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Conformations of Unsaturated Ethers

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Geometries of a series of compounds: $H_nX{=}CHOR$ (X = B, C, N, or O and R = H or CH_3) have been optimized at the 3-21G level of ab initio theory in order to understand the preference of these compounds for the syn conformation. A six-fold decomposition of the rotational barrier showed a dominant V_1 and V_2 component to the rotational barrier for both the hydroxyl and methoxyl compounds. Using the natural bond orbital (NBO) method, $\sigma \rightarrow \sigma^*$ hyperconjugative interactions are found to be present as postulated in the literature but insignificant in determining the molecular conformation. It is the molecular dipole that is found to be the primary factor determining the syn preference of these compounds, while the pseudoaromaticity, previously thought to be the dominant factor, is not present to any significant extent. Also contributing to the stability of the preferred syn conformer is an increased conjugation of the oxygen perpendicular lone pair with the double bond in the syn conformation.

Introduction

The conformational preference of methyl vinyl ether has been studied extensively, both experimentally and theoretically, over the past 20 years.[2–6] Vibrational spectroscopy[2] and electron diffraction[3] have demonstrated the syn conformation (**1a**) to be favored over the anti (**1b**). Whether the second most stable conformer is gauche (**1e**) or anti (**1b**) has not been completely settled.[4]

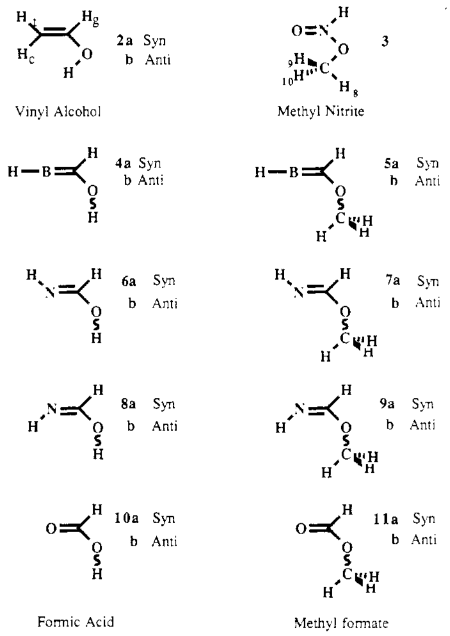
Ab initio molecular orbital calculations have confirmed that the syn conformer is the most stable[5,6] but also have been unable to establish the nature of the second conformer. The energy ordering of the gauche and anti conformer depends significantly on both the basis set and the degree of electron correlation used.[6a] The calculations have confirmed the experimental finding that the methyl group prefers to stagger the *O*-vinyl bond in both the syn (**1a**) and anti (**1b**) conformations.

This syn preference is not an isolated phenomenon. The related molecules vinyl alcohol (**2**),[7] vinyl sulfide (**12**), and methyl vinyl sulfide[8] (**13**) all prefer the syn conformation as do esters of various acids, e.g. methyl nitrite (**3**)[9] and methyl formate (**11**),[10] unless the alkoxyl group is bulky. Why are the apparently sterically more congested conformations favored? Cadioli et al.[4] argued that the preference for syn can be rationalized in much the same way as the conformations of ethane. They suggested that the syn conformation of methyl vinyl ether can be viewed as having two sp^3 oxygen lone pairs staggering the vinylic C–H bond and the *O*-methyl bond staggering the carbon–carbon bond (when this is viewed as a banana bond).

In another proposal, Bernardi et al.[5] suggested a nonbonded interaction to account for this behavior. They proposed using the out of phase s orbital combination from the out-of-plane methyl hydrogens (as a pseudo p orbital) with the p orbital from the methyl carbon as the π orbital of one molecular fragment (Figure 2a). By combining this with the π bond and the p-type oxygen lone pair, a five-center, six-electron π system is obtained. In the syn staggered conformation this leads to pseudoaromaticity, which is not possible in the anti conformation. This pseudoaromaticity will be disrupted either when the methoxy group is rotated into the anti-staggered (**1b**) or when the methyl group is rotated to give the syn-eclipsed (**1c**) conformation. Hence, the rotational barriers should be quite large (Figure 1). In contrast, the barrier to rotation of the methyl group from the anti-staggered to the eclipsed conformation (**1d**) will be lower because there is no disruption of pseudoaromaticity.

