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A MOLECULAR MECHANICS STUDY OF METHYL VINYL ETHER AND RELATED COMPOUNDS

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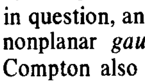
Abstract—Utilizing the known structures of methyl vinyl ether and a few related compounds including anisol and phenol, the MM2 force field has been extended so that structures of these compounds may be calculated. The energy differences between conformations and configurations for many related molecules have been examined, and on the whole these are well calculated in cases where they are known. Dipole moments and heats of formation were also studied.

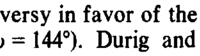
Molecular mechanics calculations have been developed to the point where they can be used to determine molecular structures and energies with an accuracy comparable with that available experimentally.[1] The present paper is concerned with the application of the molecular mechanics method to vinyl ethers and related compounds (enols, phenols, phenyl ethers).

The key compound in the vinyl ether series is methyl vinyl ether (I). The corresponding alcohol, vinyl alcohol (II), is in fact the enol form of acetaldehyde, to which it spontaneously is converted. The microwave spectrum of vinyl alcohol has been determined, and the moments of inertia are available for the major conformation.[2] The complete structure and the torsional potential have been determined by *ab initio* calculations.[3]

Methyl vinyl ether has been studied by many investigators over the years using a variety of techniques. It has long been known to exhibit internal rotation about the vinyl-oxygen bond, and to consist of an equilibrium mixture between two stable isomers. The more stable one was unequivocally determined to be the planar *s-cis* compound,[4–6] but until recently the structure of the second conformation has been the subject of controversy. Spectroscopic methods[4] suggested a *gauche* form, while electron diffraction investigations yielded contradictory results,[6] and older *ab initio* calculations[6–9] predicted a planar *s-trans* structure. Recently, accurate resolution of the torsional vibrations of the conformation by Durig and Compton[10] yielded the shape of the barrier in question, and resolved the controversy in favor of the nonplanar *gauche* conformation ($\omega = 144°$). Durig and Compton also determined the Me group rotational barriers for both conformations, which are significantly different.



I *cis*-0°



I *gauche*-144°

Some years ago we developed an extension of the MM1 force field to deal with vinyl ethers, but this was based on what is now known to be an erroneous structure for the *gauche* (then thought to be *trans*) conformation. Accordingly, we decided to update the earlier work within the context of the better force field (MM2) now available.[11,12] The present work was completed before the latest *ab initio* calculations were carried out on methyl vinyl ether[3] so we were not able to utilize that work.

The compounds examined in the present work include I–XIX.

Method

All calculations were carried out using the MM2 program described elsewhere.[12] The necessary unknown parameters were determined by the standard procedures.[13] Unfortunately, little is known experimentally of the structure of vinyl alcohol, and in particular the torsional function about the C–O bond is unknown. Phenol gives some information on the latter point, but not as much as is desired because of its higher symmetry. Only the barrier height is known for phenol.[14–16] In particular, we can evaluate only the V_2 coefficient for C_{sp^2}–C_{sp^2}–O–H linkage, but not that for H–C_{sp^2}–O–H. Similarly, the available data tells us the sum of the torsional terms C_{sp^2}–C_{sp^2}–O–C_{sp^3} and H–C_{sp^2}–O–C_{sp^3} linkages in methyl vinyl ether, but we cannot evaluate them independently. We could if we had an accurate barrier height for anisol (IV), which unfortunately is not available. The conformational preference of 1,2,3-trimethoxybenzene is known,[17,18] and can be used to place some limits on the way the coefficients are partitioned between the two functions.

It was desired to be able to calculate the heats of formation for vinyl ethers. All of the bond energy parameters needed are previously known, except that for the C–O bond of the vinyl ether type. Two relatively simple vinyl ethers have known heats of formation, ethyl vinyl ether, and dihydropyran.[19] The parameter was chosen so as to fit as well as possible these two experimental heats, however the error is somewhat large. When applied to anisol, the calculated heat of formation is 1.0 kcal/mol away from the experimental value, and

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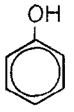
I methyl vinyl ether

