11918 *J. Am. Chem. Soc.* **1993,** *115,* 11918–11925

Molecular Mechanics (MM3). Calculations of Furan, Vinyl Ethers, and Related Compounds

Norman L. Allinger* and Liqun Yan

Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received January 19, 1993⊗

Abstract: The structures, conformational energies, and heats of formation of 21 compounds and the vibrational spectra for four molecules (vinyl alcohol, methyl vinyl ether, furan, and *p*-dioxin) were studied, and parameters were developed for the MM3 force field to describe these compounds. The structures and energies are fit well, but the spectroscopic data are fit less well (average rms error of 86 cm^{-1} over four compounds).

Introduction

Previous papers[1-10] have described the MM3 molecular mechanics force field[11] and its application to a wide variety of compounds. Molecules that contain a conjugated electronic system present special problems in molecular mechanics, which have been solved[12,13] by carrying out a quantum mechanical π-system calculation and superimposing constants determined in this way upon the regular molecular mechanics calculation. This method has been shown to work well for conjugated hydrocarbons using the MM3 force field as far as calculating structures and energies but is of somewhat limited accuracy for vibrational spectra.[5] Our goal has been to calculate bond lengths (excluding hydrogens) to within 0.005 Å, angles to within 1°, and energies to within 1 kcal/mol, and this accuracy is almost always achieved. For vibrational frequencies, however, for saturated molecules, the rms error over a wide selection of molecules is about 40 cm^{-1}. For conjugated hydrocarbons[5] and also for alkenes,[4] the accuracy is much lower, on the order of 70 cm^{-1}. This lower accuracy in the case of planar hydrocarbons is mostly a result of the couplings between both the in-plane and the out-of-plane bending frequencies that are not adequately taken into account in MM3. Fortunately, these have, as far as we have been able to determine, a negligible effect on structures and energies, so that good results are obtained for the latter, even though the spectra are of less than the desired accuracy.

Having an adequate (for now) MM3 force field for the description of aromatic hydrocarbons, we next wished to extend this kind of calculation to cover various heteroatom systems. In this paper, we will discuss only oxygen-containing systems, particularly furan and its derivatives. Nitrogen, sulfur, and carbonyl compounds will be discussed in separate papers.

Method

The π-system method used is a VESCF (variable electronegativity self-consistent field) method, as previously described.[5,12,13] The details of the quantum mechanics are all analogous to those for hydrocarbons, and the general method other than for items specified is basically the same as was used in MM2.[13]

In many kinds of simple compounds, such as vinyl ethers or vinyl alcohols, one can treat the system as being nonconjugated, but in furan, clearly the system is conjugated. With MM2, we parameterized the force field so that they could be treated either way, utilizing a type 6 oxygen for the unconjugated system and a type 41 oxygen for the conjugated system. In MM3, lone pairs are not explicitly considered on oxygen (or otherwise), and this is one significant difference from MM2. In general, the direction of a p orbital on an sp^2 atom is defined to be perpendicular to the plane of the three attached atoms. In the case of oxygen, only two atoms are attached to it, so the plane is determined by including the oxygen itself as the third atom.

Results and Discussion

π-System Parameters. In the heat of formation calculations of conjugated hydrocarbons, the modified Lo and Whitehead method was used to calculate the π-system energy with the MM3 program.[5,14] The bond energy of a conjugated C–C bond E_b(C=C) is taken to be the sum of its σ component, the σ bond energy $E_{\sigma b}$, and its π component, the π bond energy $E_{\pi b}$. Lo and Whitehead chose ethylene and benzene to parameterize these values semiempirically, since these two compounds are well known experimentally. The parameters are the equilibrium bond lengths R_e, the equilibrium bond energies E_e, and the stretching force constants k_e of ethylene and benzene. In MM2,[13] the parameters for the C–C atom pair were modified slightly from the Lo and Whitehead values to get the best fit of the heats of formation to the experimental data for a set of conjugated hydrocarbons. For MM2, the corresponding parameters for other types of π bonds were taken to be proportional to those of C–C bonds of the same lengths. This approximation works well if we are only concerned about structures, but it fails in the heat of formation calculations for the heterocycles.[15] In MM3, independent parameters for each different atom pair were developed. The parameters for the

---

⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1993.

(1) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989,** *111,* 8551, 8566, 8576.

(2) Allinger, N. L.; Rahman, M.; Lii, J.-H. *J. Am. Chem. Soc.* **1990,** *112,* 8293.

(3) Schmitz, L,. R.; Allinger, N. L. *J. Am. Chem. Soc.* **1990,** *112,* 8307.

(4) Allinger, N. L.; Li, F.; Yan, L. *J. Comput. Chem.* **1990,** *11,* 848.

(5) Allinger, N. L.; Li, F.; Yan, L.; Tai, J. C. *J. Comput. Chem.* **1990,** *11,* 868.

(6) Allinger, N. L.; Kuang, J.; Thomas, H. *Theochem.* **1990,** *209,* 125.

(7) Lii, J.-H.; Allinger, N. L. *J. Comput. Chem.* **1991,** *12,* 186.

(8) Allinger, N. L.; Chen, K.; Rahman, M.; Pathiaseril, A. *J. Am. Chem. Soc.* **1991,** *113,* 4505.

(9) Allinger, N. L.; Quinn, M.; Rahman, M.; Chen, K. *J. Phys. Org. Chem.* **1991,** *4,* 647.

(10) Chen, K.; Allinger, N. L. *J. Phys. Org. Chem.* **1991,** *4,* 659.

(11) The MM3 program is available to all users from the Technical Utilization Corporation, Inc., 235 Glen Village Court, Powell, OH 43065, to commercial users only from Tripos Associates, 1699 South Hanley Rd, 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. Note that the work described herein is believed to be correctly incorporated into MM3(93). The corresponding π-system work was also correct in MM3(91), which was limited by hydrocarbons only. In revising the hydrocarbon version to treat heteroatom systems, an error in the nonbonded resonance integral calculation was inadvertantly introduced, and it is present in the MM3(92) version only. Calculations on conjugated systems made with that version of the program are thus not correct, but the errors are usually quite small.

(12) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973,** *95,* 3893.

(13) Sprague, J. T.; Tai, J. C; Yuh, Y.; Allinger, N. L. *J. Comput. Chem.* **1987,** *8,* 581.

(14) Lo, D. H.; Whitehead, M. A. *Can J. Chem.* **1968,** *46,* 2027.

(15) (a) Tai, J. C.; Lii, J.-H.; Allinger, N. L. *J. Comput. Chem.* **1989,** *10,* 635. (b) Tai, J. C.; Allinger, N. L. *J. Am. Chem. Soc.* **1988,** *110,* 2050.

