Conformational Analysis. CXI. The Calculation of the Structures and Energies of Disulfides by the Molecular Mechanics Method

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Abstract: A force field has been developed to permit molecular mechanics calculations on dialkyl disulfides. Application of the method to a determination of the structure of 5*H*,8*H*-dibenzo[*d*,*f*][1,2 dithiocin shows that the chair conformation is more stable than the tub form for the isolated molecule. The interactions leading to this conclusion are discussed. Calculations on the 1,2,4,5-tetrathiane ring system are presented, and the conformational equilibria and barriers are discussed. Comparison with experiment is made in all cases where data exist, and predictions are made in other cases.

Previous papers[1] have described a molecular mechanics or force field method for the calculation of the structures and energies of a variety of types of compounds, including simple organic molecules containing sulfur in the form of a thiol or thioether. The disulfides constitute another large class of sulfur-containing molecules which is of special importance because of its widespread occurrence in nature. From the structural point of view, these disulfides can be looked upon as the second-row analogue of the organic peroxides.

The general methods and most of the parameters used in the present work have been described previously.[1,2] Only a few parameters are needed to extend the previous work to disulfides and polysulfides; these quantities are listed in Table I.

The S-S bond stretching force constant and bending force constants for S-S-S and C_{sp^3}-S-S were taken directly from the literature.[3,4] We were not able to find experimental values for the deformation of the C_{sp^2}-C_{sp^3}-S angle, and hence the C_{sp^3}-C_{sp^3}-S bending force constant was used as an approximation. Torsional parameters for C_{sp^3}-S-S-S, C_{sp^2}-C_{sp^3}-S-S, and S-C_{sp^3}-C_{sp^3}-S were similarly unavailable, so there were approximated by the previously determined values[1b] for S-S-S-S, C_{sp^3}-C_{sp^3}-S-C_{sp^3}, and C_{sp^3}-C_{sp^3}-C_{sp^3}-S, respectively.

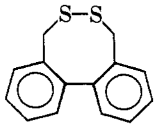
The exact nature of the barrier for C_{sp^3}-S-S-C_{sp^3} torsion is uncertain, although it has been extensively discussed. Experimental estimates[5] of the barrier to rotation for R-S-S-R vary somewhat depending on the experimental method used to obtain the data. Also, in most cases the cis and trans barriers were not individually identified although it is commonly believed a gauche form is the most stable. From calculated and observed data for the entropy and heat capacity of dimethyl disulfide, the barrier has been estimated to be 6.8 kcal/mol.[5a] A similar barrier height, 7.29 kcal/mol, has been obtained from infrared data.[5b] From Raman data the following somewhat larger barriers have been obtained: dimethyl disulfide,[5c] 9.5 kcal/mol; diethyl disulfide,[5d] 13.2 kcal/mol. An even larger barrier (cis barrier), 12.3 kcal/mol, has been estimated from NMR data.[5e] A study[5f] of the millimeter-wave rotational spectrum of H_2S_2 led to the conclusion that the barrier is very high, much higher than in H_2O_2 (cis barrier, 7.0 kcal/mol; trans barrier, 1.1 kcal/mol).[7a] We speculated that the cis barrier height should be somewhere around 10 kcal/mol, and the trans would be very close to 7 kcal/mol as found in ref 5a and 5b.

The barrier for R-S-S-R torsion has also been studied quite extensively by quantum mechanical calculations.[6] Most calculations predicted that the cis barrier would be higher than the trans, although the calculated quantities span quite a range, depending on the method used. It is worthy of mention here that Veillard and Demuynck[6b] have calculated, using the ab initio method, a cis barrier for H_2S_2 as high as 9.33 kcal/mol, being larger than the trans barrier by 3.34 kcal/mol.

Reviewing both the experimental and theoretical work available to us,[5,6] and noting the analogy with the more accurately known case of the peroxides,[7,8] we settled upon a barrier with the characteristics shown in Table I as our best choice for the experimental quantity, but note that there is considerable uncertainty here.[1,2] In general, a torsional barrier can be represented by a Fourier series expansion. In the present case, the observed curve cannot be fit with just a twofold term, but requires a minimum of two terms, a twofold and a threefold. These parameters give for dimethyl disulfide a twofold barrier with a cis barrier height of 10.6 kcal/mol and a trans barrier height of 7.0 kcal/mol, and they put the minimum in approximately the right place (Table II). According to our parameters, torsional strain is responsible for 86.2 and 99.0%, respectively, of the cis and trans barriers to rotation. Also note that the trans barrier height of 7.0 kcal/mol is in good agreement with those found from calorimetric data[5a] and from infrared data.[5b] The C-S bond was given a bond moment of 1.2 D with the negative end toward sulfur, obtained from earlier work using dimethyl sulfide as the model[1] (although the results are rather insensitive to this quantity).

