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Nonbonded Attraction in Methyl Vinyl Ether

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Abstract: A detailed ab-initio investigation of the rotational surface of methyl vinyl ether shows that two stable isomers exist, the more "crowded" cisoid-staggered conformer being the structure of lowest energy. This conformational preference is in agreement with experimental results and can be understood in terms of a nonbonded attractive interactions between the methyl group and the double bond. Furthermore, the methyl rotational barriers in the cisoid and transoid conformations have been computed and their relative magnitudes can be also interpreted in terms of nonbonded interactions.

In our continuing studies of nonbonded interactions, we have investigated the conformational properties of the molecule methyl vinyl ether, $H_3COCH{=}CH_2$. This particular molecule was selected because it can serve as a prototype for the study of nonbonded attractive interactions and their influence upon molecular conformation. In this paper, the results of ab-initio calculations are reported and compared with experimental data. The computational results, in agreement with experimental evidence,[2] show that the most stable conformation of methyl vinyl ether is the one which a chemist might have dismissed on grounds of being "sterically" unfavorable. Subsequently, it is shown that this conformational preference can be understood in terms of a qualitative MO analysis based upon the ideas developed by one of the authors[3-5] and that these ideas are in full accord with the computational data.

Ab-Initio Calculations

In order to study the conformational properties of methyl vinyl ether two rotational motions have to be investigated (see Figure 1), i.e., rotation around the C_1–O bond (described here in terms of the torsional angle θ) and rotation around the O–C_2 bond (described in terms of the torsional angle Φ). The zero values of the two torsional angles correspond to the cisoid-eclipsed (CE) conformation. The computations were performed with the GAUSSIAN 70 series of programs[6] at two different levels of sophistication. We first made a detailed study of these two rotational motions with a STO-3G[7] basis set. These computations were carried out for various values of the angle Φ (Φ = 0, 45, 90, 120, 135, 155, and 180°) and at each Φ for various values of the angle θ (θ = 0, 30, 60, and 100°). At this computational level the following bond angles and bond lengths were kept constant (see Figure 1): $\angle HC_1H = 109.5°$; $\angle HC_3H = 120°$; $r(C_3\text{–}H) = r(C_2\text{–}H) = 1.07$ Å; and $r(C_1\text{–}H) = 1.09$ Å. The remaining parameters were first optimized in the TE conformation, where important nonbonded interactions are absent, in the following order: (a) $\angle OC_2C_3$; (b) $\angle C_1OC_2$; (c) $r(C_2\text{–}C_3)$; (d) $r(C_2\text{–}O)$; (e) $\angle C_2C_3H$; and (f) $r(O\text{–}C_1)$. Furthermore, for the various conformations investigated, the following parameters were reoptimized: (i) $\angle OC_2C_3$ and $\angle C_2OC_1$ for all the conformations with θ = 0 and 60°; (ii) $\angle C_2OC_1$ for all the conformations with θ = 30 and 100° because $\angle OC_2C_3$ was found to have, in all cases, almost identical values at θ = 0 and 60° (in the computations at θ = 30° $\angle C_3C_2O$ was kept at the value obtained at θ = 0°, while for θ = 100° at the value obtained at θ = 60°); (iii) $r(C_2\text{–}O)$ for the conformations with θ = 0° (for all the conformations with the same Φ, $r(C_2\text{–}O)$ was kept fixed at the value obtained at θ = 0°).

In order to obtain more accurate estimates of the energy differences of interest, we carried out calculations for the conformations listed in Table I using a 4-31G basis set.[8] In the first stage we used the geometries optimized at the STO-3G level and these results are shown in Table I. In the second stage we reoptimized at the 4-31G level certain geometrical parameters which, on the basis of the STO-3G computations, appear to affect the energy the most, i.e., $r(O\text{–}C_2)$, $\angle OC_2C_3$, $\angle C_1OC_2$, and $\angle H_cC_1O$. The corresponding values, together with the total energies, are listed in Table II.