0002-7863/93/1515-11918$04.00/0

Table 1. Parameters Used in the Morse Potental Function

i–j	compd	$E_e^{i\text{–}j}$ (kcal/mol)	R_e (Å)	k_e ($10^5 \times$ dyn/cm)	$\alpha = (k_e/(2E_e^{i\text{–}j}))^{1/2}$ (Å^{-1})
C–C	ethylene	129.37 (129.10)[a]	1.338	9.75	2.307 (2.309)[a]
	benzene	115.58 (117.559)[a]	1.397	7.50	2.161 (2.142)[a]
C–O	pseudomolecule	126.43	1.244		2.307
	furan	98.68	1.364		2.161
O–O	molecule 1	123.69	1.150		2.307
	molecule 2	81.78	1.331		2.161

[a] The values in parentheses are directly from the experimental values. Since our method is empirical, we modified the values slightly so that the calculated heats of formation fit better to the experimental results.

Table 2. Heats of Formation and Standard Enthalpies

equation	$\Delta H°$ (kcal/mol)	ref
C (graphite) → C (gas)	$\Delta H_r = 170.89$	14
$^1/_2O_2$ (gas) → O (gas)	$\Delta H_r = 59.61$	37
$^1/_2H_2$ (gas) → H (gas)	$\Delta H_r = 52.10$	14
6C (graphite) + $3H_2$ (gas) → benzene	$\Delta H_f = 19.81$	38
2C (graphite) + $2H_2$ (gas) → ethylene	$\Delta H_f = 12.56$	39
4C (graphite) + $^1/_2O_2$ (gas) + $2H_2$ → furan	$\Delta H_f = -8.13$	39

C–C, C–O, and O–O atom pairs are listed in Table 1. The Lo and Whitehead values are in parentheses. The different parameters allowed for different atom pairs in MM3 greatly improved the heat of formation results. The standard deviation of the heats of formation of 14 compounds studied here is 0.37 kcal/mol (vide infra).

In the Lo and Whitehead work, the parameters for ethylene and benzene were derived from the experimental heats of formation and structures of these two compounds. To determine the parameters of oxygen heterocycles by this method, we needed to find two oxygen compounds with quite different C–O bond orders to take the place of ethylene and benzene. However, all the compounds we know have similar C–O bond orders (around 0.2–0.3). To solve this problem, approximations were made. Furan was taken to be the benzene-like molecule. Its bond energy was derived from its heat of formation, and the bond length was taken from a good experimental r_α value.[16] A dummy molecule with a C–O bond order of 1.0 was chosen to be the ethylene-type molecule. Its bond energy and bond length were derived from the furan values by assuming a linear relationship of these quantities with the bond order and taking the slopes to be the same as the corresponding ones for ethylene and benzene. The C–O bond order of furan was assumed to be 0.32, which is approximately the MM3 calculated value. The bond energies of furan and the dummy molecule were modified slightly later to get a better fit to the heats of formation. The α (α = bond energy/force constant) values of the C–O bond in furan and the dummy molecule were taken to be the same as those of benzene and ethylene, respectively, as a first approximation, and these turned out to be our final values because they gave reasonable results.

The data used to derive the C–O bond energy of furan are listed in Table 2. The bond energies of the C–C single bond and double bonds in furan were calculated from a linear equation of bond energy and bond order derived from the ethylene and benzene bond energies as listed in Table 1. The bond orders of the C–C single and double bonds are 0.48 and 0.85, respectively.

The values of the parameters for the C–O atom pair should be approximately the average of the values of the C–C and O–O atom pairs. By knowing those for the C–O and C–C atom pairs, the parameters for the O–O atom pair can be derived, and the values are listed in Table 1 as dummy 1 and dummy 2. Dummy 1 is the ethylene-like molecule for the O–O atom pair, and dummy 2 is the benzene-like molecule for the O–O atom pair.

The nonbonded resonance integral H_{ij}' is set to be proportional to the corresponding overlap integral[17] $S_{\pi\pi}$ as in eq 1

$$H_{ij}' = \mathrm{CB}^* S_{\pi\pi}(W_i + W_j) \tag{1}$$

where $S_{\pi\pi}$ was calculated following Mulliken's work.[17] The term p in their method was defined as in eq 2,

$$p = (Z_A + Z_B)R^*\mathrm{DB} \tag{2}$$

where Z_A and Z_B are the effective nuclear charges of atoms A and B, respectively, and R is the distance between the two atoms.

The proportionality constants CB and DB were chosen so that the nonbonding resonance integral H_{ij}' merges with bonding resonance integral H_{ij} near 1.4 Å for the C–O atom pair and 1.3 Å for the O–O atom pair. The final values of CB and DB for the C–O atom pair are 0.235 and 0.710. These values for the O–O atom pair are 0.175 and 0.535.

The first ionization potential of oxygen was increased by 15% from the experimental value in the MM2 calculations in order to get the correct C–C bond order in furan.[15] This adjustment was thought to compensate for the exclusion of the non-neighbor resonance integrals. However, in MM3, this adjustment is still necessary, even though we have included resonance integrals between all atom pairs. The value used in the MM3 program is 18.06 eV, which is 18% higher than the experimental value of 15.30 eV.

MM3 Parameters. After we had determined all of the parameters involved in the VESCF calculation, the problem was reduced to a general molecular mechanics parameterization. The new parameters used for furan, vinyl alcohol, and their derivatives are listed in Table 3.

Stretching Parameters. The C_{sp^2}–O (represented by C–O) bond orders and lengths calculated by MM3 and the bond lengths determined by experiment for several molecules are listed in Table 4. The experimental methods used to measure those bond lengths varied from one molecule to another and therefore gave different types of bond lengths.[15] In the MM3 calculation, bond lengths are fit to r_g values from electron diffraction whenever they are available. In this study, where we have to compare our bond lengths to microwave or X-ray data, systematic adjustments have been made before the comparison. We added 0.006 Å to the r_s values from MW values, 0.002 Å to r_a and r_α from ED values, and 0.007 Å to r_α from room-temperature X-ray values. The experimental methods used and the correction values are listed in the tables for each of the individual molecules. The values shown in Table 4 are the values after the correction.

Furan and dibenzofuran are the only two compounds that have C–O bonds in five-membered rings which can have the stretching constant and the natural bond length different from the open-chain compounds. Poor agreement was found in the dibenzofuran C–O bond length when we chose l_0 to fit furan. We could adjust the slope of the bond length and bond order equation to fit both compounds. However, this would result in a physically unreasonable l_0–P_{ij} relationship, and as was discussed in the MM2 work,[15] we believe that this disagreement is due to an artifact in the experimental measurement. So we chose to fit furan very well and let the C–O bond lengths in dibenzofuran be calculated to be 1.392 Å, shorter than the experimental value by 0.014 Å. This discrepancy is mostly an "experimental artifact" that comes from the fact that the X-ray bond lengths are measured between centers of electron density and the lone pairs on oxygen cause the center of electron density to be positioned farther from the carbons than are the nuclei.[54] The remaining discrepancies in bond lengths are real. It is noted that the experimental values, apart from the C–O bonds, are systematically too short, which suggests that the thermal motion corrections may be a bit too small.