Dimethyl disulfide,[9] allyl mercaptan,[10] cyclohexasulfur,[11] 1,3,5-trithiane,[12] and 3,3:6,6-bis(pentamethylene)-*S*-tetrathiane[18a] were used as model compounds from which to obtain, through trial and error, most of the necessary parameters. The experimental and calculated results for these compounds are summarized in Table II.

Having now the necessary force field to deal with disulfides, some problems of current interest involving such structures were examined. We first looked at the compound 5*H*,8*H*-dibenzo[*d*,*f*][1,2]dithiocin, an interesting disulfide whose x-ray structure has recently been reported[15] (see Table III).



5*H*,8*H*-dibenzo[*d*,*f*][1,2]dithiocin

Models show that there are two reasonable conforma-

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* University of Georgia.

Table I. Parameters for the Geometry Calculation

Bond	Bond Stretching l_0, Å	k, mdyn/Å
S–S	2.024	3.10

Angle	Angle Bending θ_0, deg	k, mdyn Å/rad^2
C_{sp^3}–S–S	102.9	1.168[3]
C_{sp^2}–C_{sp^3}–S	109.5	0.42
S–S–S	104.0	0.77[4]

Torsional Parameters

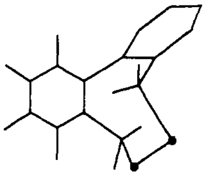
$$E_T = V_2(1 - \cos 2\theta)/2 + V_3(1 + \cos 3\theta)/2$$

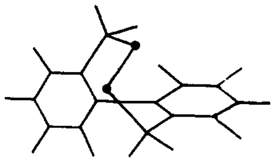
Dihedral angle	Torsional constants, kcal/mol V_2	 V_3
S–C_{sp^3}–C_{sp^2}–H		0.30
S–C_{sp^3}–C_{sp^2}–C_{sp^2}		0.30
C_{sp^2}–C_{sp^3}–S–S		1.45
S–C_{sp^3}–C_{sp^3}–S		1.45
S–C_{sp^3}–S–C_{sp^3}		1.45
H–C_{sp^3}–S–S		0.80
C_{sp^2}–C_{sp^3}–S–H		0.80
S–C_{sp^3}–S–S		0.80
C_{sp^3}–C_{sp^3}–S–S		0.80
C_{sp^3}–S–S–C_{sp^3}	−7.6	1.70
C_{sp^3}–S–S–S	−7.6	1.70
S–S–S–S	−7.6	1.70

tions for this compound; the central eight-membered ring can be either in a chair or tub conformation as shown.[17] They also show the dihedral angle at the S–S bond is about 60° in the chair and 90° in the tub. Since the observed dihedral angle in dimethyl disulfide is 84°, one might suppose that tub form would be the stable one. However, the chair

Table III. A Comparison of Experimental and Calculated Bond Lengths and Bond Angles for 5*H*,8*H*-Dibenzo[*d,f*] [1,2] dithiocin and Its Open-Chain Analogue, Dibenzyl Disulfide

Bond length (Å) or bond angle (deg)	Present work (calcd) Chair	 Tub	Wahl[15] (x ray) chair	Lee[16] (x ray) open chain
S–S	2.027	2.027	2.035 ± 0.001	2.029 ± 0.005
C–S	1.820	1.821	1.835 ± 0.003	1.840 ± 0.013
S–S–C	103.4	104.5	104.3 ± 0.1	102.9 ± 0.5
C–S–S–C	64.1	89.5	56.4 ± 0.2	92.1
ϕ–ϕ	69.5	88.9	67.2 ± 0.2	





was found in the crystal.[15] Of course crystal packing forces might change the order of stability of the conformations in the crystal, relative to the gas phase, but perhaps there is some other explanation which might be uncovered by detailed calculations.

The calculated steric energy and its components for both the chair and tub conformations are given in Table IV. We in fact calculate the chair conformation to be 1.34 kcal/mol lower in energy than the tub form, with most of this energy difference due to torsional interactions.