The potential energy curves for rotation about the O–C_2 bond, determined at the STO-3G and 4-31G levels, are shown in Figure 2. Here, we report only one curve at the 4-31G level, since the relative energies with and without geometry reoptimization are almost identical. The two curves at the STO-3G and 4-31G levels are very similar and predict that only two stable isomers exist: the CS (Φ = 0°) and TS (Φ = 180°) conformations. In both cases the planar CS conformer is the most stable isomer. The experimental studies[2] have suggested the existence of two rotamers of methyl vinyl ether with the more stable isomer having a planar cis conformation in accord with the ab initio result. However, there is some disagreement between the theoretical and experimental results about the structure of the less stable rotamer. Electron diffraction data[2c] suggest that it has a nonplanar heavy-atom skeleton with Φ in the range 80–110°, while the present computational results indicate a planar transoid form (Φ = 180°). It must be emphasized that this latter result has been obtained after a sophisticated geometry optimization. On the other hand, various assumptions were made in the least-squares refinement of the structural

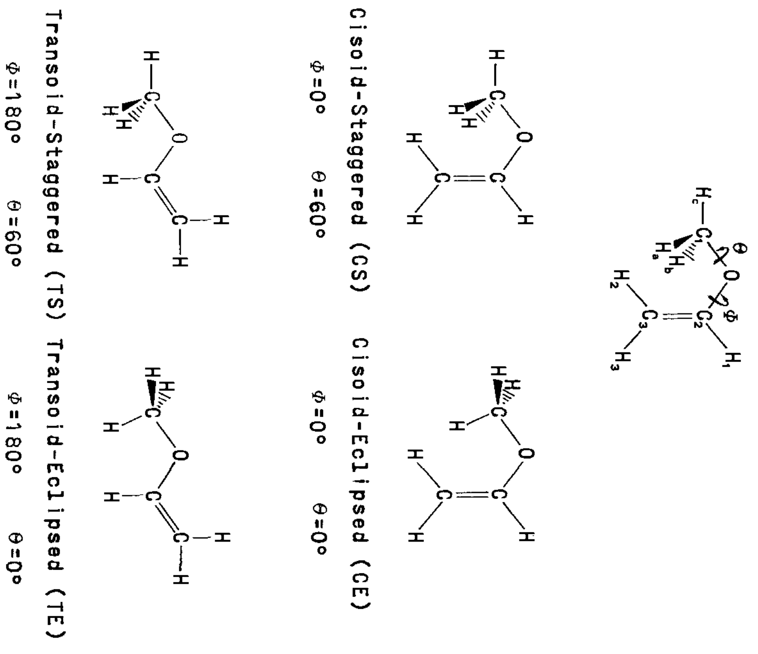


Figure 1. Reference system and conformations of methyl vinyl ether.

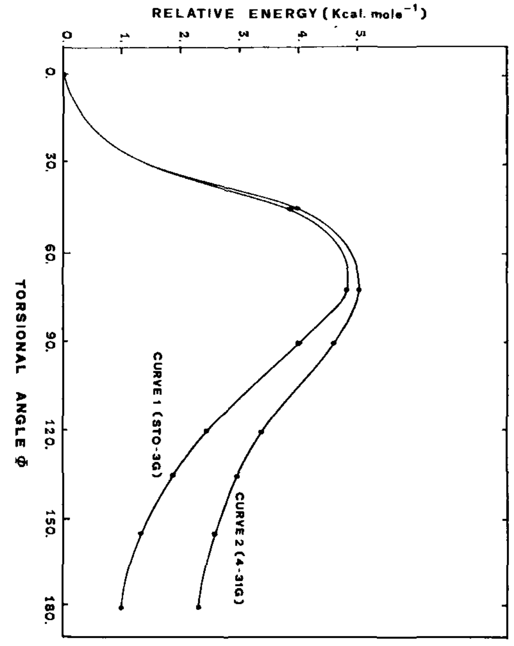


Figure 2. Minimal path for vinyl rotation.

parameters obtained by electron diffraction, the most severe being that the bond angles and bond distances were the same in the two rotamers. The present computations show, instead, that the cisoid rotamer has geometric parameters which differ significantly from those of a second isomer with $\Phi \geq 90°$. As a result of the present detailed optimization, reasonable values of the various geometric parameters have now become available for various conformations of interest and it seems reasonable to suggest a reexamination of the experimental data. In this connection, it should be pointed out that it is conceivable that the second stable isomer is indeed the one suggested by Owen and Seip[2c] because this geometry is stabilized by a hyperconjugative interaction between the π ethylenic system and the C_1-O bond.