Open-chain compounds have similar bond orders (around 0.20), except for the nonplanar molecules divinyl ether and diphenyl

---

(16) Liescheski, P. B.; Rankin, D. W. K. *J. Mol. Struct.* **1989**, *196*, 1.

(17) Mulliken, R. S.; Rieke, C. A.; Orloff, D.; Orloff, H. *J. Chem. Phys.* **1949**, *17*, 1248.

Table 3. MM3 Parameters[a]

Torsional Parameters (kcal/mol)

bond type	V_1	V_2	V_3
1 1 1 41	0.00	0.00	0.70
41 1 1 41	0.00	0.00	1.91
5 1 1 41	−1.20	−0.90	0.60
5 1 2 41	0.00	0.00	0.54
1 1 41 2	0.00	0.00	0.45
5 1 41 2	0.00	0.00	0.45
1 2 2 41	0.00	10.00	0.00
2 2 2 41	−0.45	10.00	0.00
5 2 2 41	−0.25	10.00	0.00
41 2 2 41	0.00	10.00	0.00
1 2 41 1	0.00	10.11	0.00
1 2 41 2	0.00	10.00	0.00
2 2 41 1	0.00	12.00	−2.10
5 2 41 1	−0.80	11.00	2.10
2 2 41 2	0.20	6.00	−0.80
5 2 41 2	0.00	9.00	0.40
2 2 41 73	−0.10	10.80	0.00
5 2 41 73	0.74	9.00	0.00
2 2 2 41	0.35	11.50	0.00, *5
2 2 41 2	0.45	13.50	−0.70, *5

Stretching Parameters (md/Å, Å)

bond type	K_s	l_o	K_{slope}	L_{slope}	bond moment
1 41	5.40	1.420			1.50
2 41	12.20	1.218	8.20	0.172	0.55
2 41	11.60	1.225	8.20	0.162	0.855, *5
41 73	7.20	0.960			

Electronegativity Corrections (Å)

bond type	Δl_o	bond type	Δl_o
2 41 41 73	0.021	2 5 2 41	−0.005
2 41 41 2	0.012		

Bond Angles (md·Å/rad^2, deg)

		type		
bond type	K_b	1	2	3
1 1 41	0.90	107.5		
5 1 41	0.92	110.0	108.9	108.7
1 2 41	0.50	120.0		
2 2 41	1.05	119.5	120.8	
5 2 41	0.80	108.0		
2 41 1	1.00	109.1		
2 41 2	0.95	112.0		
2 41 73	0.85	107.0		
2 2 41	1.15	120.0	116.6, *5	
2 41 2	1.15	116.4, *5		

Out-of-Plane Bending Parameter (md·Å/rad^2)

bond type	K_{oop}
2 41	0.15

[a] Asterisk denotes four- and five-membered rings. Atom type: 1, sp^3 carbon; 2, sp^2 carbon; 41, sp^2 oxygen; 5, hydrogen; and 73, hydrogen attached to an oxygen.

ether. However, they have very different C–O bond lengths. The C–O bond lengths in methyl vinyl ether and anisole are around 1.360 Å, while those in *p*-dioxene and 3,4-dihydro-1,2-pyran are around 1.40 Å. We chose to fit the first two compounds because the experimental data of the latter two are not very accurate. In the case of *p*-dioxene, the C_{sp^2}–O bond is even longer than the C_{sp^3}–O bond by experiment, which is unreasonable. The C–O bonds attached to a hydrogen as in phenol and vinyl alcohol or attached to a C_{sp^2} as in *p*-dioxin are around 1.38 Å. By adding electronegativity corrections to these two cases, the C–O bond lengths were calculated in agreement with experiment for those molecules. The O–H and O–C_{sp^3} bonds are pure σ bonds, and their lengths do not vary much from molecule to molecule.

Bending Parameters. Bending parameters of the four types of angles C=C—O, C—O—C, C—O—H, and C—O—C_{sp^3} are the bending parameters of most concern in this study. The calculated values for these angles for different compounds are summarized in Table 5 according to the angle type.

Torsional Parameters. Seventeen torsional parameters are involved in the calculations. The torsion angle 2-2-2-41 occurs in several compounds, but the values are equal to 0° or 180° in all of these compounds; thus, the torsional parameters here cannot be uniquely assigned. The V_2 term of the 2-2-2-41 parameter was assigned a value of 10.0, which is the general value of the V_2 term when the central bond is a C=C bond. 1-Naphthol and 2-vinylfuran, studied for their heats of formation, contain 2-2-2-41 angles. This angle is 0° in 1-naphthol and in 2-vinylfuran when the vinyl group is cis to oxygen. No energy difference between *cis*- and *trans*-2-vinylfuran is available. Therefore, the V_3 term was set to be 0 for 2-2-2-41, and we chose an appropriate value of V_1 to fit the heat of formation of 1-naphthol (which was −0.45). As a result, *cis*-2-vinylfuran is more stable than *trans*-2-vinylfuran by 0.1 kcal/mol. Other parameters were chosen so as to fit the torsional frequencies of four compounds, vinyl alcohol, methyl vinyl ether, furan, and *p*-dioxin, as well as the energy differences and the torsional angles of different conformations and the rotational barriers. The vibrational frequencies will be discussed later. The torsional frequencies do not fit to experiment very well in the two cyclic compounds because of the large couplings in the torsional motions. The energy differences between the different conformations and the corresponding dihedral angles are summarized in Table 6.

Bond Moments. The dipole moment of a conjugated compound is calculated as the vector sum of the σ moment and the π moment. The π moment is considered to be overestimated in the current MM3 VESCF calculation, even though it is much better than that from the SCF method in the MM2 program.[15] Therefore, the π moment is calculated from the coordinates of the atoms and the π charges at these sites and then multiplied by a factor of 0.65 (to allow for the moments induced in the σ system by the π system). The calculated dipole moments and the experimental values are compared in Table 7. The calculated moments do not allow for the induced moments in the molecule (except for the π system), but these could be allowed for by the IDME method if desired.[18] A comparison of the *x*, *y*, and *z* components of the molecular dipole was also made wherever they were available. The σ dipole moment of furan is opposite to the π moment and larger in value. Therefore, the total dipole moment of furan is in the direction of the σ moment, and it points from the ring (positive) to the oxygen (negative). It is interesting that the dipole moment of pyrrole is quite similar in magnitude to that of furan, but it points in the opposite direction (from nitrogen into the ring). This is because the lower electronegativity of the nitrogen leads to both a reduced value for the σ moment and an increased value for the π moment. These facts are reproduced by MM3.