The same arguments were employed earlier to explain the conformational preference of CH_3XCH_3 systems[11] and the basic concept can be traced to Hehre's[12] proposal explaining the preference of methyl groups to eclipse double

Chart I



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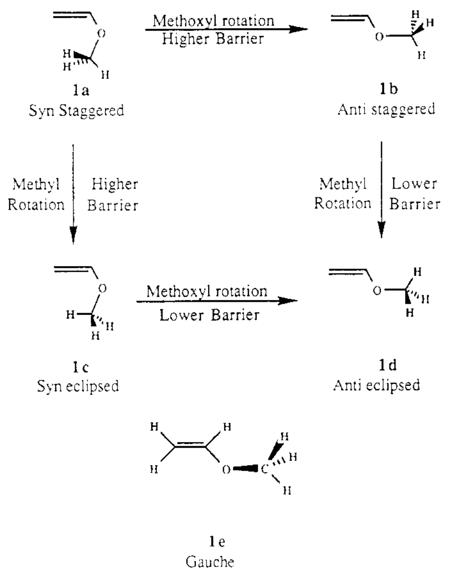

Figure 1. Conformations of methyl vinyl ether and relative rotational barriers, assuming the presence of a pseudoaromatic interaction.

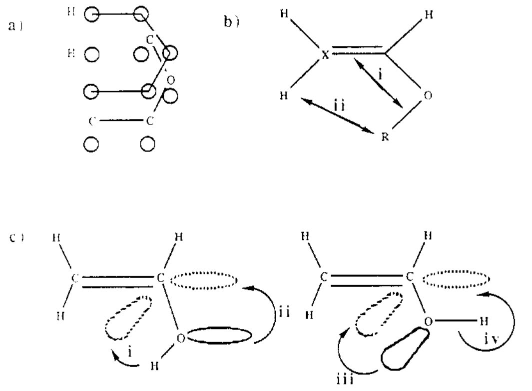

Figure 2. Orbital interactions. (a) Six-electron, five-center pseudoaromatic configuration; (b) orbital repulsions between (i) RO and C=X bonds, (ii) the X–H and R–O bonds; (c) hyperconjugative interactions between: (i) OH σ and CH σ^*, (ii) oxygen lone pair and CC σ^*, (iii) oxygen lone pair and CH σ^*, (iv) OH σ and CC σ^*.

bonds. The idea has been intriguing to chemists, and the conformational preferences of heterocycles,[13] the crotyl cation and anion,[14] substituted phenonium ions,[15] sulfides,[16] and methyl nitrate,[17] among others, have been rationalized using this explanation.

Larson et al.[18] suggested that hyperconjugative interactions between the in-plane oxygen lone pair and the C–C σ^* or C–H σ^* orbitals (Figure 2c) could be responsible for the preferred conformation of vinyl alcohol, methyl vinyl sulfide, etc. They argued that the C–C σ^* should be a better acceptor than the C–H σ^*; hence, the syn conformation should be favored over the anti. These interactions also should be present in methyl vinyl ether.

Because of the similarity between vinyl alcohol and methyl vinyl ether, we undertook a comparative study of these systems to determine the relative importance of the interactions which stabilize the various conformations. In addition, we have examined the series of compounds, $H_nX{=}CHOR$, where X = B (**4**, **5**), C (**1**, **2**), N (**6**–**9**), or O (**10**, **11**) and R = H or CH_3 (Chart I), in order to understand the changes in these interactions with systematic variations in the polarity of the π bond. In the ethers (R = CH_3), "pseudoaromaticity" is possible, but not in the corresponding alcohols (R = H).