In looking more closely at the torsional interactions, one finds that the interactions about the central bond in C–S–S–C and S–S–C–H favor the tub form by 0.7 and 0.8 kcal/

Table II. A Comparison of Calculated and Observed Molecular Geometries, Energy Differences, and Dipole Moments

	Calcd, Å or deg	Obsd Å or deg	
	Dimethyl Disulfide	E.D.[9a]	M.W.[9b]
C–S	1.818	1.806 ± 0.002	1.810
S–S	2.030	2.022 ± 0.003	2.038
S–S–C_{sp^3}	103.7	104.1 ± 0.3	102.8
S–C_{sp^3}–H	107.5	106.5 ± 1.0	108.9
C_{sp^3}–S–S–C_{sp^3} (ω)[a]	83.2	83.9 ± 0.9	84.7
	Allyl Mercaptan		M.W.[10]
C–S	1.822		1.819
S–H	1.347		1.335
C_{sp^2}–C_{sp^3}–S	110.9		110.9
C_{sp^3}–S–H	96.3		96.5
C_{sp^2}–C_{sp^2}–C_{sp^3}–S (ω)[a]	120.0		124 ± 0.05
C_{sp^2}–C_{sp^3}–S–H (ω)[a]	57.5		50
	Cyclohexasulfur		X ray[11]
S–S	2.029		2.057 ± 0.018
S–S–S	102.2		102.2 ± 1.6
S–S–S–S	74.4		74.5 ± 2.5
	1,3,5-Trithiane		X ray[12]
S–C	1.810		1.818 ± 0.003
C_{sp^3}–S–C_{sp^3}	99.6		100.7 ± 0.5
S–C_{sp^3}–S	114.9		115.2 ± 0.5

Dimethyl disulfide (optimized geometries)	Calculated and experimental energies, kcal/mol E (calcd)	 ΔE (calcd)	 ΔE (obsd)[5,9b]
Gauche	−6.75	0.00	0.00
Anti	0.26	7.01	6 ~ 12 (?)
Eclipsed	3.85	10.60	
Gauche (H's on C eclipsed)	−5.58	1.17	1.6

Dipole moments	Calcd, D	Obsd, D
Dielectric constant (1.0)		
Dimethyl sulfide	1.57	1.56[13]
Dimethyl disulfide	1.74	1.90[14]

[a] (ω) indicates the dihedral angle about the central bond.

Table IV. Steric Energy and Its Components for the Chair and Tub Conformations of 5*H*,8*H*-Dibenzo[*d*,*f*] [1,2] dithiocin

Steric energy components	Steric energy, kcal/mol		ΔE (chair − tub)
	Chair	Tub	
van der Waals			
1,4 energy	7.13	7.30	0.17
Other	−2.66	−2.76	−0.10
Compression	0.48	0.40	−0.08
Bending	1.38	1.40	0.02
Stretch–bend	−0.02	0.06	0.08
Torsional	10.91	12.43	1.52
Torsion-bend	0.01	−0.25	−0.26
Dipole	0.66	0.66	0.00
Steric energy	17.89	19.23	1.34

mol respectively. On the other hand, torsion about the C–C–S–S bonds in the tub is about 2.5 kcal/mol higher, and that about the central bond connecting the two benzene rings is 0.5 kcal/mol higher than that found in the chair form. The remaining torsional interactions are similar. Thus we may conclude that the chair form should in fact be more stable than the tub, it is simply a matter of different torsional forces operating in different directions, and that is the predicted balance, which is consistent with what is found experimentally.

We next turn our attention to the 1,2,4,5-tetrathiane ring system, several derivatives of which have recently been studied.[18] By way of introduction, we might recall that cyclohexane exists preferentially in a chair conformation, and a "flexible form" constitutes the second stable conformation. The energy of the latter is 5-6 kcal/mol above that of the former. There is an energy barrier of about 10 kcal separating the two forms. The flexible form is calculated to be most stable in the twist conformation, which pseudorotates through a boat conformation to another twist, with the boat conformations being approximately 1.5 kcal in energy above the twist. This information is summarized in Table V, the energies given being those calculated from our current force field. Experimental values for these quantities are available with the exception of the twist-boat energy difference, and are similar to the calculated quantities.