$CH_3OCH=CH_2$

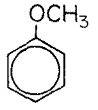
II vinyl alcohol

$CH_2=CHOH$

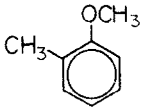
III phenol



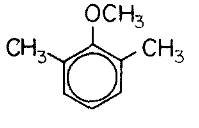
IV anisol



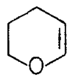
V *o*-methylanisol



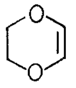
VI 2,6-dimethylanisol



VII 2,3-dihydropyran



VIII 1,4-dioxene



IX methyl 1-propenyl-ether-*cis*
X -*trans*

$CH_3CH=CHOCH_3$

XI 2-methoxybut-2-ene-*cis* (Z)
XII -*trans* (E)

$CH_3CH=CH(CH_3)OCH_3$

XIII ethyl vinyl ether

$CH_2=CHOCH_2CH_3$

XIV ethyl 1-propenyl ether-*cis*
XV -*trans*

$CH_3CH=CHOCH_2CH_3$

XVI 1,2-dimethoxyethylene-*cis*
XVII -*trans*

$CH_3OCH=CHOCH_3$

XVIII 1,2-dimethoxypropene-*cis*
XIX -*trans*

$CH_3O(CH_3)C=CHOCH_3$

this is probably the kind of accuracy that can be expected for these compounds.

For the calculation of the dipole moment we have one adjustable parameter, which is the C_{sp^2}–O bond moment. Our dipole moment calculation is based upon simple additivity of bond moments, and is not highly accurate. It is possible to calculate much better dipole moments within the framework of molecular mechanics, if induction is allowed for.[60] This can be done in principle, but the calculational scheme has not been worked into the molecular mechanics program at hand.

The bond moment for the bond in question was therefore chosen so as to reasonably well reproduce a variety of dipole moments including that of methyl vinyl ether, for which we calculate the value 1.10 D. The experimental values are 0.96 D in the gas phase (microwave),[5] or up to 1.35 D from dielectric constant measurements in solution.[20,21]

The new parameters developed for vinyl and aromatic ethers and alcohols are collected in Table 1. The remaining parameters used in the calculation but not given here are the standard MM2 ones.[11,12]

RESULTS AND DISCUSSION

Among the items examined in the present work were exact structures, rotational barriers, dipole moments, and heats of formation, and a number of equilibria between isomers and conformations. In some cases comparison with experiment is possible, in other cases the calculations yield predictions.

The calculated and experimental geometries of the more interesting and experimentally better studied compounds, I–IV, VII and VIII, are collected in Table 2, and the corresponding moments of inertia are given in Table 3. The latter are known from the microwave spectra for a few compounds and conformations. One usually expects that the calculated and experimental values will differ by up to 1%, due to the difference in the definition of bond lengths and angles in microwave spectroscopy from that in electron diffraction (on which our force field is based). Discrepancies larger than about 2% probably signal real errors in our calculated structures.

The calculated and experimental results pertaining to the inversion barriers for cyclic molecules VII and VIII are collected in Table 4, while the energy differences between the conformational and configurational isomers of methoxyethylenes IX–XIX can be found in Table 5. The results presented in the Tables 2–5 are discussed in some detail below.

The calculated and experimental values of the dipole moments are collected in Table 6. A comparison between them is difficult because the experimental data represent varying degrees of accuracy. Some of them were obtained by means of microwave spectra. They correspond to the gas state and are quite accurate. Others were measured in benzene solutions where solvation can play an important role. The results obtained are quite satisfactory for all but two compounds for which experimental data are available for comparison. The discrepancies (compounds IX and XIV) will be discussed below.

Too little is known about the heats of formation of vinyl and aromatic alcohols and ethers to enable parameterization of the usual accuracy and reliability. The calculated heats of formation for vinyl ethers are

Table 1. Extention of the 1977 force field for vinyl and aromatic ethers and alcohols[11,12]