Several groups have reported optimizations or partial optimizations of methyl vinyl ether[5,6] and vinyl alcohol.[19,20] Both semiempirical[21] and ab initio[22] investigations for HN=CHOR have appeared in the literature, while the compounds HB=CHOR (R = H and CH_3) have never been prepared and no previous computations appear to have been reported. Finally, formic acid and methyl formate have already been examined frequently.[23]

Methods

The ab initio calculations reported here were carried out with the GAUSSIAN 82 program, employing its standard methods and basis sets.[24,25] Geometries were taken from the Carnegie-Mellon Archive[20] where available or optimized at the HF/3-21G level for all molecules reported. The influence of electron correlation was assessed by computing single-point energies at the MP2/6-31G*//3-21G level[25] (with frozen core) for methyl vinyl ether and methyl formate. Comparable data for vinyl alcohol and formic acid from the Carnegie-Mellon Archive[20] are also included.

The intramolecular interactions were analyzed using the HF/3-21G wave functions with the natural bond orbital set of methods,[26] using the program G82NBO.[27] The steps of the method involve natural population analysis (NPA),[26b] the formation of localized natural bond orbitals (NBO),[26a] and finally, the formation of natural localized molecular orbitals (NLMOs)[26c] by allowing the natural bond orbitals to delocalize to full occupancy. Natural population analysis[26b] has been shown to give atomic changes which are less subject to basis set artifacts than the Mulliken procedure. While both are presented, we have relied on NPA for our analysis.

The Fourier component analysis (using eq 1 below) of the rotational barriers[28] was carried out to the sixth-fold

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Table I. Calculated Dipole Moment and Absolute (au) and Relative (kcal/mol) Energies of the Compounds X═CHOR (R = H and CH_3)

	HF/3-21G//3-21G			HF/6-31G*//3-21G			MP2/6-31G*//3-21G		
	energy		dipole moment	energy		dipole moment			
molecule	total	rel		total	rel		total	rel	expt
HB═CHOH (**4**)									
syn	−138.28122	0.00	1.87						
anti	−138.27979	0.90	1.91						
HB═$CHOCH_3$ (**5**)									
syn-eclipsed	−177.09236	3.24	1.69						
syn-staggered	−177.09753	0.00	1.70						
anti-eclipsed	−177.09197	4.05	1.77						
anti-staggered	−177.09383	2.32	1.69						
H_2C═CHOH, vinyl alcohol (**2**)									
syn	−152.04176[a]	0.00	1.28	−152.90097[b]	0.00	1.05[d]	−153.39199[c]	0.00	0.00
anti	−152.03690[a]	3.06	2.24	−152.89765[b]	2.28	2.10	−153.39524[c]	2.07	1.08[e]
H_2C═$CHOCH_3$, methyl vinyl ether (**1**)									
syn-eclipsed	−190.85027	3.16	1.33	−191.90847	3.58	1.17	−192.46756	3.85	3.80[f]
syn-staggered	−190.85530	0.00	1.28	−191.91415	0.00	1.12	−192.47370	0.00	0.00[f]
anti-eclipsed	−190.84835	4.36	2.25	−191.90906	3.20	2.02	−192.46746	3.92	2.73[f,g]
anti-staggered	−190.84987	3.41	2.16	−191.91072	2.13	1.96	−192.46920	2.82	1.26[f,g]
HN═$CHOCH_3$ (NH anti to oxygen) (**6**)									
syn	−167.95683	0.00	1.41	−168.92023		1.22	−169.43419		
anti	−167.94236	9.08	4.40						
HN═$CHOCH_3$ (NH anti to oxygen) (**7**)									
syn-eclipsed	−206.76744	1.42	0.82						
syn-staggered	−206.76971	0.00	0.88						
anti-eclipsed	−206.76497	9.24	4.35						
anti-staggered	−206.76593	8.65	4.30						
HN═$CHOCH_3$ (NH syn to oxygen) (**8**)									
syn	−167.95178	0.00	2.26						
anti	−167.95049[a]	0.81	2.94						
HN═$CHOCH_3$ (NH syn to oxygen) (**9**)									
syn-eclipsed	−206.76186	2.23	2.87						
syn-staggered	−206.76542	0.00	2.76						
anti-eclipsed	−206.76313	1.44	3.34						
anti-staggered	−206.76401	0.88	3.29						
O═CHOH formic acid (**10**)									
syn	−187.70019[a]	0.00	1.40	−188.77054[b]	0.00	1.62	−189.28636[c]	0.00	0.00
anti	−187.68868[a]	7.23	4.55	−188.76098[b]	6.02	4.37	−189.27763[c]	5.46	3.90[h]
O═$CHOCH_3$ methyl formate (**11**)									
syn-eclipsed	−226.51318	0.69	1.83	−227.78500	1.19	2.03	−228.39305	1.00	2.03
syn-staggered	−226.51428	0.00	1.80	−227.78697	0.00	1.99	−228.39464	0.00	0.00
anti-eclipsed	−226.50299	7.08	4.88	−227.77686	6.34	4.77	−228.38498	6.09	
anti-staggered	−226.50308	7.03	4.85	−227.77728	6.09	4.75	−228.38483	6.15	4.75[i,j]