Molecular Structures and Energies. The structures of 13 compounds were calculated, and they are listed individually in Tables 8–20. (Tables 13–18 are in the supplementary material.) The structures of some heterocyclic compounds, together with the numbering systems used, are shown in Figure 1.

The two stable conformers of vinyl alcohol are the cis and trans conformers with the dihedral angles C=C—O—H equal to 0° and 180°, respectively. The most stable one detected in microwave studies[19,20] is cis planar. The trans has not been observed experimentally, but *ab initio* data on it are available[21] (MP2/6-31G*). The potential energy calculated by *ab initio* methods[21] was used as a reference in our parametrization.

---

(18) (a) Dosen-Micovic, L.; Jeremic, D.; Allinger, N. L. *J. Am. Chem. Soc.* **1983**, *105*, 1716. (b) Dosen-Micovic, L.; Jeremic, D.; Allinger, N. L. *J. Am. Chem. Soc.* **1983**, *105*, 1723.

(19) Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399.

(20) (a) Rodler, M.; Bauder, A. *J. Am. Chem. Soc.* **1984**, *106*, 4025. (b) Mulliken, R. S.; Rieke, C. A.; Orloff, D.; Orloff, H. *J. Chem. Phys.* **1949**, *17*, 1248.

(21) Nobes, R. H.; Radom, L.; Allinger, N. L. *J. Mol. Struct.* **1981**, *85*, 185.

Table 4. C–O Bond Orders and Bond Lengths (Å)

	exp	exp method[a]	MM3 (bond length/order)	Δ	Δ correctn
furan	1.366	ED + MW + LC	1.372/0.323	0.006	
dibenzofuran	1.406	X-ray	1.392/0.249	−0.014[c]	−0.004
vinyl alcohol	1.378	MW	1.378/0.229	0.000	
phenol	1.380	MW	1.382/0.217	0.002	
methyl vinyl ether	1.359	ED + MW	1.360/0.236	0.001	
anisole	1.363	ED	1.366/0.223	0.003	
p-dioxene	1.409	MW	1.359/0.213	−0.050[b]	
3,4-dihydro-1,2-pyran	1.411	MW	1.361/0.233	−0.050[b]	
p-dioxin	1.401	ED	1.379/0.195	−0.022[b]	
dibenzo-*p*-dioxin	1.389	X-ray	1.379/0.204	−0.010[c]	0.000
rms					0.003
avg					0.002

[a] ED = electron diffraction, MW = microwave, and LC = liquid-crystal NMR. All values were corrected to r_g (see text). [b] These values are mostly due to experimental error and were not included in the rms calculation. [c] These values measure positions of electron density instead of nuclear positions. Add 0.010 Å as a correction.

Table 5. Bond Angles of Oxygen Heterocycles (deg)

	C_{sp^2}—O—C_{sp^2}			C═C—O		C—O—H or C—O—C_{sp^3}	
	exp	MM3		exp	MM3	exp	MM3
furan	106.74(7)	106.4		110.49(7)	110.4		
dibenzofuran	104.1	104.5		112.7	112.3		
			exo	124.3	126.5		
p-dioxin	109.8(5)	113.5		124.2(45)	123.3		
dibenzo-*p*-dioxin	116.4(5)	117.0		121.8(6)	121.5		
			exo	117.7(6)	118.7		
cis-vinyl alcohol				126.2	125.2	108.3	108.3
phenol				121.1	121.3	108.9	108.8
cis-methyl vinyl ether				127.3(18)	127.8	116.8(18)	116.6

Table 6. Energy Differences between Conformations (kcal/mol)

		exp	MM3	Δ
vinyl alcohol[21]				
C═C—O—H =	0 (s-cis)	0.0	0.0	0.0
	90	4.3	4.40(95)	0.10
	180 (s-trans)	1.8	1.77	0.05
phenol[40]				
C═C—O—H =	0 (s-cis)	0.0	0.0	0.0
	90	3.29–3.47 (avg 3.38)	3.30(90)	−0.08
methyl vinyl ether[23]				
C═C—O—C =	0 (s-cis)	0.0	0.0	0.0
	44 (transition state)	7.02	6.95(70)	−0.07
	138 (gauche)	1.70	2.44(149)	0.74
	180 (transition state)	3.44	2.80	−0.64
Me rotnl barrier				
cis		3.81	3.55	−0.26
gauche		1.50	1.70	0.20
anisole[41]				
C═C—O—C =	0	0.0	0.0	0.0
	90	−2.4	1.1	−1.3
3,4-dihydro-1,2-pyran[24]				
planar–twist		11.7	11.66	−0.04
p-dioxene[24]				
planar–twist		11.8	11.77	−0.03

The most stable conformer of methyl vinyl ether is cis, and it has a planar skeleton. Its structure was studied by a combination of ED and MW.[22] The second stable conformer is gauche with the C═C—O—C dihedral angle of 138° rather than trans planar. The entire potential energy curve was determined from studies on the far-infrared and Raman spectra.[23] Our calculation agrees with experiment very well. The stable conformers of phenol and anisol are also planar with the hydrogen or the methyl group in the molecular plane.

Table 7. Dipole Moments of Oxygen Heterocycles (debye)

		exp	MM3	Δ
furan[15a]		0.67	0.67	0.00
		1.03 ± 0.02	0.91	−0.12
	μ_a	0.91 ± 0.01	0.84	−0.07
	μ_b	0.48 ± 0.03	0.39	−0.09
benzofuran[15a]		0.79	0.85	0.06
dibenzofuran[43]		0.88 ± 0.06 (B)	1.01	0.13
vinyl alcohol[19]		1.016 ± 0.009	1.076	0.001
	μ_a	0.616 ± 0.007	0.654	0.038
	μ_b	0.807 ± 0.006	0.778	−0.029
phenol[44]		1.224	1.336	0.112
methyl vinyl ether[19]		0.96 ± 0.02	0.97	0.01
anisole[15a]		1.30 ± 0.03	1.32	0.02
3,4-dihyro-1,2-pyran[26]		1.400 ± 0.008	1.271	−0.129
	μ_a	1.240 ± 0.002	0.996	−0.244
	μ_b	0.588 ± 0.010	0.716	0.128
	μ_c	0.278 ± 0.008	0.331	0.053
dioxene[25]		0.939 ± 0.008	0.876	−0.063
divinyl ether[27]		0.782 ± 0.026	0.706	−0.076
	μ_a	0.349 ± 0.012	0.343	−0.006
	μ_b	0.662 ± 0.009	0.570	−0.092
	μ_c	0.225 ± 0.035	0.238	0.013

A very precise determination of the furan structure was carried out by Liescheski and Rankin.[16] They determined the structure by a combined analysis of data obtained by ED, MW, and liquid-crystal NMR spectroscopy. Therefore, considerable effort was put into fitting the structure of this molecule. The MM3 errors in the bond lengths are within 0.005 Å, and those in the bond angles are within 0.3°. The moments of inertia were fit with errors of 0.3–0.6%. Since the microwave moment of inertia corresponds to an r_α geometry and the MM3 geometry is r_g, the MM3 moments of inertia should be approximately 0.5% larger than those of experiment.