Bond Stretching	l_0(Å)	k(mdyn/Å)	Bond moment (D)
$C_{sp^2}-C_{sp^2}$	1.337	9.60	0
$C_{sp^2}-O$	1.355	6.00	0
O-H	0.972	7.2	-0.7
Angle bending	Ø(degree)	k(mdyn/rad^2)	
$C_{sp^2}-C_{sp^2}-O$	124.3	0.70	
$H-C_{sp^2}-O$	116.4	0.54	
$C_{sp^3}-O-C_{sp^2}$	110.8	0.77	
$C_{sp^2}-O-H$	108.0	0.35	
LP-O-H	101.0	0.24	
$C_{sp^2}-O-LP$	103.26	0.35	
$O-C_{sp^2}-C_{sp^3}$	120.0	0.50	
Torsion	V_1	V_2	V_3 (kcal/mol)
$C_{sp^3}-C_{sp^2}-O-C_{sp^3}$	2.3	4.0	0
$C_{sp^2}-C_{sp^2}-O-LP$	0	0	0
$C_{sp^2}-C_{sp^2}-O-C_{sp^3}$	3.53	2.3	-3.53
$C_{sp^2}-C_{sp^2}-O-H$	2.0	1.7	-2.0
$H-C_{sp^3}-O-C_{sp^2}$	0	0	0.53
$H-C_{sp^2}-O-C_{sp^3}$	3.0	3.1	0
$H-C_{sp^2}-O-LP$	0	0	0
$H-C_{sp^2}-C_{sp^2}-O$	0	16.25	0
$C_{sp^3}-C_{sp^2}-C_{sp^2}-O$	-1.2	16.25	0
$C_{sp^2}-C_{sp^2}-C_{sp^2}-O$	0	16.25	0
$O-C_{sp^2}-C_{sp^2}-O$	-2.0	16.25	0
$H-C_{sp^2}-O-H$	2.94	1.50	-1.10
$C_{sp^3}-C_{sp^3}-O-C_{sp^2}$	0	0	0.4
$H-C_{sp^3}-C_{sp^2}-O$	0	0	0.54
Heat of Formation (kcal/mol)	Normal	Strainless	
$C_{sp^2}-O$	-20.14*	-18.12	
O-H (enol)	-27.20	-28.60	

* This value is given incorrectly in the original QCPE version of the program.

given in Table 7, together with the few known experimental values. The calculated values for these compounds are regarded as only approximate.

Methyl vinyl ether (I). Until recently the conformational equilibrium of I posed a significant problem. The available experimental data concerning the second stable conformation of the molecule were interpreted in terms of a nonplanar *gauche* structure, or a planar *s-trans* one.[2] The early *ab initio* calculations which involved optimization of several geometrical parameters indicated that the *s-trans* isomer was more stable than the *gauche*,[6–9] in disagreement with the recent experimental determination of the torsional function about the C-O bond.[10] Electron correlation must be included before the *gauche* conformation is calculated to be more stable, but the difference in energy between conformations is small.[3] As is well known, while small basis set calculations deal well with saturated hydrocarbons,[22] superficially similar molecules containing atoms with lone pairs, such as hydrogen peroxide, do not have their torsional functions reproduced at all well unless a sufficiently large basis set including polarization functions is used, and in this case it is necessary to include electron correlation as well. The available results do, however, raise doubts about the results of published calculations for methoxylated benzenes,[17] for which the experimental data concerning the second conformation are either lacking or unconvincing.

The calculated and experimental structural results for I are summarized in Table 2. The bond lengths and angles are all reproduced to within three standard deviations of the electron diffraction values. The largest errors are in the C-O bond lengths, of which the C_{sp^3}-O is not an adjustable quantity for the present work. The C_{sp^2}-O bond is purposely made to come out too long, so as to better fit the same bond in phenol, which comes out too short. This is a systematic difference between alcohols and ethers (between methyl alcohol and dimethyl ether, for example[24]) which is found experimentally, but cannot be reproduced using the parameters available in a force field of the present kind. To reproduce this experimental trend it would be necessary to use different natural bond lengths for alcohols and for ethers. While this could be done, and would yield better results, and economy of parameters has dictated that we forgo this refinement at present.

Table 2. The calculated and experimental bond lengths and angles for the molecules I-IV, VII and VIII