[a] Reference 20. [b] Reference 20, 6-31G**//6-31G*. [c] Reference 20, MP4SDTQ/6-31G**//6-31G*. [d] Reference 7. [e] Reference 19b. [f] Durig, J. R.; Compton, D. A. C. *J. Chem. Phys.* **1978**, *69*, 2028. [g] The experimental value is the gauche–syn energy. [h] Hocking, W. H. *Z. Naturforsch* **1976**, *31A*, 1113. [i] Blom, C. E.; Gunthard, H. H. *Chem. Phys. Lett.* **1981**, *84*, 267. [j] Ultrasound measurements give a value of 2.4 kcal/mol; Choi, P. K.; Naito, Y.; Takagi, T. *Chem. Phys. Lett.* **1985**, *121*, 169.

term by performing single-point calculations at 30, 60, 90, 120, 150, and 180 °C using the rigid rotor approximation.

$$V(\Theta) = \sum \tfrac{1}{2} V_n (1 - \cos (n\Theta)) \qquad n = 1\text{–}6 \qquad (1)$$

Results

A. Energies and Rotational Barriers. The energies, relative energies, and calculated dipole moments from the 3-21G optimizations and the MP2/6-31G*//3-21G single-point calculations are shown in Table I. The energy ordering of the methyl vinyl ether conformers is predicted correctly by the calculations at all levels of theory, although larger basis sets and electron correlation give improved agreement with experiment (2.82 kcal/mol at MP2/6-31G*//3-21G vs 1.26 kcal/mol for experiment). Calculated energies also predict the correct ordering of conformers for vinyl alcohol (2.07 vs 1.08 kcal/mol), formic acid (5.46 vs 3.90 kcal/mol), and methyl formate (6.15 vs 4.75 kcal/mol), although here, too, the experimental energy is overestimated at both 3-21G and MP2/6-31G*. Dipole moments are also overestimated at the SCF level, since the major correction is from single excitations.

For the X═CHOR series, the syn–anti energy shown in Table I depends on the group X and is largely independent of whether R is H or CH_3 (for the ethers, the comparison is between the two staggered conformers). The boron compounds are an exception to this, with the ether (**5**) having a greater preference for the syn conformer than the alcohol (4, 2.32 vs 0.90 kcal/mol, respectively). The energy required for the rotation of the methoxyl group increases gradually as X is varied from boron (2.32 kcal/mol) to oxygen (7.03 kcal/mol). Figure 3 shows a plot of the electronegativity[29] of X vs anti–syn energy, which gives reasonably good correlation. Rotation of the methyl group from the staggered to the eclipsed is consistently larger in the syn conformation than in the anti.

In either case, the rotational barrier is affected by the electronegativity of atom X and the presence of eclipsing interactions. The former is best illustrated by the conformational energy differences in the anti conformation where eclipsing exists for **1b**, **5b**, **7b**, **9b**, and **11b**. There,

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(28) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371.

(29) The Allred-Rochow electronegativity values have been used throughout: Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958** *5*, 269.