The experimental structures of *p*-dioxene and 3,4-dihydro-1,2-pyran are nonplanar. The potential energy surfaces of these two compounds were determined by Tecklenburg and Laane[24] using far-infrared and Raman spectra. The twisted (half-chair) conformations have the lowest energy, from both far-infrared[24] and MW studies.[25,26] The dihedral angles between the

---

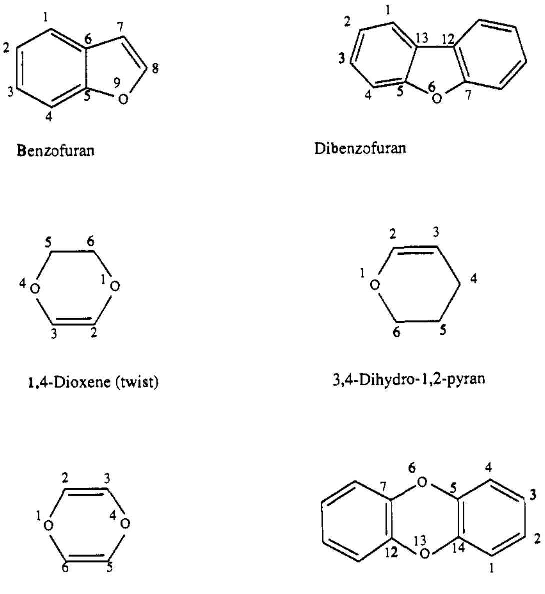
(22) Pyckhout, W.; Van Nuffel, P.; Van Alsenoy, C.; Van Den Enden, L.; Geise, H. J. *J. Mol. Struct.* **1983**, *102*, 333.

(23) Sullivan, J. F.; Dickson, T. J.; Durig, J. R. *Spectrochim. Acta* **1986**, *42A*, 113.

(24) Tecklenburg, M. M. J.; Laane, J. *J. Am. Chem. Soc.* **1989**, *111*, 6920.

(25) Wells, J. A.; Malloy, T. B., Jr. *J. Chem. Phys.* **1974**, *60*, 2132.

(26) Lopez, J. C.; Alonso, J. L. *Z. Naturforsch.* **1985**, *40A*, 913.



Benzofuran Dibenzofuran

1,4-Dioxene (twist) 3,4-Dihydro-1,2-pyran

p-Dioxin Dibenzo-p-dioxin

Figure 1. Structures of oxygen heterocycles.

Table 8. Structure of *cis*-Vinyl Alcohol (bonds in Å and angles in deg)

	exp(NMW)[20] r^a	exp(corr) $r_g = r + 0.006$	MM3 r_g	Δ
C=C	1.326(5)	1.332	1.341	0.009
C—O	1.372(4)	1.378	1.378	0.000
O—H	0.960(3)	0.966	0.960	−0.006
C1—H	1.097(5)	1.103	1.096	−0.007
C2—H_c	1.086(4)	1.092	1.100	0.008
C2—H_t	1.079(4)	1.085	1.100	0.015
C=C—O	126.2		125.2	-1.0
C—O—H	108.3		108.3	0.0
$I_x{}^b$	1.407		1.445	2.70%
$I_y{}^b$	7.949		7.991	0.52%
$I_z{}^b$	9.363		9.435	0.77%

[a] Type of *r* was not specified in the paper. It is probably r_s. [b] The unit is g·cm² × 10^{-39}.

Table 9. Structure of Methyl Vinyl Ether (bonds in Å and angles in deg)

	expt(ED + MW)[22] r_g	MM3(cis) r_g	Δ	MM3(gauche) r_g
C=C	1.337(20)	1.342	0.005	1.337
C_{sp^2}—O	1.359(15)	1.360	0.001	1.366
O—C_{sp^3}	1.427(7)	1.426	−0.001	1.428
C1—H	1.095(3)	1.097	0.002	1.096
C2—H_c	1.095(3)	1.098	0.003	1.100
C2—H_t	1.095(3)	1.100	0.005	1.100
C=C—O	127.3(18)	127.8	0.5	122.9
C—O—C	116.8(18)	116.6	−0.2	113.8
C=C—O—C		0.0		149.4
I_x	4.605	4.644	0.85%	2.374
I_y	13.135	13.314	1.36%	18.519
I_z	17.215	17.400	1.07%	19.724

Table 10. Structure of Phenol (bonds in Å and angles in deg)

	exp(MW)[44] r_s	exp(corr) $r_g = r_s + 0.006$	MM3 r_g	Δ
$(C{=}C)_{Ph}$	1.391–1.395	1.397–1.401	1.396–1.404	
C—O	1.374	1.380	1.382	0.002
O—H	0.957	0.963	0.960	−0.003
C=C—O, 2-1-7	121.1		121.3	0.2
6-1-7			118.9	
C—O—H	108.9		108.8	−0.1
I_x	14.855		14.966	0.75%
I_y	32.019		32.339	1.01%
I_z	46.874		47.305	0.92%

Table 11. Structure of Anisole (bonds in Å and angles in deg)

	exp(ED)[45] r_a	exp(corr) $r_g = r_a + 0.002$	MM3 r_g	Δ
$(C{=}C)_{Ph}$	1.398(3)	1.400	1.399	−0.001
C_{sp^2}—O	1.361(15)	1.363	1.366	0.003
O—C_{sp^3}	1.423(15)	1.425	1.425	0.000
C—O—C	120.0(2.0)		117.9	-2.1

Table 12. Structure of Furan (bonds in Å and angles in deg)

	exp(ED + MW + LC)[16] r°_α	exp(corr) $r_g = r^\circ_\alpha + 0.002$	MM3 r_g	Δ
C—O	1.3641(7)	1.366	1.372	0.006
C=C	1.3640(9)	1.366	1.361	−0.005
C—C	1.4303(19)	1.432	1.431	−0.001
C2—H	1.0864(14)	1.088	1.092	0.004
C3—H	1.0862(16)	1.088	1.097	0.009
C—O—C	106.74(7)		106.4	−0.3
C=C—O	110.49(7)		110.4	−0.1
C=C—C	106.14(6)		106.4	0.3
I_x	8.885		8.911	0.29%
I_y	9.079		9.133	0.59%
I_z	17.970		18.044	0.40%