	I s-cis		I gauche		II		III		IV		VII	VIII	
	calc.	exp.[5]	calc.	exp.	calc.	exp.[2]	calc.	exp.[27b]	calc.	exp.[29]	calc.	calc.	exp.[38]
$C_{sp^2}-C_{sp^2}$	1.342	1.341	1.341	n.m.[c]	1.340	1.332 ass.	1.397- 1.402	1.391- 1.395	1.396- 1.406	1.398± 0.003	1.341	1.341	1.338± 0.010
$C_{sp^2}-C_{sp^3}$											1.503		
$C_{sp^2}-O$	1.368	1.360± 0.003	1.366	n.m.	1.359	1.373	1.362	1.374	1.372	1.361± 0.015	1.366	1.364	1.403± 0.016
$C_{sp^3}-O$	1.419	1.428± 0.003	1.420	n.m.					1.419	1.423± 0.015	1.423	1.422	1.400± 0.015
O-H					0.972	0.956 ass.	0.972	0.957					
$C_{sp^2}-C_{sp^2}-O$	128.6	127.7± 1.4	124.3	n.m.	124.4	126.0	121.3 121.1	121.1	125.2 118.6	n.r.[e]	125.6	123.6	123.4± 0.5
$C_{sp^2}-O-C_{sp^3}$	117.5	118.3± 1.1	114.7	n.m.					118.4	120.0± 2.0	115.5	112.9	
$C_{sp^2}-O-H$					108.8	108.87	108.9	108.9					
$C_{sp^2}-C_{sp^2}-O-C_{sp^3}$	0	0	141.9	144[10]					0		0.7	12.5	n.r.
$C_{sp^2}-C_{sp^2}-O-H$					0	0	0	0[d]					
twist angle											28.7	29.7	29.9± 1.5

[a] (The angle between the C=C and C-C bonds) see also Ref. 45.

[b] see also Ref. 14,15

[c] not measured. [d] Small out-of-plane distortions of $C_{sp^2}-C_{sp^2}-O-H$ angle were reported in Ref. 14 and 15.

[e] not reported.

Table 3. The calculated and experimental values of moments of inertia (in amÅ^2)

		I_A	I_B	I_C
Methyl vinyl ether I	calc.	27.380	82.272	106.290
s-cis	exp.[5,6a]	27.738	79.127	103.678
gauche	calc.	14.883	111.981	118.115
Vinyl alcohol s-cis II	calc.	8.835	47.108	55.943
	exp.[2]	8.475	47.875	56.396
Phenol III	calc.	89.067	196.025	285.091
	exp.[27]	89.439	192.789	282.228
Anisol IV	calc.	99.646	331.441	427.639
2,3-dihydropyran VII	calc.	98.033	106.372	186.668
1,4-dioxene VIII	calc.	89.777	101.344	177.448
	exp.[38]	88.754	101.770	176.475

Table 4. Barriers to interconversion for 2,3-dihydropyran VII and 1,4-dioxene VIII (in kcal/mol)

	VII		VIII	
Type of barrier	calc.	exp.	calc.	exp.
half-chair--bent	none found	7.6±0.6[40] 8.4[39] 6.6±0.3 ($\Delta G^{\ddagger}$)[42]	none found	7.64±0.6[40] 8.26[39] 7.62±0.15 (E_a)[43] 7.32±0.21 ($\Delta G^{\ddagger}$)[43]
to planarity	9.46	17.22±2.14[40] 16.7[39]	5.98	18.64±2.16[40] 19.5[39]

The moments of inertia for the *cis* isomer were also examined, as these can be compared with the experimental values. We note that I_A is calculated to have too small a value, while the other moments have calculated values which are too large, by about 3% (Table 3). Most of these errors are attributable to the C–O bond length, but we have chosen to accept this discrepancy for reasons explained earlier.

For rotation of the vinyl group about the C–O bond, we have matched the experimental data of Durig.[10] Taking the *cis* form to have a dihedral angle of 0°, and a relative energy of zero, our calculated values (with experimental values in parentheses) give energy minima for the *gauche* conformations at $\omega = 140°$ (144°) 1.07 kcal/mol (1.15), and the energy barriers come at values for the dihedral angles of *ca.* 60° and 180.0° with energy maxima of 5.94 (6.33) and 4.87 (5.07) kcal/mol, respectively.

Nothing is known experimentally about the geometry of the *gauche* isomer, except for the dihedral angle of the skeleton, which is reproduced adequately. The rotational barriers for the Me groups are known from the Raman work[10] to have the values 4.60 and 1.37 kcal/mol for the stable *cis* and *gauche* forms, respectively. Our calculated values are 4.41 and 2.61 kcal/mol. A similar conformational dependence of the magnitude of Me group rotational barriers was suggested previously for methyl vinyl ketone.[25]

The dipole moment and heat of formation data are summarized in Tables 6 and 7 respectively.