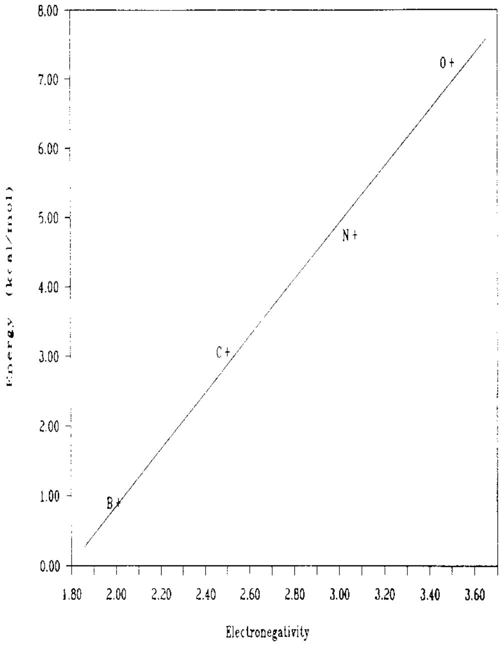

Figure 3. Plot of electonegativity of atom X vs the anti–syn energy in the molecules $H_nX{=}CHOH$ (The energies of compounds 6 and 8 have been averaged).

the energy difference declines from 1.73 kcal/mol for **5b** to 0.05 kcal/mol for **11b**. There is a similar trend in the syn series, but it is disrupted as eclipsing interactions are either present (as in **1a** and **9a**) or absent (**5a**, **7a**, and **11a**).

Table II shows the 6-fold decomposition of the rotational barriers of the alcohols and ethers studied. The V_1 term is usually associated with the dipole component of the barrier or steric effects, although, in principle, it could also include differences in conjugation and hyperconjugation energy[30] when these have a periodicity of 360°. The "pseudoaromaticity" proposed by Bernardi et al.[5] is an example of such an interaction. A positive value of V_1 indicates a preference for the syn conformer.

The V_2 term is normally associated with conjugative and hyperconjugative effects that have a periodicity of 180°. Conjugation of the oxygen out of plane lone pair with the π system and hyperconjugation of the oxygen in plane lone pair with the C–C σ^* or C–H σ^* are examples of interactions that would be components of V_2.

The large magnitude of the V_1 and V_2 terms shows that they are principally responsible for the rotational barrier of the methoxyl or hydroxyl group. The main difference between the rotational barrier of the RO group of the alcohols and ethers is in the V_3 term with the ethers having a larger and positive value, indicating a preference for the eclipsed conformer. There are other, less significant differences in the V_4, V_5, and V_6 terms. The similarity between the decomposition of the barriers of the alcohol and ethers suggests that the rotational barriers have similar origins. As a corollary, it is likely that the preference for the syn conformer shown by these two groups of compounds also has a common origin.

For methyl rotation, the major component of the rotational barrier is the V_3 term. This is compatible with a barrier similar in origin to that of ethane and also a barrier arising from pseudoaromaticity, since for methyl rotation, this force would be manifested in the V_3 term. Although a pseudoaromatic interaction is possible in all ethers of the series, the V_3 component of the barrier is larger for rotation in the syn conformer than in the anti where there is an eclipsing interaction between the methyl and X–H bond (e.g. for **1** and **8**). The magnitude of this barrier falls off dramatically, and the difference between the syn and anti is reduced in compounds **5**, **7**, and **11**.