By way of contrast, we may now look at the tetrathiane ring system. Because of the lower symmetry, more conformations need to be considered, and the necessary information is also summarized in Table V.

The relationship between the conformational characteristics of cyclohexane and tetrathiane is rather remote. First we note that the tetrathiane is also more stable in the chair form, but only by 1.1 kcal/mol. However, it is in the twist-boat manifold that the major contrast with cyclohexane occurs. In this case there are two (mirror image) energy minima in the manifold, as opposed to six for cyclohexane. There are also two maxima, and they are very large compared to those in cyclohexane. The less symmetrical twist form, which corresponds to an energy minimum in cyclohexane, and the less symmetrical boat, which corresponds to an energy maximum, are neither minima nor maxima in this case, but simply points on the side of the potential well. The extreme instability of the symmetrical boat form is noteworthy. It results, of course, because both of the disulfide linkages possess the unfavorable cis orientation in this conformation. The energy barrier which separates the chair from the twist conformation is larger than in cyclohexane, but not as large as the barrier which separates the two twist conformations from each other. Therefore, the twist-boat arrangement does not pseudorotate, but rather one twist form goes to the other by going back through the chair form.

While there appear to be no experimental conformational data on the above parent molecule, derivatives of this ring system have been studied fairly extensively,[18] and we can compare the calculated and experimental results available on some of these systems.

First, let us compare 1,1,4,4-tetramethylcyclohexane with cyclohexane itself. Note that there is an unfavorable repulsion between the axial methyls and the gauche methylene groups. This repulsion decreases the stability of the chair form, relative to cyclohexane, but has little influence on the twist form. The result is that the energy difference between the chair and the twist form becomes much less in the methylated cyclohexane than it was in cyclohexane itself. The methyl groups lead to a highly unfavorable interaction when they occupy the prow and stern positions in the symmetrical boat (Table V). The other conformations for the methylated cyclohexane have energies similar to those found for cyclohexane itself.

We might expect analogous effects from the methyl groups in 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane. Thus, the twist-boat energy difference should be significantly decreased relative to the unmethylated parent ring system. Since in the latter the chair was more stable by only 1.1 kcal/mol, it is not surprising that in this case the twist form becomes slightly more stable, by a calculated amount of 0.7 kcal/mol. Bushweller[18] has concluded from spectral studies that the twist form is more stable than the chair in this molecule by 0.4 kcal/mol. (This value was erroneously given as 0.8 kcal/mol in earlier papers, but has subsequently been corrected.) The interference of the methyl groups raises still higher the energy barrier corresponding to the symmetrical boat conformation. Bushweller's measurements[18] show that this conformation must have an energy of greater than 16.

Table V. Conformations and Energies (kcal/mol)

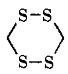
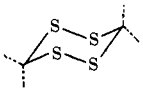
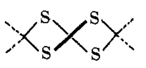
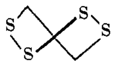
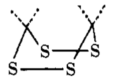
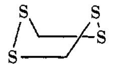
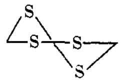
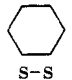
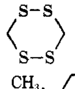
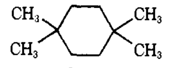
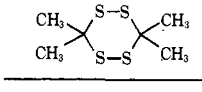
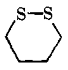
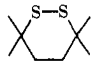
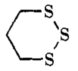
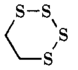
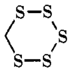
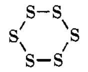
Compd	Chair	D_2 twist	C_2twist	C_{2v} boat	C_2 boat	$C_2^{\ddagger}$
						
	0.0	5.3	5.3	6.8	6.8	9.2
	0.0	1.1		18.9	4.5	14.2
	0.0	3.1		17.4	5.8	8.7
	0.7	0.0		31.7	4.5	15.6

Table VI. Conformations and Energies (kcal/mol) of Some Cyclic Polysulfides

Compd	Chair	Twist (symmetry)	Boat (symmetry)
	0.0	3.9 (C_2)	10.9 (C_S)
	0.0	2.4 (C_2)	22.5 (C_S)
	0.0		3.3 (C_S)
	0.0	7.5 (C_2)	14.7 (C_S)
	0.0	10.2 (C_2)	14.8 (C_2)
	0.0	18.4 (D_2)	19.7 (C_{2v})