Table III compares the theoretical and experimental results while the computational details are given in Table IV. It must be noticed again that, while the rotational barrier of the methyl group computed at the STO-3G level agrees

Table I. Geometrical Parameters[a] for Various Conformations of Methyl Vinyl Ether Computed at the STO-3G Level, Together with the Corresponding Energies Computed at the STO-3G and 4-31G Levels

	($\Phi = 0°, \theta = 60°$)	($\Phi = 45°, \theta = 49, 47°$)	($\Phi = 72.46°, \theta = 60°$)	($\Phi = 90°, \theta = 60°$)	($\Phi = 120°, \theta = 60°$)	($\Phi = 135°, \theta = 60°$)	($\Phi = 155°, \theta = 60°$)	($\Phi = 180°, \theta = 60°$)
$r(C_1-O)$	1.4371	1.4431[b]	1.4431[b]	1.4446	1.4427	1.4432	1.4413	1.4431[b]
$r(O-C_2)$	1.3924	1.4054	1.4060	1.4114	1.4058	1.4042	1.4007	1.3950[b]
$r(C_2-C_3)$	1.3148	1.3153[b]	1.3153[b]	1.3111	1.3121	1.3112	1.3116	1.3153[b]
$\angle C_1OC_2$	113.99	112.62	110.74	109.69	109.54	110.02	110.94	111.77
$\angle OC_2C_3$	129.09	127.56	124.75	123.46	122.38	122.08	121.52	121.19
$\angle H_1C_2C_3$	121.63	121.99[b]	121.99[b]	121.78	122.04	122.02	122.03	121.99[b]
$\angle C_2C_3H_2$	122.96	120.00[c]	120.00[c]	121.69	121.27	121.58	121.58	121.26
$\angle H_2C_3H_3$	115.49	120.00[c]	120.00[c]	116.75	116.73	117.10	117.23	117.07
Tilt angle[d]	−3.79[e]	0[c]	0[c]	1.60[f]	1.48[f]	1.39[f]	1.45[f]	−3.31[e]
Total energy (STO-3G)	−189.496 28	−189.489 95	−189.488 59	−189.489 87	−189.492 27	−189.493 33	−189.494 10	−189.494 75
Total energy (4-31G)	−191.633 86	−191.627 47	−191.625 85	−191.626 56	−191.628 44	−191.629 09	−191.629 57	−191.630 15
Nuclear energy	121.181 56	120.611 02	120.385 93	119.986 92	119.566 21	119.350 61	119.207 77	119.055 53

[a] Bond lengths in Å and angles in deg. [b] Optimized for the TE conformation at the STO-3G level (see Table III). [c] Not optimized. [d] Tilt angle of the local threefold axis of the methyl group to the CO bond. [e] Tilt angle optimized in the H_cC_1O plane (a positive tilt corresponds to a H_cC_1O angle > 109.5°). [f] Tilt angle optimized in the H_aC_1O angle > 109.5°).

Table II. Geometrical Parameters[a] and Total Energies (au) Computed at the 4-31G Level

	($\Phi = 0°, \theta = 60°$)	($\Phi = 90°, \theta = 60°$)	($\Phi = 120°, \theta = 60°$)	($\Phi = 135°, \theta = 60°$)	($\Phi = 155°, \theta = 60°$)	($\Phi = 180°, \theta = 60°$)
$r(O-C_2)$	1.3748	1.3935	1.3885	1.3863	1.3840	1.3830
$\angle OC_2C_3$	128.69	123.55	122.85	122.77	122.51	122.32
$\angle C_1OC_2$	119.85	116.75	116.20	116.48	117.19	117.88
Tilt angle[b]	−3.35[c]	1.62[d]	1.56[d]	1.48[d]	1.45[d]	−3.31[c]
Total energy	−191.636 02	−191.628 92	−191.630 57	−191.631 21	−191.631 65	−191.632 08

[a] Bond lengths in Å and angles in deg. [b] Tilt angle of the local threefold axis of the methyl group to the C–O bond. [c] Tilt angle optimized in the H_cC_1O plane. [d] Tilt angle optimized in the H_aC_1O plane.

Table III. Cisoid–Transoid Energy Differences and Methyl Rotational Barrier for Methyl Vinyl Ether

Transformation	Exptl, kcal/mol	STO-3G, kcal/mol	4-31G, kcal/mol
TS–CS	1.15 ± 0.25[a,b]	0.96	2.47
CE–TE		1.34	−0.40
CE–CS	3.83 ± 0.1[b]	4.14	2.97
TE–TS		1.84	0.89

[a] Experimental energy difference between the two isomers. [b] See ref 21b.

well with the experimental value, the agreement is poorer for the value computed at the 4-31G level.