Table II. Decomposition of Rotational Barriers for $H_nX{=}CHOR$

molecule	hydroxyl (R = H) rotation	methoxyl (R = CH_3) rotation	methyl rotation (R = CH_3)	
			syn	anti
HB=CHOR				
V_1	2.17	1.59	0.76	1.05
V_2	0.06	0.69	0.04	−0.59
V_3	0.65	1.92	−2.83	−0.87
V_4	−0.03	0.54	−0.13	−0.35
V_5	0.01	0.07	0.01	0.37
V_6	0.00	−0.22	0.01	−0.19
H_2C=CHOR				
V_1	3.10	3.52	1.33	0.69
V_2	2.98	3.36	−0.17	−0.22
V_3	0.76	1.42	−2.52	−0.51
V_4	0.40	0.22	0.10	0.01
V_5	0.68	0.16	0.01	0.00
V_6	0.38	0.05	−0.07	0.01
HN=CHOR (NH anti to oxygen)				
V_1	8.92	8.16	−0.02	0.82
V_2	6.64	5.96	0.29	−0.21
V_3	0.98	1.21	−0.40	−0.17
V_4	0.07	0.16	0.05	0.00
V_5	0.01	0.28	0.07	0.00
V_6	0.00	−0.11	−0.39	0.02
HN=CHOR (NH syn to oxygen)				
V_1	2.18	1.43	2.63	0.65
V_2	5.49	4.41	0.54	−0.18
V_3	0.87	1.07	−1.59	−0.18
V_4	0.21	0.13	2.29	0.00
V_5	0.22	0.15	−1.27	0.00
V_6	0.21	0.04	−0.80	0.01
O=CHOR				
V_1	7.40	6.33	0.34	0.04
V_2	8.71	8.32	−0.32	0.35
V_3	0.38	1.27	0.10	0.86
V_4	−0.17	0.02	−0.19	0.03
V_5	0.17	0.09	−0.18	0.14
V_6	0.16	0.02	0.18	−0.51

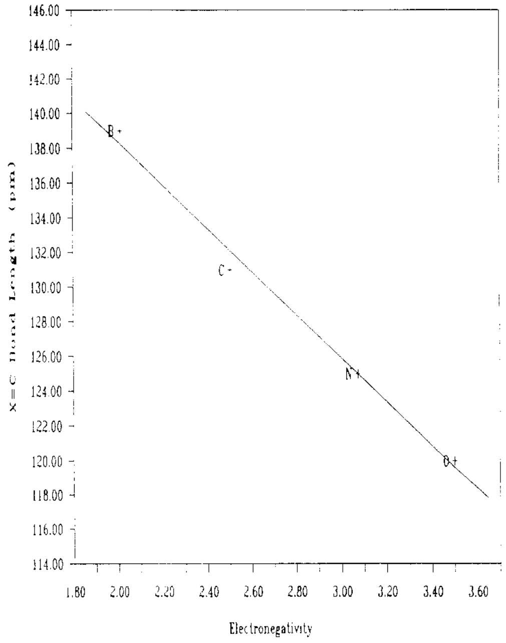

Figure 4. Plot of electronegativity of atom X vs the C=X bond length.

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Table III. Selected Bond Lengths (Å) and Angles (deg) for $H_nX{=}CHOR$ (R = H and CH_3)