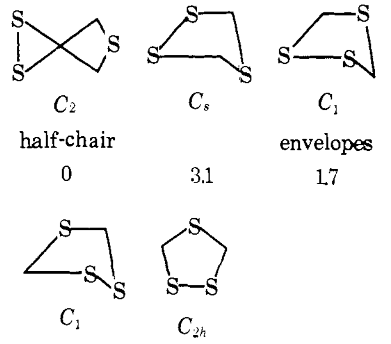
kcal/mol (because the molecule never reaches it), but he was unable to ascertain the true value. He also found experimentally that the twist-chair transformation ($\Delta G^{\ddagger}$) required 16 kcal/mol, while we calculate 15.6 kcal/mol. The correspondence between the calculated and observed values for the tetramethyltetrathiane is excellent, and the calculated values for the parent ring system can therefore be accepted with reasonable confidence.

The conformational characteristics of 1,2-dithiane are similar to those found in 1,2,3,4-tetrathiane. However, the chair form is now more stable than the twist form by 3.9 kcal/mol, more than three times that found in 1,2,3,4-tetrathiane. As expected, the introduction of four methyls to 1,2-dithiane at 3,4 positions decreases the twist-chair energy difference by 1.5 kcal/mol relative to the unmethylated ring system. The methyl groups again lead to a highly unfavorable interaction in the symmetrical boat form (C_s). The details of the calculations are summarized in Table VI. NMR measurements[5e] show that barriers ($\Delta G^{\ddagger}$) for the chair-chair transformation in 1,2-dithiane and 3,3,6,6-tetramethyl-1,2-dithiane are respectively 11.6 and 13.6 kcal/mol, while the calculated values are 11.7 and 13.4 kcal/mol.

The conformational characteristics of 1,2,3-trithiane are rather peculiar. Although the chair form is still the most stable, and there are two (mirror image) energy minima in the twist-boat manifold, the symmetrical twist form (C_2) is not an energy minimum, but rather is a point on the side of the potential well. The symmetrical boat form (C_s) corresponds to the energy minimum. This unusual fact results from the high torsional barrier at the *cis*-S-S- bond. The barrier for the chair-chair transformation is calculated to be 12.3 kcal/mol (experimental value,[19] 13.2 kcal/mol).

1,2,3,4-Tetrathiane, pentathiane, and cyclohexasulfur all have conformational characteristics similar to 1,2-dithiane. There are for each of these compounds two energy minima in the twist-boat manifold, with the symmetrical twist (C_2) being at the minimum and the chair form being the most stable conformation. The presence of additional sulfur atoms in the six-membered ring increases the energy difference between chair and twist forms. The twist-boat energy difference decreases in going from 1,2,3,4-tetrathiane by cyclohexasulfur, being 6.9 kcal/mol in 1,2,3,4-tetrathiane and 1.3 kcal/mol in cyclohexasulfur. NMR data show[18a] that the barrier for the chair-chair transformation in pentathiane should be greater than 15 kcal/mol. The actual value has not been obtained, while we calculate it to be 17.4 kcal/mol. The experimental values for the chair-chair inversion barriers for 1,2,3,4-tetrathiane and cyclohexasulfur are unavailable. The calculated values are 14.7 and 29.9 kcal/mol, respectively.

Finally, we would like to examine the 1,2,4-trithiolane ring structure which is of current interest. Tjan and coworkers[20] studied the alkyl derivatives of 1,2,4-trithiolane by NMR spectroscopy and suggested that these compounds exist as a mixture of two conformers showing pseudorotation with a barrier estimated to be smaller than 6 kcal/mol. Recently Guiman and co-workers[21] showed from studies by vibrational and photoelectron spectroscopy that 1,2,4-trithiolane exists only in the half-chair form with C_2 symmetry and about a 40° dihedral angle along the S-S bond.



Relative energies 0 3.1 1.7

Relative energies 0.3 4.5

Our calculations show that the C_2 conformation with a 45.9° dihedral angle along the S-S bond is the most stable, being favored over the C_s envelope form by 3.1 kcal mol^{-1}, which corresponds to the pseudorotational barrier between the C_2 forms.

Acknowledgment. The authors are indebted to the National Institute of Arthritis and Metabolic Diseases for support of this work (Grant AM-14042).