Vinyl alcohol (II). The only structural data available are the moments of inertia.[2] From these, with assumed values for some geometric parameters, a "structure" was derived. Our calculated structure is in reasonable agreement with the "experimental" one. The C–O bond length is calculated to be too short, as was previously discussed, and the C–C–O angle is calculated to be somewhat too small. The serious discrepancy between the calculated and observed moments of inertia lies in the value for I_A, which is with respect to an axis running approximately from the midpoint of the C–C bond through the midpoint of C–O bond. The small value for the C–C–O angle calculated tends to make this calculated moment too large. Again, the problem is to fit both the ether and the alcohol at the same time, and we have weighted the fit in the direction of the ether, since from a

Table 5. Strain energy differences in methoxyethylenes IX-XIX (in kcal/mol)

	ΔE *s-cis* → *gauche*		ΔE *cis* → *trans*[a]	
Molecule	calc.	exp.	calc.	exp.
IX	-3.51	n.m.[b]	0.17	0.1[45]
X	1.10	1.0±0.3[51]		
XI	1.23	n.m.	-1.93	ΔH=2.47[46], ΔG=1.46[46],-1.40[50c]
XII	-3.82	n.m.		
XIII	1.06	0.8±0.2[52] 0.85[53]		
XIV	-3.59	n.m.	0.28	ΔH=-.47[45]
XV	1.05	1.10±0.25[53]		
XVI			1.60	1.455±0.054[54]
XVII				
XVIII			.47	ΔH=-1.34[44], ΔG=-0.97[44]
XIX				

[a] The energy difference between Entgegen and Zusammen isomers in case of the tri-substituted double bond.

[b] n.m. not measured.

[c] Estimated on the basis of the K value reported in Ref. 50.

Table 6. Calculated and experimental dipole moments (Debyes)

Molecule	calc.	exp.
I	1.10	0.96±0.02[5] 1.05[59] 1.30[20] 1.35[21]
II	1.24	1.016±0.009[2]
III	1.24	1.224[14] 1.28[27] 1.50±0.04[50]
IV	1.10	1.30±0.03[55]
V	.84	1.0[53]
VI	1.09	n.m.[a] 1.32±0.02[56]
VII	1.36	1.38[57] 1.44[47]
VIII	0.76	0.939±0.008[38]
IX	0.90	1.30[48]
X	1.16	1.23[48]
XI	1.36	n.m.[a]
XII	1.09	n.m.
XIII	1.10	1.14[48]
XIV	0.90	1.40[48]
XV	1.16	n.m.
XVI	1.60	n.m.
XVII	1.18	n.m.
XVIII	1.76	n.m.
XIX	1.03	n.m.

[a] not measured

Table 7. Calculated and experimental heats of formation of vinyl and aromatic ethers (kcal/mol)

Compound			Compound		
	calc.	exp.		calc.	exp.
I	-24.73		XI	-38.15	
IV	-16.27	-17.27±0.93[61]	XII	-40.08	
V	-24.81		XIII	-31.86	-33.63±0.20[61]
VI	-31.14		XIV	-41.16	
VII	-31.67	-29.9±0.4[61]	XV	-40.88	
VIII	-36.08		XVI	-61.24	
IX	-32.89		XVII	-59.70	
X	-32.72		XVIII	-66.75	
			XIX	-67.21	

structural point of view the ethers are the more important group of compounds.

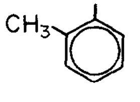
There is no experimental information on the other conformation in equilibrium with the *cis* isomer, or on the torsional potential function that interconnects the two. There are some fairly careful *ab initio* calculations on the subject, however.[3] The latter indicated that the other isomer was *trans*, not *gauche* as in the case of the ether. The energy of the *trans* isomer was calculated to be 1.8 kcal/mol above that of the *cis*, and the torsional barrier separating the two isomers is 4.3 kcal/mol high, measured from the *cis* isomer. This barrier occurred at a torsional angle of 87°. The molecular mechanics torsional parameters were chosen so as to reasonably reproduce this data, together with that on phenol (below). There are two torsional functions involved. In phenol there occurs only the C_{sp^2}–C_{sp^2}–O–H barrier, and the V_2 constant was chosen to reproduce this. In vinyl alcohol, there occurs in addition the atom sequence H–C_{sp^2}–O–H, and the potential here was chosen so as to reproduce both the energy difference between the isomers (calculated 1.8 kcal/mol), and the geometry (torsional angle 84°) and energy (4.3 kcal/mol) of the barrier.