Several aspects of the computational results listed in Tables I, II, and IV are of interest. (i) Recalling that the ethylenic C-C bond length computed with the same basis set is 1.306 Å[9] we find that the corresponding C-C bond lengths in the various conformations of methyl vinyl ether are all larger than the ethylene value. (ii) The agreement between the values of the geometrical parameters computed at the minimal and extended levels is quite good, except for the $\angle C_1OC_2$ angle, whose value increases significantly going from the STO-3G to the 4-31G basis set. However, this increase, 6-7°, is less than that of the ∠HOH angle in H_2O for the same change of basis sets (10°).[10] (iii) The value of the $O-C_2$ bond length is not significantly altered during rotation.

A comment regarding the reliability of the basis set is necessary. Specifically, Pople and co-workers[11] have found that methyl rotation barriers are well reproduced by the basis sets used in our work. However, it is true that in cases involving a small barrier, like the CE-TE barrier, a basis set dependence may be manifested. It would be interesting to see how other good quality basis sets work in such cases.[12]

Nonbonded Attractions in Methyl Vinyl Ether

In this section we shall trace the key factors dictating the unexpected conformational preference of methyl vinyl ether.

Since "steric effects" should favor a trans conformation, the comparative discussion will involve the CS and TS conformations. The analysis presented here is based on a qualitative MO approach and involves the following steps: (a) sequential dissection of the molecule under consideration into component fragments; (b) construction of the group MO's of each fragment by means of one-electron MO (OEMO) theory or explicit calculations; (c) examination of the key group orbital interactions which obtain in the course of the union of the component fragments to yield the composite system in a specified geometry.

In the course of our analysis, we shall make use of the following general results of one-electron MO theory.

(a) The interaction of a doubly occupied MO, ϕ_i, with a vacant MO, ϕ_j, leads to two-electron stabilization which is inversely proportional to the energy separation of the two MO's, $E_i - E_j$, and directly proportional to the square of their overlap integral, S_{ij}. This is a well-known result of perturbation theory[13] and the approximations involved in its derivation are valid for the systems studied in this work.[14] The algebraic expression for the two-electron stabilization is given below:

$$\Delta E_{ij}^2 = S_{ij}^2(K - E_i)^2/(E_i - E_j) \qquad (1)$$

(b) The interaction of two doubly occupied MO's, ϕ_i and ϕ_j, leads to net four-electron destabilization which increases as the overlap integral of the two MO's, S_{ij}, and the mean of their energies, $(E_i + E_j)/2$, increase.[15] This result is obtained by application of the variational method to the case of a two-orbital four-electron interaction and involves no additional assumptions other than the usual approximation of the interaction matrix element as a linear function of the overlap integral. The algebraic expression for the four-electron destabilization is given below:

$$\Delta E_{ij}^4 = \frac{4S_{ij}^2}{1 - S_{ij}^2}(E_0 - K) \qquad (2)$$

where E_0 is the mean of the energies of the ϕ_i and ϕ_j MO's before mixing.

Methyl vinyl ether can be dissected into fragments A and B. In turn, fragment B can be further dissected into the elementary fragments B_a and B_b, the wave functions of which are known. This kind of "theoretical surgery" is shown below.

We first proceed to construct the π MO's of fragment B from the π MO's of the methyl group (fragment B_a) and the double bond (fragment B_b). Figure 3 depicts the inter-

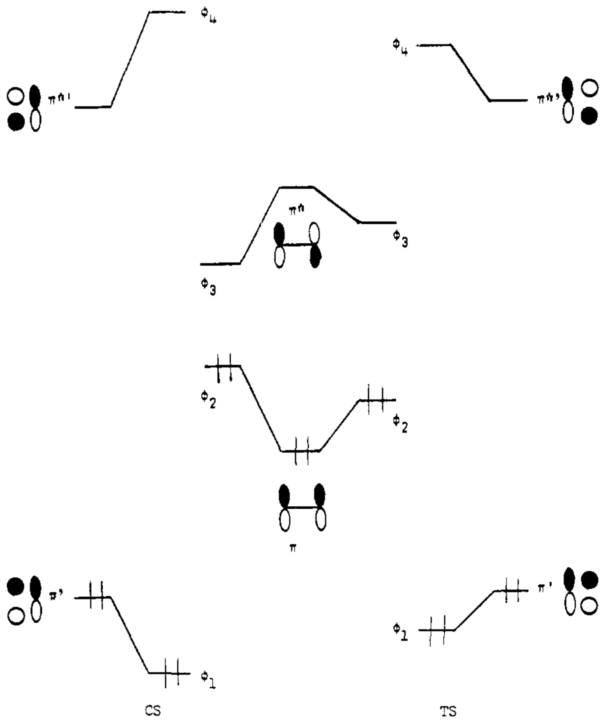


Figure 3. Interaction diagram of the $B_a + B_b$ union in a CS and TS conformation.