molecule	X=C	C_2O	OR	XCO	COR	XCH_g[a]	H_8CO[b]	H_9CO[b]
HB=CHOH (**4**)								
syn	1.393	1.407	1.165	132.69	112.40	117.59		
anti	1.393	1.411	1.165	123.39	111.22	119.81		
$HB{=}CHOCH_3$ (**5**)								
syn-eclipsed	1.396	1.388	1.440	132.35	118.63	117.47	112.02	108.70
syn-staggered	1.397	1.391	1.434	130.62	115.87	118.70	106.85	110.75
anti-eclipsed	1.395	1.399	1.438	123.52	118.75	120.28	111.68	108.88
anti-staggered	1.394	1.404	1.436	123.27	116.41	120.45	106.20	111.29
$H_2C{=}CHOH$, vinyl alcohol (**2**)								
syn	1.314	1.376	0.966	127.16	112.74	122.67		
anti	1.311	1.387	0.962	121.90	112.57	121.70		
$H_2C{=}CHOCH_3$, methyl vinyl ether (**1**)								
syn-eclipsed	1.315	1.370	1.441	129.72	122.67	125.14	112.73	108.06
syn-staggered	1.315	1.370	1.437	128.07	119.16	125.50	105.95	111.02
anti-eclipsed	1.312	1.374	1.438	122.38	119.71	123.79	111.54	108.77
anti-staggered	1.312	1.379	1.438	122.10	117.57	123.55	106.54	111.32
HN=CHOH (NH anti to oxygen) (**6**)								
syn	1.245	1.360	1.007	122.08	110.54	128.19		
anti	1.242	1.369	1.009	120.14	113.16	125.89		
$HN{=}CHOCH_3$ (NH anti to oxygen) (**7**)								
syn-eclipsed	1.247	1.355	1.452	123.88	119.77	127.19	110.21	107.71
syn-staggered	1.248	1.353	1.449	122.80	117.72	127.60	105.35	110.46
anti-eclipsed	1.242	1.361	1.489	120.72	120.05	126.12	111.64	108.61
anti-staggered	1.243	1.364	1.440	120.52	117.99	125.97	105.84	111.35
HN=CHOH (NH syn to oxygen) (**8**)								
syn	1.246	1.374	1.013	129.16	114.09	121.50		
anti	1.242	1.376	1.013	123.55	113.81	120.92		
$HN{=}CHOCH_3$ (NH syn to oxygen) (**9**)								
syn-eclipsed	1.246	1.371	1.444	130.72	123.55	120.89	112.58	108.01
syn-staggered	1.246	1.370	1.442	129.37	119.88	121.34	105.61	111.15
anti-eclipsed	1.243	1.369	1.441	124.11	120.05	121.13	111.31	108.64
anti-staggered	1.243	1.372	1.441	123.84	121.08	118.18	106.14	111.13
O=CHOH, formic acid (**10**)								
syn	1.198	1.351	0.969	124.61	112.65	125.88		
anti	1.192	1.354	0.964	122.55	114.75	123.66		
$O{=}CHOCH_3$, methyl formate (**11**)								
syn-eclipsed	1.200	1.344	1.458	125.45	119.75	125.14	109.96	107.53
syn-staggered	1.200	1.343	1.456	124.60	117.93	125.50	105.26	110.26
anti-eclipsed	1.193	1.348	1.443	123.25	120.62	123.79	111.22	108.35
anti-staggered	1.193	1.349	1.446	123.05	118.92	123.55	105.77	111.00

[a] See **2** (Chart I) for numbering scheme. [b] See **3** (Chart I) for numbering scheme.

B. Structure. The average bond lengths of selected bonds are shown in Table III. As expected, the lengths of the C=X bonds are inversely proportional to the electronegativity of atom X (Figure 4).[31] The C_2O bond is also shortened as X becomes more electronegative, but this effect is not as pronounced as for the C=X bond length. These two bond lengths show a slight conformational effect in that the C=X bond length is slightly longer in the syn conformer and the C_2O bond is slightly shorter. Most other bond lengths show little variation as the conformation of the molecule is varied, and the individual values are within 0.005 Å of the average.

In contrast, many of the bond angles show significant deviations as the conformation is changed (see Table III). Note in particular, the decrease in the XCO angle as the conformation is changed from syn to anti in all examples. Although the magnitude of the change is dependent upon X and R, the XCO angle decreases in every case. We propose that this is a result of repulsions between (a) the oxygen-hydrogen (or methyl group) and carbon-X bond orbitals, and (b) the hydroxyl hydrogen (or methyl) and the hydrogens on atom X (Figure 2b), where these are present. As the electronegativity of X increases, the electron density in the region of C_2 should decrease, thus allowing more facile rotation of the OR group. This hypothesis is supported by Figure 5, which shows that there is a direct relationship between the bond angle difference and electronegativity.

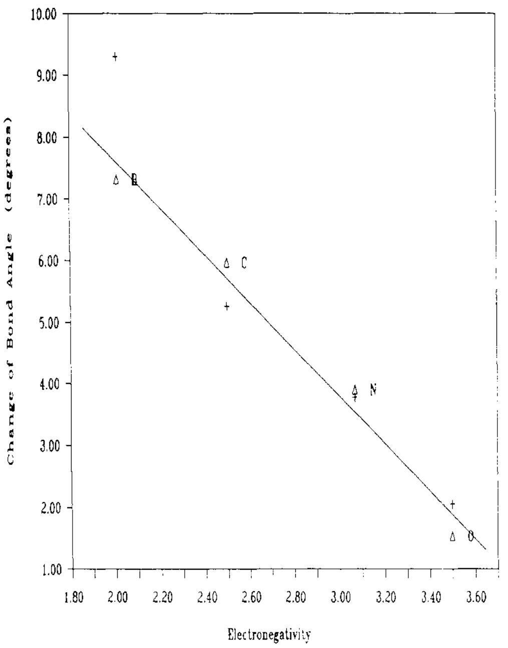

Figure 5. Plot of electronegativity of atom X vs the change in the XCO bond angle: $H_nX{=}COCH3$ (+); HnX=COH (△). The linear relationship is for the latter series.