O—C=C—O plane and the C—C bond in dioxene and the C—C=C—O plane and the C—C bond in pyran were determined to be 35.1° and 36.5°, respectively, by IR and 29.9° and 30.5° by MW. The values calculated by MM3 are 30.3° and 30.4°, respectively. The transition states for interconversion of the two twist forms of dioxene and pyran are boat forms by far-infrared and Raman spectra.[24] The relative energies of the boat forms above the twist forms are 11.0 and 9.9 kcal/mol for dioxene and pyran, respectively. They also determined the energy differences between the planar and twist forms and found that these values (11.8 and 11.7) are slightly higher than (and probably within experimental error of) the energy differences between the boat and twist forms. In MM3, we could choose different values of the 2-2-41-1 parameter and let either the planar or the boat forms come out to be the transition states for interconversion of the two twist forms. However, we have already fit the 2-2-41-1 parameter to the rotational potential curve of methyl vinyl ether. The most stable conformer of methyl vinyl ether is the planar cis form. The planar conformers were then calculated to be the transition states by MM3. The boat forms are neither transition states nor stable conformers according to the MM3 calculations. Other torsional parameters involved in *p*-dioxene and 3,4-dihydro-1,2-pyran were adjusted so that the calculated relative energies of the planar forms agree with the energies of the planar forms measured by experiment. The values are included in Table 6.

Divinyl ether has several possible rotameric forms, which may be described by two unique dihedral angles (C=C—O—C and C—O—C=C) about the C_{sp^2}—O bonds. The microwave study[27] pointed to the [180, −60] conformer as the most stable one, whereas the electron diffraction[28] was interpreted as showing that a near-planar [180, 180] conformer was the most stable. A combined analysis of previous spectroscopic work and *ab initio* calculations at the 4-21G level was reported by Pyckhout et al.,[29] and they concluded that at 300 K, the rotameric mixture of divinyl ether consists of 80% [143.5, -17.6] and 20% [180, 180] conformers. Higher level *ab initio* calculation at the 6-31G*[30] indicated a mixture of conformations, principally with [143, -17] and [180, 180] conformers, 90% and 10%, respectively. Efforts were made with MM3 to fit the energy potential to the 6-31G* results. However, the two conformers with [143, -143] and [143, 143] dihedral angles were calculated to be more stable than the [143,

---

(27) Hirose, C.; Curl, R. F., Jr. *J. Mol. Spectrosc.* **1971**, *38*, 358.

(28) Barricelli, L. L.; Bastiansen, O. *Acta Chem. Scand.* **1949**, *3*, 201.

(29) Pyckhout, W.; Van Alsenoy, C.; Geise, H. J.; Van Der Veken, B.; Pieters, G. *J. Mol. Struct.* **1985**, *130*, 335.

(30) Bowen, J. P.; Reddy, V. V.; Patterson, D. G., Jr.; Allinger, N. L. *J. Org. Chem.* **1988**, *53*, 5471.

Table 19. Structure of Divinyl Ether (bonds in Å and angles in deg)

		exp(MW + ED)[29] r_α	exp(corr) $r_g = r_\alpha + 0.002$	MM3 r_g	Δ
C═C,	1-2	1.338	1.340	1.337	–0.003
	4-5	1.339	1.341	1.341	0.000
C—O,	2-3	1.395	1.397	1.381	–0.016
	3-4	1.388	1.390	1.376	–0.014
C—H,	4-9	1.102	1.104	1.096	–0.008
	2-8	1.103	1.105	1.096	–0.009
	1-6	1.105	1.107	1.100	–0.007
	1-7	1.101	1.103	1.100	–0.003
	5-10	1.103	1.105	1.100	–0.005
	5-11	1.103	1.105	1.099	–0.006
C═C—O,	1-2-3	118.5		122.9	4.4
	3-4-5	124.2		127.3	3.0
C—O—C,	2-3-4	118.8		119.3	0.5
C═C—O—C,	1-2-3-4	145.0		145.2	0.2
	2-3-4-5	–13.0		–12.8	0.2
I_x		5.356		5.347	–0.17%
I_y		26.05		26.865	3.13%
I_z		30.08		30.937	2.85%

Table 20. Structure of Diphenyl Ether (bonds in Å and angles in deg)

conformer	exp(ED)[36] r^a C2	C1	MM3 r_g C2	Δ
C—O	1.358(32)	1.382(30)	1.391	0.033
C═C_{av}	1.402(6)		1.398	–0.004
C—O—C	115.4(33)	117.5(25)	117.3	1.9
C═C—O—C	42.6(88)	29.4(82)	42.3	–0.3
C—O—C═C	42.6(88)	69.9(43)	42.3	–0.3

[a] Type of *r* was not specified in the paper.

Table 21. Conformational Energies of Divinyl Ether (kcal/mol)

conformation	4-21G[29]	6-31G*[30]	MM2[20]	MM3
[0, 180]		1.36	1.45	0.87
[180, 180]	1.58	0.46	0.46	0.61
[28.9, 28.9]	1.07	2.99	2.45	0.59 [31, 31]
[143, –17]	0.00	0.00	0.00	0.00 [145, –13]
[143, 143]		1.06	–0.10	0.13 [162, 162]
[143, –143]			–0.10	

Table 22. Heats of Formation (kcal/mol)

eq	wt	$H_f°$ calc	$H_f°$ [39] exp(err)	difference (calc – exp)	compound
1	1	–8.61	–8.13(0.2)	–0.48	furan
2	1	20.08	19.95(1.1)	0.13	dibenzofuranm
3	0	3.39	6.65(0.9)	–3.26	2-vinylfuran
4	2	–2.85	–3.25(0.2)	0.40	divinyl ether
5	2	5.21	5.43(0.5)	–0.22	phenyl vinyl ether
6	2	12.71	12.44(0.4)	0.27	diphenyl ether
7	2	–23.72	–23.06(0.2)	–0.66	phenol
8	2	–30.56	–30.77(0.3)	0.21	2-methylphenol
9	2	–31.93	–31.65(0.3)	–0.28	3-methylphenol
10	2	–38.45	–38.71(0.3)	0.26	2,6-dimethylphenol
11	2	–6.66	–7.15(0.2)	0.49	1-naphthol
12	2	–33.65	–33.68(0.2)	0.03	ethyl vinyl ether
13	2	–16.85	–16.24(0.2)	–0.61	anisole
14	2	–24.03	–24.30(0.1)	0.27	ethyl phenyl ether
15	2	–29.62	–29.93(0.4)	0.31	dihydro-2*H*-pyran

Standard deviation = 0.37

Average Experimental error = 40.37

Best Values: C═O[a] = 67.481; O—C3[a] = –21.146; O—H[a] = –38.545

[a] The parameters C═O, O—C3, and O—H are the enthapy incremnets for each C═O, O—C_{sp^3}, and O—H bond, respectively.