References and Notes

(1) (a) For paper CX, see A. Y. Meyer and N. L. Allinger, *Tetrahedron*, **31**, 1971 (1975); (b) N. L. Allinger and M. J. Hickey, *J. Am. Chem. Soc.*, **97**, 5167 (1975).
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Conformational Analysis. CXII. Conformations, Energies, and Electronic Absorption Spectra of α,β-Unsaturated Aldehydes and Ketones[1,2]

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Abstract: A previously described molecular mechanics method for the calculation of the structures and energies of hydrocarbons with delocalized electronic systems has been extended to include molecules containing a conjugated carbonyl group. In cases where a comparison with experimental data can be made, the agreement is good. Electronic spectra were calculated using a VESCF method including doubly excited states in the configuration interaction. The presence of two $\pi \rightarrow \pi^*$ transitions close to the observed absorption maxima, not found in calculations employing only singly excited states, is indicated by these calculations.

In previous papers a molecular mechanics method for the calculation of structures and energies of hydrocarbons with delocalized electronic systems was developed.[4,5] This method includes a quantum mechanical π system calculation (VESCF) in the iterative energy minimization sequence. The purpose of the VESCF calculation is to provide bond orders, from which the stretching and torsional force constants for the conjugated system are deduced. Calculations on a variety of conjugated hydrocarbons generally yielded structures and energies in good agreement with experimental data.

The Method

In the present paper is described an extension of the force field for delocalized hydrocarbon systems to include compounds containing a carbonyl group. Conformations and energies of α,β-unsaturated aldehydes and ketones will be discussed. Since there is a continued interest in the spectroscopic properties of these molecules,[6-8] we have also calculated their electronic spectra by the VESCF-Cl method,[5,9-11a] including all singly and doubly excited electronic configurations, and using geometries obtained from the force field calculations. The resonance and two-center repulsion integrals were calculated as described in ref 5.[11b]

Parameters. The basic force field used in the present work is essentially the same as previously described.[4,5] A number of new parameters, specific for the conjugated carbonyl system, were evaluated by fitting calculated values to experimental data. The data used in the parameterization were the electron diffraction structure of acrolein;[12,13] the cis-trans energy difference for acrolein,[14] 3-buten-2-one[15] (methyl vinyl ketone), and methacrolein;[16] and the barrier to internal rotation in acrolein.[14] The value for the cis-trans energy difference in methacrolein had to be taken from liquid-phase experiments, as a vapor-phase value is not available. A comparison of the cis-trans energy differences in 3-buten-2-one and *trans*-pent-3-en-2-one in solution and in the vapor phase suggests that the inconsistency is small.[15] The parameters involving the unsaturated carbonyl system are summarized in Table I.

Attempts to reproduce the barriers to methyl group rotation in 3-buten-2-one, methacrolein, and crotonaldehyde met with some difficulties. In previous work[17] it was found that no torsional contribution for eclipsing a methyl group hydrogen and a double bond was necessary to reproduce the barrier to methyl group rotation in propene and other simple (unconjugated) alkenes. However, using the same approach and numerical values for methacrolein, essentially free rotation of the methyl group was calculated. The experimental barrier is 1.34 ± 0.06 kcal/mol (microwave).[18] Similarly, the corresponding barrier in isoprene was calculated to be only about half of that experimentally observed.[19a] Logically, it would seem that the torsional constant for a methyl attached to an unsaturated carbon should not in general be a constant, but should be a function of the bond order. The torsional force constants for eclipsing pure single and double bonds, respectively, were therefore used to construct a linear relationship between bond order and torsional constant. The latter were then calculated from the former using this relationship for different molecules as needed.[19b] No new parameters were necessary. This approach gave barriers to methyl group rotation in isoprene, methacrolein, and crotonaldehyde of 2.88, 1.53, and 1.82 kcal/mol, respectively. The calculated values compare favorably with the experimental ones 2.62,[19a] 1.34,[18] and 1.73[20] kcal/mol, respectively. Satisfactory barriers were calculated for *cis*- and *trans*-1,3-pentadiene, 0.55 and 1.83 kcal/mol, respectively (experimental[21] 0.74 and 1.81 kcal/mol). Similar calculations on hydrocarbons were reported earlier by Dodziuk.[22] Since the bond orders at the α,β bond for the compounds considered in this paper are quite similar, a single value for the torsional contribution, $V_3 = 1.37$ kcal/mol (see Table I), was used, which corresponds to the bond order calculated for the central bond in acrolein. In the general case the calculation of the torsional parameter should be made part of the computer program. The same