Table IV. Geometrical Parameters[a] and Energies (au) Computed at the STO-3G and 4-31G Levels

	CE		TE	
	STO-3G	4-31G	STO-3G	4-31G
$r(C_1-O)$	1.4371	(1.4371)	1.4431	(1.4431)
$r(O-C_2)$	1.3924	1.3769	1.3950	1.3811
$r(C_2-C_3)$	1.3148	(1.3148)	1.3153	(1.3153)
$\angle C_1OC_2$	117.27	123.19	113.97	119.94
$\angle OC_2C_3$	131.81	130.54	121.07	122.26
$\angle H_1C_2C_3$	121.63	(121.63)	121.99	(121.99)
$\angle C_2C_3H_2$	122.96	(122.96)	121.26	(121.26)
$\angle H_2C_3H_3$	115.49	(115.49)	117.07	(117.07)
Tilt angle[b]	−4.51	−3.06	−2.64	−1.86
Total energy	−189.489 68 (−191.628 68)[c]	−191.631 29	−189.491 81 (−191.628 44)[c]	−191.630 65
Nuclear energy	120.374 36	120.074 87	118.858 42	118.546 35

[a] Bond lengths in Å and bond angles in deg. [b] Tilt angle of the local threefold axis of the methyl group to the C−O bond computed in the H_cC_1O plane. [c] Energy value computed at the 4-31G level with the geometry optimized at the STO-3G level.

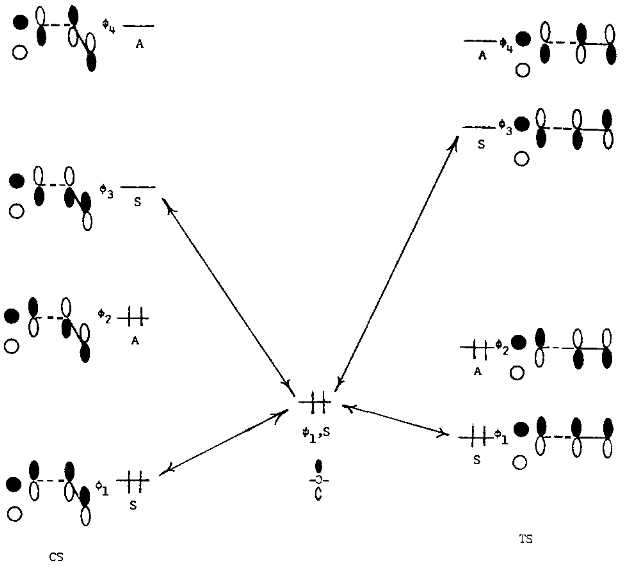
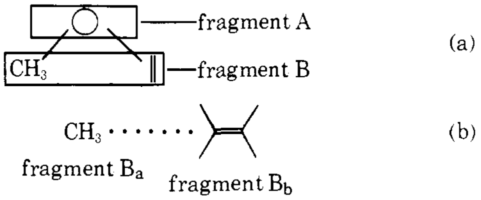


Figure 4. Interaction diagram of the A + B union for the CS and TS conformation of methyl vinyl ether. Arrows indicate the dominant orbital interactions. Symmetry labels refer to the pseudosymmetry of the $B_a + B_b$ MO's.



actions between the π type MO's of the methyl group and the π MO's of the double bond. The key difference between the two conformations CS and TS is that in the former case the two 1s AO's of the methyl hydrogens H_a and H_b can overlap with the $2p_z$ AO of the outer olefinic carbon, while in the latter case they cannot. On the basis of the general principles outlined before, we predict that the two-electron stabilization resulting from the $\pi'-\pi^*$ and $\pi-\pi^{*\prime}$ interactions will favor the TS conformation since the appropriate MO overlap integrals are greater for the TS than the CS conformer. Similarly, the four-electron destabilization arising from the $\pi-\pi'$ interaction will also favor the TS conformation since $S_{\pi\pi'}(\mathrm{CS}) > S_{\pi\pi'}(\mathrm{TS})$.

Once we have examined the energetics of the MO interactions which obtain in the course of the union of the π systems of the methyl group and the double bond, we return to the interaction diagram of Figure 3 in order to make certain observations about the π MO's of fragment B. Specifically, it can be seen that, as a result of the orbital interaction pattern discussed before, the energies of the various π MO's of fragment B vary as follows, depending upon the geometry of union.