The dipole moment calculated for this molecule depends not only on the value chosen for the C–O bond moment, but also on the value chosen for the H–O bond moment. The acidity of vinyl alcohols and phenols are in between those of ordinary alcohols and carboxylic acids. Hence the electron density about the hydroxylic proton should be much lower in this compound than it is in an ordinary alcohol. Not wanting to introduce an extra parameter set to deal with these compounds, we have chosen to treat the hydroxylic hydrogen of a vinyl alcohol as we treat the acidic proton of a carboxylic acid,[26] (except for the heat of formation parameter, or bond energy). The dipole moment calculated for vinyl alcohol then comes out in reasonable agreement with experiment.[1]

Phenol (III). An experimental structure is available from several studies.[14–16,27] The agreement of the calculations with experiment is reasonable, except that the C–O bond length is calculated to be too short, as explained above. The torsional barrier was fit as discussed earlier, and the calculated moments of inertia and dipole moment are satisfactory.

The stable form of phenol is planar, and the energy maximum occurs when the hydroxyl hydrogen has a dihedral angle of 90° with the ring. The experimental values for the barrier height are given as 3.29[15] to 3.40[14] and 3.47[16] kcal/mol. An old *ab initio* value is 5.15 kcal/mol.[28] Our value is 3.70 kcal/mol.

Anisol (IV). An electron diffraction study of IV[29] and a microwave study of the *p*-fluoro derivative[30] both yielded planar structures for the heavy atom skeleton, disproving a suggestion of nonplanarity based on Kerr constants.[31] Similarly, arguments in favor of a nonplanar arrangement on the basis of dipole moments[18] seem unacceptable. The calculations yielded a planar stable structure, with a broad maximum corresponding to a 90° dihedral angle between the ring and the OMe group. The experimental determination of the barrier height for rotation about the C_{sp^2}–O bond in anisol is complicated by the presence of the other rotational top in the molecule, and the values deduced differ considerably. The IR spectrum of the liquid yielded a value of 6 kcal/mol[32,33] for the barrier, while infrared intensity measurements gave 2.6 kcal/mol[34]. Seip and Seip[29] failed to reproduce the electron diffraction data using a simple two-fold barrier with values of 2.3 or 6 kcal/mol for V_2. A value of 3.6 kcal/mol was reported for the gas phase, but is probably inaccurate because of coupling of the torsional modes.[35] The largest reported value for the barrier was obtained from the Raman spectrum on the solid, and was 11.53 kcal/mol.[36] This value is difficult to compare with our calculated value of 1.88 kcal/mol, which refers to the isolated molecule. On the other hand, the calculated value for the barrier to rotation about the C_{sp^3}–O bond of 4.68 kcal/mol is close to that of the corresponding solid phase Raman value of 5.28 kcal/mol.[36]



Va

o-Methylanisol(V) *and* 2,6-*dimethylanisol*(VI). The calculations gave a planar structure (Va) for *ortho*-methylanisol, while a structure with the OMe group perpendicular to the ring was found for VI. These results are in accordance with experimental evidence. It is generally recognized that 2,6-disubstitution forces the OMe group out of the plane of the benzene ring, while one *ortho* substituent does not.[37]

2,3-*Dihydropyran* (VII) *and* 1,4-*dioxene* (VIII). The reported geometry of VIII was largely assumed by Wells and Malloy,[38] while no experimental structure for VII is available. A comparison of the C_{sp^2}–O and C_{sp^3}–O bond lengths for dioxene VIII with the corresponding experimental values for the molecules I–IV and the calculated values seems to indicate that the structure reported in Ref. 38 is of limited accuracy. The calculated and experimental values of the barriers for the ring inversion for VII and VIII are collected in Table 4. Two barriers to chair–chair interconversion of these rings were reported on the basis of Raman and IR spectra: a half-chair-to-bent form barrier, and a barrier to planarity.

We were not able to detect any metastable structure (postulated in Refs. 39 and 40) as the "bent" form. Moreover, the calculated values of the barriers to planarity for both molecules are much closer to the reported values of the half-chair-to-bent barriers than to the barriers ot planarity. The metastable form was not detected experimentally, but was postulated[39–41] from the shape of the torsional potential well of the half-chair form, and thus represents a large extrapolation of the actual experimental data. We believe that the experimental findings for the molecules VII and VIII could better be interpreted in terms of one barrier to interconversion, i.e. the barrier to planarity. Although our result for the barrier 2,3-dihydropyran may be too big (9.46) and that for dioxene may be too small (5.98 kcal/mol), we believe that the corresponding experimental errors are substantially underestimated in Refs. 39, 40, 42 and 43.