Table 24. Vibrational Frequencies of *s-cis*-Vinyl Alcohol (cm^{-1})

	sym	assignment	exp[49]	calc	diff
	A′				
1		O—H str	3584	3588	4
2		CH_2 str asym	3130	3110	–20
3		CH str	3096	3078	–18
4		CH_2 str sym		3014	
5		C═C str	1649	1674	25
6		CH_2 bend	1421	1480	59
7		CH rock	1310	1345	35
8		COH bend	1282	1226	–56
9		C—O str	1112	1135	23
10		CH_2 rock	952	931	–21
11		CCO bend	516	537	21
	A″				
12		CH_2 wag	975	1134	159
13		CH_2 wag	819	970	151
14		CH_2 twist	713	622	–91
15		OH tor	475	457	–16
rms					69
avg					18

–17] conformer by 0.10 kcal/mol. The relative energies of different conformations are summarized in Table 21.

The 2-2-41-2 and 5-2-41-2 parameters were adjusted to fit the conformational preferences of divinyl ether to the experimental results. Three stable conformers with the dihedral angles [145, –13], [162, 162], and [31, 31] were found by MM3. In accordance with the microwave spectrum and *ab initio* calculations, the [145, –13] conformer is the most stable one. The energy of the conformer with [162, 162] is higher that that of the lowest one by 0.32 kcal/mol. This latter conformer could be the one observed by electron diffraction, which has been claimed to be trans and near-planar. The [180, 180] conformer is always a transition state in MM3 no matter how we change the two torsional parameters 2-2-41-2 and 5-2-41-2. At first, this seemed unreasonable. However, when we looked at the structure in more detail, we found that the distance between the hydrogens on carbon 2 and 4 is relatively small (2.12 Å) in the planar conformation. In order to avoid this large van der Waals repulsion, the two C–O bonds are twisted out of planarity, and thus, the stable conformer becomes [162, 162]. This disagrees with microwave and *ab initio* results which found the [180, 180] conformer to be the second most stable conformer. However, no previous experiments, including the microwave spectrum, showed definite evidence that the second stable conformer is planar. Also, the *ab initio* calculations published did not say that the force constant matrix of the [180, 180] conformer has all positive eigenvalues. From the above analysis, the experimentally observed trans,trans conformer should be the conformer with [162, 162]. The [180, 0] conformer is also a transition state. The conformer with the dihedral angles of about [143, –143] with C_s symmetry is neither a ground state nor a transition state in MM3. The results are summarized in Table 21.

The conformational preferences of diphenyl ether are also controversial. Possible rotamaric forms can be found by rotating the two C═C—O—C torsional angles in the molecule. Semiempirical calculations[30–33] showed that the most favorable conformations are structures with angles of rotation about the C–O bonds of 30–52° and that the molecule as a whole has C_2 symmetry. In a UV[34] study, it was also assumed that the angles of rotation are about 50°. An analysis of IR[35] led to a different conclusion, namely that the most stable conformation of diphenyl ether has different torsional angles around the two C–O bonds. The electron diffraction[36] fit both models mentioned above to the observed experimental distribution. The two sets of data obtained are listed in Table 20. The MM3 calculation showed that the C_2 conformer with the C═C—O—C dihedral angles of 42.3° is the most stable conformation.

---

(31) Gallaso, V.; De Alti, G.; Bigotto, A. *Tetrahedron* **1971**, *27*, 6151.

(32) Zubkov, V. A.; Birshtein, T. M.; Milevskaya, I. S. *J. Mol. Struct.* **1975**, *27*, 139.

(33) Hernander-Laguna, A. S. G. *J. Chim. Phys. Phys. Chim. Biol.* **1978**, *75*, 83.

(34) Higasi, K. Dipole, Molecule, and Chemistry. *Res. Inst. Appl. Electron*; Sapporo, 1965.

(35) Katon, J. E.; Feairholler, W. R.; Lippincott, J. E. R. *J. Mol. Spectrosc.* **1964**, *13*, 72.

(36) Naumov, V. A.; Ziatdinova, R. N. *Zh. Strukt. Khim.* **1984**, *25*, 88.

Table 25. Vibrational Frequencies of *s-cis*-Methyl Vinyl Alcohol (cm^{-1})

	sym	assignment	exp[50]	exp[51]	MM3	MM3 – exp
1	A′	CH_2 asym str	3131	3130	3117	–13
2		CH str	3073	3055	3069	14
3		CH_3 asym str	3015	3017	3020	3
4		CH_2 sym str	3024	2991	2977	–14
5		CH_3 sym str	2875	2866	2876	10
6		$C{=}C$ str	1614	1616	1679	63
7		CH_3 asym bend	1482	1473	1531	58
8		CH_3 sym bend	1455	1452	1498	46
9		CH_2 bend	1394	1393	1439	46
10		CH bend	1323	1323	1279	–44
11		COC asym str	1222	1222	1191	–31
12		CH_3 rock	1159	1200	1155	–45
13		CH_2 rock	814	1013	1030	17
14		COC sym str	965	895	853	–42
15		CCO bend	589	589	583	–6
15		COOC bend	334	327	331	4
17	A″	CH_3 asym str	2961	1960	2975	15
18		CH_3 asym bend	1462	1460	1490	30
19		CH_3 rock	1090	1159	1173	14
20		CH_2 and CH twist	1014	966	1158	192
21		CH_2 wag	896	815	980	165
22		CH and CH_2 twist	702	704	660	–43
23		O—CH_3 tor	235	245	261	16
24		CC—OC tor	250	234	312	78
rms						62
avg						22

Table 26. Vibrational Frequencies of Furan (cm^{-1})

	sym	assignment	exp[52]	MM3	MM3 – exp
1	A1	CH(a) str	3159	3134	–25
2		CH(b) str	3128	3108	–20
3		ring str	1483	1587	104
4		ring str	1380	1385	5
5		C—H def ip	1140	1087	–53
6		C—H def ip	1061	1013	–48
7		ring str	986	946	–40
8		ring def ip	873	803	–70
9	B1	CH(a) str	3148	3129	–19
10		CH(b) str	3120	3100	–20
11		ring str	1556	1553	–3
12		C—H def ip	1270	1319	49
13		C—H def ip	1171	1180	9
14		ring (def + str)	1040	1025	–15
15		ring def ip	873	751	–122
16	A2	C—H def oop	863	1209	346
17		C—H def oop	728	782	54
18		ring def oop	613	499	–144
19	B2	C—H def oop	839	1133	294
20		C—H def oop	745	630	–115
21		ring def oop	601	534	–67
rms					116
avg					6

Heats of Formation. These were calculated for 15 compounds of which 14 were weighted, and the values are listed in Table 22. The standard deviation is 0.37 kcal/mol, which is comparable to the experimental errors for the same set of compounds.

As we mentioned before, there are two possible stable conformers of 2-vinylfuran with the vinyl group cis or trans to the oxygen. No experimental information is available on the conformational equilibrium. This equilibrium can be changed in the MM3 calculation by changing the 2-2-2-41 and 5-2-2-41 parameters. The 5-2-2-41 parameters occur in many compounds and were set in order to get the smallest standard deviation in the heat of formation calculations. The 2-2-2-41 parameters were chosen in part to fit the heat of formation of naphthol. The errors here may be considerable.