Table V. π Bond Orders of the CS and TS Conformations of Methyl Vinyl Ether

Atom pair	Predicted π bonding in CS relative to TS	π bond orders (STO-3G)[a]	
		CS conformation	TS conformation
$H_{ab}-C_1$	−	0.9628	0.9653
$H_{ab}-O$	−	0.3929	0.3998
$H_{ab}-C_2$	−	−0.0583	−0.0424
$H_{ab}-C_3$	+	0.1105	0.0932
C_1-O	+	0.0541	0.0447
C_1-C_2	+	−0.0520	−0.0377
C_1-C_3	−	−0.0404	−0.0333
$O-C_2$	+	0.1736	0.1485
$O-C_3$	−	−0.3731	−0.3672
C_2-C_3	−	0.7655	0.7732

[a] Optimized geometries.

$$E_1(\mathrm{CS}) < E_1(\mathrm{TS})$$

$$E_2(\mathrm{CS}) > \mathrm{E}_2(\mathrm{TS})$$

$$E_3(\mathrm{CS}) < E_3(\mathrm{TS})$$

$$E_4(\mathrm{CS}) > E_4(\mathrm{TS})$$

This pattern is not surprising to the theoretical organic chemist since it reflects nothing more than the fact that the CS conformation resembles an antiaromatic structure and the TS conformation a nonaromatic structure. The changes in the energies of the π MO's which accompany the TS → CS transformation are characteristic of the changes in the energies of the π MO's accompanying nonaromatic → antiaromatic transformation.

We are now prepared to consider the construction of the composite system of methyl vinyl ether from the π system of fragment B and the oxygen lone pair AO. The orbital interactions which obtain in this union are depicted in Figure 4. On the basis of the principles outlined before, we can determine that the $\psi_1-\phi_3$ interaction is more destabilizing in the TS conformation. This four-electron destabilization which favors the CS conformation in the A + B union will more than compensate for the four-electron destabilization term which favors the TS conformation in the $B_a + B_b$ union since we expect that the overlap integral $S(\psi_1\phi_1)$ will

Table VI. π-Overlap Populations for the Various Conformations of Methyl Vinyl Ether

Atom pair	CS		CE		TS		TE	
	STO-3G	4-31G	STO-3G	4-31G	STO-3G	4-31G	STO-3G	4-31G
(1) $H_{ab}-C_1$	0.3667	0.3737	0.3689	0.3857	0.3677	0.3801	0.3684	0.3827
(2) $H_{ab}-O$	−0.0119	−0.0366	−0.0128	−0.0343	−0.0119	−0.0362	−0.0127	−0.0373
(3) $H_{ab}-C_2$	−0.0010	0.0013	−0.0004	−0.0008	−0.0008	0.0014	0.0003	0.0000
(4) $H_{ab}-C_3$	0.0014	0.0057	0.0001	0.0004	0.0001	0.0004	0.0000	0.0002
(5) C_1-O	0.0077	−0.0029	0.0044	−0.0182	0.0064	−0.0048	0.0051	−0.0101
(6) C_1-C_2	−0.0016	−0.0058	−0.0008	−0.0008	−0.0011	−0.0038	−0.0008	−0.0020
(7) C_1-C_3	−0.0004	−0.0018	0.0000	0.0008	0.0000	−0.0003	0.0000	0.0000
(8) $O-C_2$	0.0247	0.0077	0.0248	0.0037	0.0211	−0.0044	0.0218	−0.0042
(9) $O-C_3$	−0.0039	−0.0177	−0.0037	−0.0179	−0.0048	−0.0197	−0.0049	−0.0207
(10) C_2-C_3	0.1899	0.2526	0.1897	0.2535	0.1915	0.2577	0.1909	0.2573
Total π-overlap population	0.5716	0.5803	0.5702	0.5721	0.5682	0.5704	0.5675	0.5659

be much larger in the case of A + B union relative to the $S(\pi\pi')$ overlap integral in the $B_a + B_b$ union. Furthermore, the two-electron stabilizing term which favors the TS conformation in the $B_a + B_b$ union will be dominated by the two-electron stabilizing term which favors the CS conformation in the A + B union because of a larger MO overlap integral and a smaller energy difference between the interacting orbitals. In general, the four-electron destabilization of the first union favoring the least crowded structure will tend to be counteracted by the four-electron destabilization of the second union which favors the more crowded structure. As a result, the relative two-electron stabilization which is greater in the second union than in the first union will favor a greater overall stabilization of the more crowded structure.

