	1	0.250	0.050	0.657
5	6	1	6	1	0.250	−2.000	1.720
					Bond Stretching		
					k_s	l_0	
5	1	6			5.70	1.416	
		6			0.010(*k*)	1.300(*c*)	0.0050(*d*)
					Electronegativity Correction		
	1	1	1	6	−0.007		
	56	56	56	6	−0.007		
					Angle Bending		
					k_θ	θ_0	
	1	1	6		0.830	107.5	1
	1	1	6		0.830	107.0	2
	1	1	6		0.830	107.9	3
	5	1	6		0.820	110.0	1
	5	1	6		0.820	108.9	2
	5	1	6		0.820	108.7	3
	6	1	6		0.540	108.6	1
	6	1	6		0.540	108.6	2
	6	1	6		0.540	108.6	3
	1	6	1		0.820	107.2	
	1	56	6		0.770	107.6	2
	5	56	6		0.450	108.7	1
	5	56	6		0.450	108.7	2
	5	56	6		0.450	108.7	3
4	56	6	56		0.424	107.0	1
4	6	56	56		0.340	109.3	1
4	6	56	56		0.340	109.2	2
4	6	56	56		0.340	108.4	3

[a] Parameters are given in terms of atom types: 1 is an alkane carbon, 51 is a cyclobutane carbon, 5 is hydrogen attached to carbon, 21 is hydrogen attached to oxygen, and 6 is alcohol (or ether) oxygen. For additional information refer to the users' manual (ref 4).

values of the CCOH dihedral angles, the molecule can be present as either a boat-like or chair-like six-membered ring. The structural parameters obtained in the ED study are reported in Table XXX together with the corresponding MM3 values.

Heats of Formation. With MM3 it is possible to do the heat of formation calculation from either a straight bond energy scheme in which the zero point energies and thermal energies are automatically included in the bond parameters, or these may be separately calculated and included.[3] We have used only the former method to study heats of formation in the present work.

As earlier studies have shown, the heats of formation of alcohols and ethers can be well fit by the standard bond energy scheme, although quite a few parameters are needed. A total of nine heat of formation parameters are in principle required. These parameters were evaluated by least-squares fitting to the data listed in Table XXXI.[78] The final results show that quite a good fit was obtained, with a standard deviation between the MM3 calculations and experiment of 0.38 kcal/mol. Since the saturated hydrocarbon standard deviation was 0.43 kcal/mol, a value smaller than that has to be regarded as fortuitous. But clearly the results

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(77) Kinneging, A. J.; Mom, V.; Mijlhoff, F. C.; Renes, G. H. *J. Mol. Struct.* **1982**, *82*, 271.

(78) Experimental heats of formation are taken from (a) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970. (b) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1977.

are quite good, and one should be able to rely on heats of formation calculated by MM3 for compounds of this class.

All of the heat of formation input and output data are given in Table XXXI. The meaning of the terms is as usual.[3,8] The nine parameters to be evaluated are listed under "best values" in footnote *a*. These include bond energies for the CO and OH bond and structural terms when an oxygen is attached to a methyl, a secondary carbon, or a tertiary carbon. (If attached to a primary carbon, this is zero.) If two oxygens are simultaneously attached to a carbon along with zero, one, or two hydrogens, these terms are respectively OCO, OC1O, and OC2O. When two oxygens are attached to adjacent carbons, we have the term OCCO. These are the parameters used in this work. In Table XXXI are given the number of times each of these parameters appears in a given compound. sumh is the contribution to the heat of formation from the hydrocarbon portion of the molecule which is not being evaluated here but utilizes parameters carried over from the hydrocarbon work.[3]

Looking at the results in Table XXXI, a problem occurs at line 29, isopropyl *tert*-butyl ether. We believe this is an experimental error, since the more hindered compound di-*tert*-butyl ether (line 31) and also diisopropyl ether (line 28) show much smaller errors.

3-Oxabicyclo[3.2.2]nonane (line 36) shows a large error, and since there is nothing exceptional about this compound that we can see, we believe this is an experimental error also. The experimental value for 1-heptanol (line 13) is also clearly in error, and we also suspect the value for 1,3-propanediol (line 19), as this appears to be a rather ordinary structure. We have included 39 compounds in the heat of formation calculations, so the set is well over-determined, and the results should be reliable. Parameters necessary for calculating strainless heats of formation and strain energies were derived and are shown in Table XXXII.

Concluding Remarks

An MM3 parameter set has been derived which permits one to calculate with experimental accuracy various structures, conformational energies, heats of formation, and other properties for a series of alcohols and ethers. The studies have been sufficiently extensive that we believe these parameters will be applicable to compounds of this class in general. Vibrational spectra may also be calculated, although with more limited accuracy. As with the hydrocarbons, we believe that the addition of some selected cross terms into the force field will permit vibrational spectra to be calculated with considerably higher accuracy, but these are expected to have little effect on structures and energies.

The complete set of structural parameters (Table XXXIII), together with the heats of formation parameters are included in MM3(90). A copy of the full MM3 parameter set may also be obtained from the author upon request.

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Molecular Mechanics Calculations (MM3) on Aliphatic Amines

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Abstract: The MM3 force field has been extended to cover aliphatic amines. The structures of eight compounds have been examined and are generally fit to approximately within experimental error, including dipole moments and conformational equilibria. The heats of formation available (20 compounds) have been fit by a heat of formation parameterization. The vibrational spectra for four simple compounds have also been examined and, excluding the Bohlmann bands, fit to an rms error of 35 cm^{-1}. Hydrogen bonding has been examined in the ammonia dimer and in ethylenediamine.

Introduction

Molecular mechanics calculations have become increasingly convenient for the determination of molecular structures and many other properties in recent years.[1] The MM2 force field[2] has been widely used for such calculations and in general does a creditable job of giving structures and energies for a wide variety of molecules, including aliphatic amines.[4] However, over the years various flaws were found in MM2,[5] and it was decided some time ago to develop a new force field (MM3), by going back to the beginning and correcting these known significant errors in the original formulation. The MM3 force field for aliphatic hydrocarbons has been published.[6] Several other common functional groups have been and are now being examined by using MM3, and this paper is concerned specifically with the aliphatic amines.

The MM2 force field handled aliphatic amines reasonably well.[4] One dissatisfying feature of that force field stemmed from the fact that lone pairs were explicitly introduced into various compounds, including amines, in order to fit experimental data that

Table I. Methylamine (Å/deg)

	MM3	MW[13]	ED[8]	MW[11]
C-H	1.110 1.110	1.093		1.099
C-N	1.463	1.474	1.4652	1.471
N-H	1.016	1.014		1.010
H-C-H	108.71 107.79	109.47		108.0
C-N-H	112.29	112.1		
H-N-H	106.42	105.85		107.1
N-C-H	111.01 110.27			110.3
dipole (D)	1.29	1.336		

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[1] Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, D.C., 1982.