Table 28. MM3 Calculated Resonance Energies

compound	RE (kcal/mol)
vinyl alcohol	0.00
methyl vinyl ether	–0.87
ethyl vinyl ether	–0.87
divinyl ether	0.00
phenol	15.01
anisol	13.89
ethyl phenyl ether	13.92
phenyl vinyl ether	15.40
diphenyl ether	31.53
1-naphthol	23.81
3,4-dihydro-1,2-pyran	–1.38
1,4-dioxene	–5.39
p-dioxin	–8.00
1,3-butadienyl methyl ether	–1.00
dibenzo-*p*-dioxin	20.10
furan	12.88
2-vinylfuran	11.72
difuran	21.18
benzofuran	21.95
dibenzofuran	33.99

We were unable to fit in any reasonable way the heat of formation of 2-vinylfuran. Since this seems like quite an ordinary kind of molecule, one would expect that the calculated value for the heat of formation would be reasonably good. The experimental value was reported as long ago as 1929, and it is our suspicion that this value is simply less accurate than the experimentalists supposed (0.9 kcal/mol). Accordingly, we have weighted this compound 0 in the least-squares fitting.

Strain energies of these molecules may be calculated from the data in Table 23, which is in the supplementary material.

Vibrational Spectra. Vibrational spectra of vinyl alcohol, methyl vinyl ether, furan, and *p*-dioxin were calculated. The results are listed in Tables 24–27. (Table 27 is in the supplementary material.) The two open-chain compounds were fit to experiment reasonably well; however, the rms error of the difference between the calculated and experimental values for the cyclic compounds is quite large (average of 86 cm^{-1} for the four compounds). The experimental data used for the first three compounds are gas-phase values and those for *p*-dioxin are liquid-phase values.

The vibrational frequencies of the torsional motions related to the 5-2-2-5 parameter were calculated too high in all four compounds. In addition, we calculated the spectra of fluoroethylene and *cis*- and *trans*-difluoroethylene and found that the same problem exists. This problem was noticed earlier in the hydrocarbon calculations.[4,5] We could lower the V_2 term of the 5-2-2-5 parameter from the programmed value (11.5 kcal/mol) to fit the spectra better. However, if we use a smaller V_2 term, the rotational barrier of ethylene will be much lower than the experimental result, which is already too low by about 19 kcal/mol. This situation seems to be a consequence of the form of the torsional potential. Exploratory calculations have shown that the results for both the frequencies and the rotational barriers can be greatly improved by adding a 4-fold Fourier term to the torsional energy function. Some additional cross terms would also improve the situation, as was found earlier for hydrocarbons.

---

(37) Moore, W. J. *Physical Chemistry*, Fourth ed.; 1973; p 70.

(38) Cox, J. D. *Thermochemistry of Organic and Organometallic Compounds*; 1970.

(39) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermodynamic Data of Organic Compounds*, Second ed.; University of Sussex: Sussex, 1986.

(40) (a) Pedersen, T.; Larsen, N. W.; Nygaard, L. *J. Mol. Struct.* **1969**, *4*, 59. (b) Forest, H.; Dailey, B. P. *J. Chem. Phys.* **1966**, *45*, 1736. (c) Bist, H. D.; Williams, D. R. *Bull. Am. Phys. Soc.* **1966**, *11*, 826.

(41) Vincent, M. A.; Hillier, I. H. *Chem. Phys.* **1990**, *140*, 35.

(42) Ogata, T.; Kozima, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2344.

(43) McClellan, A. L. *Table of Experimental Dipole Moments*; 1974; Vol. 2.

(44) Larsen, N. W. *J. Mol. Struct.* **1979**, *51*, 175.

(45) Seip, H. M.; Seip, R. *Acta Chem. Scand.* **1973**, *27*, 4024.

(46) Dideberg, O.; Dupont, L.; Andre, J. M. *Acta Crystallogr.* **1972**, *B28*, 1002.

(47) Peixoto, E. M. A.; Iga, I.; Mu-Tao, L. *J. Chem. Res.* **1980**, *111*, 1864.

(48) Singh, P.; McKinney, J. D. *Acta Crystallogr.* **1978**, *B34*, 2956.

(49) Kunttu, H.; Dahlqvist, M.; Murto, J.; Rasanen, M. *J. Phys. Chem.* **1988**, *92*, 1495.

(50) Van Den Enden, L.; Geise, H. J. *J. Mol. Struct.* **1983**, *97*, 139.

These things are, however, beyond the boundaries of MM3 and will not be implemented now.

Resonance Energies. These are calculated as previously described.[5,55] Two parameters are needed, a value for a C–O (2–41) single bond as occurs in vinyl ether and a corresponding correction factor when there are two such bonds attached to a common oxygen as in divinyl ether. It is found that the best values for these quantities are –47.25 and –14.02 kcal/mol, respectively. When the resonance energies are calculated using these values, numbers are obtained as are shown in Table 28. Simple derivatives are seen to have resonance energies of zero, or approximately so. Phenol has a value of 15.01 kcal/mol, similar to benzene and to anisole. Extra conjugation, as in phenyl vinyl ether, gives essentially the same number, and diphenyl ether shows approximately twice that value. 1,4-Dioxene is interesting because it has a significant negative resonance energy (–5.39 kcal/mol). This results from putting too many electrons in the π system, and the number gets worse for *p*-dioxin (–8.00 kcal/mol). The value for furan is 12.88 kcal/mol, and the furan derivatives show resonance energies that are similar to what might have been expected.

Acknowledgment. The authors are indebted to Dr. Kuohsiang Chen for carrying out some of the calculations described in this work. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Supplementary Material Available: Tables 13–18, showing structural data, Table 23, showing strain energy data, and Table 27, showing spectral data, for compounds described herein (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(51) Cadioli, B.; Gallinella, E.; Pincelli, U. *J. Mol. Struct.* **1982**, *78*, 215.

(52) (a) Rico, M.; Barrachina, M.; Orza, J. M. *J. Mol. Spectrosc.* **1967**, *24*, 133. (b) Pouchan, C.; Raymond, J.; Sauvaitre, H.; Chaillet, M. *J. Mol. Struct.* **1974**, *21*, 253.

(53) Connett, J. E.; Creighton, J. A.; Green, J. H. S.; Kynaston, W. *Spectrochimica Acta* **1966**, *22*, 1859.

(54) Coppens, P. In *Topics in Current Physics, Neutron Diffraction*; Dachs, H., Ed.; Springer-Verlag: Berlin, 1978; p 71.

(55) Tai, J. C.; Yang, L.; Allinger, N. L. *J. Am. Chem. Soc.*, previous paper in this issue.