The previous analysis focused upon the energetics of changes which accompany the union of two fragments in a specified geometry, i.e., it was an "energy approach". Further insights are gained by adopting a "charge transfer approach". In this case, conceptual simplicity can be achieved by using perturbation theory with neglect of overlap. This approach and the principles involved have been discussed in our previous work.[3a]

Neglect of overlap will automatically eliminate the effects of four-electron repulsive interactions upon bonding. However, we have already seen that overlap repulsion may favor the more "crowded" conformer relative to a "uncrowded" geometry. Hence, one does not lose essential information by neglecting overlap in the "charge transfer approach".

In the "charge transfer" approach, we are concerned with the bonding changes which occur in the two conformations, CS and TS, as a result of the ψ_1–ϕ_3 stabilizing interaction which gives rise to charge transfer from ψ_1 to ϕ_3. From the nodal properties of ϕ_3, it can be seen that charge transfer will increase bonding between the 1s AO's of H_a and H_b and the $2p_z$ AO of the outer carbon. Furthermore, the increase in the $H_{a,b}(1s)$–$C_3(2p_z)$ bond order will be greater for the CS than the TS conformation because the $O(2p_z)$–ϕ_3 interaction is stronger in the former case. In addition, orbital overlap between the AO's is appreciable in the CS and zero in the TS conformation, e.g., the positive $H_{a,b}(1s)$–$C_3(2p_z)$ bond order is felt only in the CS conformation. Hence, we can say that there is an attractive nonbonded 1,5 interaction which favors the CS over the TS conformation.

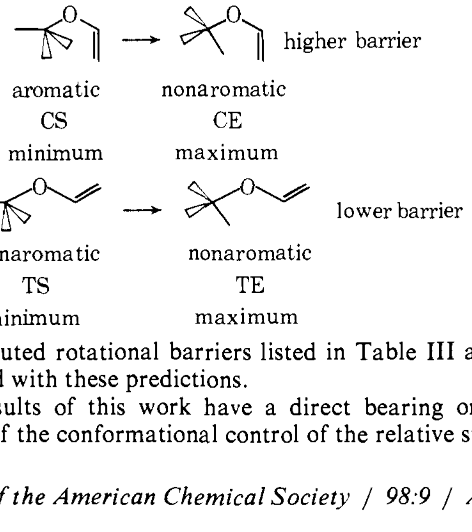
A further examination of the consequences of charge transfer by means of the interaction diagram of Figure 4 leads to clear-cut predictions about the relative magnitude of π bonding between any pair of atoms in the CS and TS conformations. Recalling that the $O(2p_z)$–ϕ_3 interaction is stronger and leads to greater charge transfer in the CS conformation, one can predict whether a certain π interaction between any pair of atoms will be more bonding or antibonding in the CS conformation relative to the TS conformation. These predictions are given in Table V along with the corresponding π bond orders calculated at the STO-3G level. It can be seen that the consequences of charge transfer in the relative π bonding of the CS and TS conformations, as predicted by our orbital symmetry approach, are confirmed by the ab-initio calculations. Specifically, the percentage of correct predictions is 90%! The π-overlap population for atom pairs as well as the total π-overlap population for a particular conformation are shown in Table VI. Keeping in mind the predictions shown in Table V, we see from Table VI that the percentage of correct predictions concerning the relative π bonding in the CS and TS conformations is 70%. However, the discrepancies are small and can be understood by reference to the fact that the predictions were based upon a rigid rotor model while the ab-initio calculations refer to geometry optimized structures. For example, the π bond order O–C_3 was correctly predicted by our approach while the O–C_3 π overlap population was not. This disagreement arises in the smaller C_1OC_2 and OC_2C_3 angles in the TS relative to the CS conformation which force a larger O–C_3 π overlap. We also see from Table VI that the total π overlap population (STO-3G) is greater for the CS than for the TS conformation. This result is paralleled by the total energies calculated at the STO-3G level and is in accord with our theoretical analysis which attributes the lower energy of the CS conformation relative to the TS conformation to π interactions.