Methoxyethylenes (IX–XIX). These compounds exhibit simultaneously two types of isomerism, i.e. *cis–trans* (or *Z–E*) geometrical isomerism around the double bond, and rotational isomerism around the C_{sp^2}–O bond. Taskinen *et al.*[44–49] published a series of studies of vinyl ethers in which they analyzed *cis–trans* equilibria assuming the presence of a single rotational isomer for each configuration shown. The conformation was taken to be *s-cis* for the *E*-isomer, while for the *Z*-isomer, only in the case of bulky R_1 and R_3 substituents would R_1 take up a *gauche* conformation. Otherwise it would be anti to the double bond. The results of our calculations do not support these assumptions. For the compounds we studied, the *trans* (*E*) isomer in each case consisted of about 85/15 *s-cis*/*gauche* conformation, and no stable *s-trans* species was found. The *cis* (*Z*) isomer was calculated to have only one conformation, since the molecule cannot assume a planar *s-cis* structure. We found that this isomer has a preferred nonplanar *gauche* structure regardless of the nature of R_1 and R_3, while the Taskinen group advocated a planar *s-trans* conformation unless R_1 and R_3 were large. The argument[45] is based on the value of the entropy change for the interconversion IX $\rightleftharpoons$ X, which led them to conclude that the planar (i.e. *s-trans*) conformation was the second stable form here, as well as in the case of methyl vinyl ether I. This conclusion is, however, contrary to recent experimental data.[10] The energy differences between the *cis–trans* and *s-cis–gauche* structures for molecules IX–XIX are collected in Table 5. The agreement between the calculated and experimental findings is satisfactory for all but three results, namely the *cis–trans* energy differences between the isomeric 2-methoxybutenes XI and XII, the ethyl 1-propenyl ethers XIV and XV, and the 1,2-dimethoxypropenes XVIII and XIX. The assignments of the *E*/*Z*-structures to these molecules is questionable because of the similarity between the conformations, and a lack of a decisive criteria for their differentiation, such as proton–proton vicinal coupling constants through a double bond. This led Taskinen[46] and Benndorf *et al.*[50] to exactly opposite conclusions concerning the configurational assignments of the *E*- and *Z*-forms. We tested a wide variety of potential functions describing the C_{sp^3}–C_{sp^2}–O–C_{sp^3} torsional potential in the 2-methoxybutenes, but were unable to reproduce the Taskinen result. Therefore, we believe that the Benndorf groups conclusion is the correct one, and the *E*-isomer XI is less stable than the *Z* (XII).

cis (*Z*) *trans* (*E*)

A similar problem was encountered with the 1,2-dimethoxypropenes XVIII and XIX. We believe that also in this case Taskinen[44] reversed the conformational assignment and incorrectly assigned the *trans* compound (XIX) as the more stable one.

The value of -0.47 kcal/mol reported by Taskinen and Liukas[45] for the $E \rightarrow Z$ energy difference for ethylpropenyl ethers XIV, XV seems questionable too, because we expect this figure to be close to the corresponding value for the methyl ethers IX and X (experimental $+0.1$, calculated $+0.2$).

As discussed above, the accuracy of the calculated dipole moments is fairly good for all but two compounds, i.e. *cis*-alkoxypropenes $CH_3CH{=}CH(OR)$ IX ($R{=}CH_3$), and XIV ($R{=}C_2H_5$). Several reasons may account for this discrepancy. The first and the most important consists in the limitations of the calculational method used, which is based on additivity of bond moments. This approach is expected to be too crude to account for dipole moment changes induced by varying degrees of conjugation upon rotation about the O–C_{sp^3} bond. Another reason for the disagreement may be due to solvent effects, since the calculations refer to gaseous state while the experimental data were obtained for benzene solutions. Finally, the accuracy of the experimental determination of the dipole moments for IX and XIV[48] is probably low, since the moments were calculated on the basis of insufficient data obtained for mixtures of isomers in solution ($\mu = 1.296$ D for a mixture of 92.7% of IX and 7.3% of X and $\mu = 1.246$ D for a mixture of 19.7% of XIV and 80.3% of XV).

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