We now turn to a comparison of the π overlap populations computed at the STO-3G and 4-31G levels. The correlation between the predicted relative π bonding in the conformations CS and TS and the calculated π overlap populations is, as in the STO-3G calculation, quite good for the 4-31G calculation with the percentage of correct predictions being 80%. In the interconversions CS → TS, CE → TE, CS → CE, and TS → TE we find, with both basis sets, a decrease in the total π overlap population when the interconversion involves a decrease in nonbonded attraction. It is important to point out that when the basis set is changed from STO-3G to 4-31G the magnitude of the long-range π-overlap population, $H_{a,b}$–C_3, increases. That is, an improvement in the quality of the basis set results in an increase in nonbonded attraction as reflected in the $H_{a,b}$–C_3 π-overlap population. This increase is largest in the CS conformation in which nonbonded attraction is the largest.

In summary, a MO analysis of the relative π energies of the CS and TS conformations leads to the prediction that the former will be more stable, a preference which can be attributed to a nonbonded attractive interaction between the methyl group and the double bond. Once more, we emphasize that the term nonbonded attraction denotes a stabilizing effect brought about by virtue of having two atoms or groups in proximity to each other. A similar approach can be used for comparing the stabilization of the CE and TE conformations relative to that of the CS conformation. Since appreciable H_{ab}-C_3 π-bonding overlap obtains only in the CS conformation, we would expect this conformation to have lower energy than either the CE or TE conformation. This expectation is confirmed by the ab initio calculations as can be seen in comparing the results contained in Tables I, II, and IV. Also, the total π-overlap population (Table VI) is larger for the CS than the CE and TE conformations. In short, there is excellent agreement between the qualitative predictions of the OEMO model and the ab-initio results. This state of affairs has, in fact, led us to seek additional "reasons" for the success of the OEMO model and we hope to report on that at a later date. The second important result of the ab-initio calculations concerns the relative magnitude of the methyl rotational barrier in the cisoid and transoid conformations. These values are listed in Table III. Once more, the MO analysis outlined before can be effectively utilized to interpret these interesting results. The barrier in the cisoid geometry will correspond to the energy difference between the CS and CE conformations with the CS conformation being an energy minimum and the CE conformation being an energy maximum. On the other hand, the barrier in the transoid geometry will correspond to the energy difference between the TS and the TE conformation with the TS conformation being the energy minimum and the TE conformation the energy maximum. It is immediately obvious that rotation of the methyl group in the cisoid geometry will be unfavorable relative to that in the transoid geometry because in the former case an $H_{a,b}$-C_3 attractive interaction is destroyed in the process while such a destructive effect is absent in the transoid geometry. In other words, we expect that the energy minimum CS will be more stable than the energy minimum TS and the two energy maxima CE and TE will be comparable in energy.

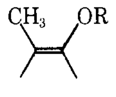
A simplifying reduction of the above detailed analysis of the conformational properties of methyl vinyl ether can be accomplished by recourse to the concept of aromaticity shown to be directly applicable to problems of geometrical and conformational isomerism.[5] Specifically, methyl vinyl ether is a 6π-electron system and, thus, the preferred conformation is predicted to be the CS conformation which corresponds to a Hückel aromatic system.

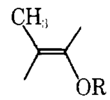
Furthermore, the relative magnitude of the rotational barriers and energy differences between cisoid and transoid conformation can be predicted by considering the aromatic, nonaromatic, or antiaromatic character of the minima and maxima of the rotational curve. These predictions are outlined below:



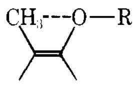
The computed rotational barriers listed in Table III are in full accord with these predictions.

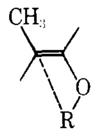
The results of this work have a direct bearing on the question of the conformational control of the relative stability of geometric isomers. For example, Okuyama et al.[16] have studied the relative stability of pairs of cis and trans α,β-unsaturated ethers, such as the ones shown below:



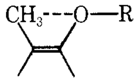


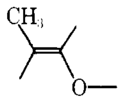
It was found that when R is isopropyl or *tert*-butyl, the cis isomer is more stable, while when R is methyl or isobutyl, the reverse situation obtains. Now, a CH_3-OR attractive nonbonded interaction will obtain in the cis isomer and an R-C_1 attractive nonbonded interaction will be possible only in the trans isomer simply because of steric reasons. In other words, when R is a "small" alkyl group, one compares the following two structures:





Nonbonded attraction obtains in both geometric isomers and the greater stability of the trans isomer can be taken as a measure of the relative strength of the two different kinds of attractive nonbonded interactions. On the other hand, when R is a "bulky" alkyl group, one compares the following two structures:





Nonbonded attraction obtains only in the cis isomer which is found to be more stable than the trans isomer.

In closing, we can say that the concept of nonbonded attraction leads to many detailed electronic predictions which are supported by ab-initio calculation.[17]

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