Evidence for the repulsion of the OR or OH groups and the X-H bond is found in the following. The difference in the XCO angle between the anti-eclipsed and anti-

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[31] Schleyer, P. v. R.; Kost, D. *J. Am. Chem. Soc.* **1988**, *110*, 2105.

Table IV. C1–H9 Bond Orders for Methyl Vinyl Ether

conformer	Wiberg[a]	Mulliken population
syn-eclipsed	0.00147	0.00013
syn-staggered	0.00436	0.00411
anti-eclipsed	0.00181	-0.00005
anti-staggered	0.00033	0.00002

[a] Reference 31.

Table V. π Molecular Orbital Eigenvalues for Methyl Vinyl Ether

conformer	1A″	2A″	3A″
syn-eclipsed	-0.64108	-0.50143	-0.33849
syn-staggered	-0.64310	-0.49816	-0.34291
anti-eclipsed	-0.64173	-0.50127	-0.33267
anti-staggered	-0.64125	-0.49893	-0.33578

staggered bond is never more than 0.3°. In contrast, the corresponding angles for the syn conformation vary from 0.85 to 1.73°. Further, the energy difference between syn-eclipsed and syn-staggered varies from 3.16 and 2.23 kcal/mol for compounds **1** and **9**, respectively, where the eclipsing is present and 1.42 and 0.69 kcal/mol in compounds **7** and **11** where it is not. As additional evidence of this steric effect, the XCO angle is larger in ethers than alcohols for the syn conformation, but very similar in the anti conformer. The differences in the COH angles of the alcohols are minimal; however, the COC angles of the ethers are larger in the eclipsed conformation than the corresponding staggered conformation.

C. Pseudoaromaticity. Is pseudoaromaticity present or absent? Bernardi et al.[5] found that the overlap populations between the methyl hydrogens and the C_1 carbon were significantly greater in the syn conformation. Our results (Table IV) show more than 1 order of magnitude increase upon rotation of methyl from eclipsed to staggered. The Wiberg index[32] also shows a substantial increase.

However, comparison of the absolute value of 0.004 for the overlap population against those overlaps of normal covalent bonds (C–H bonds typically have values between 0.350 and 0.450), and a crude estimation of the energy differences suggests that any such overlap is likely to amount to much less than the conformational energy difference of 3.41 kcal/mol calculated for methyl vinyl ether. The more quantitative NBO analysis shows that there is no significant interaction between the methyl hydrogens and the carbon–carbon π system; a value of less than 0.5 kcal/mol is estimated by second-order perturbation theory. Thus, it is unlikely that "pseudoaromaticity" is present to an extent sufficient to account for the relative stability of the methyl vinyl ether conformations.

As an additional criterion, we considered the energies of the three A″ bonding molecular orbitals. These are shown in Table V. It is expected that the aromaticity would be manifested in the 1A″orbital and there is a lowering in the energy of this orbital in the syn vs anti staggered conformation. However, a similar estimate of the effect of this energy lowering suggests that it, too, is only a fraction of the amount required to explain the conformational preference for syn. Further, there are many changes in this orbital besides the interaction between the hydrogen and π bond. There is a larger difference between staggered and eclipsed in the 3A″ orbital, but this change is seen in both the anti and syn conformations and is probably due to methyl rotation.

Examination of the three A″ MO's shows that the signs of the coefficients on C1 and the methyl hydrogens are the same. Although this is favorable for overlap, the magnitude of the coefficients, particularly those of the 1A″, are such that overlap is small and unlikely to be as important as proposed by Bernardi et al. Also working against significant overlap is the distance of 2.9 Å between the terminus of the π bond and the methyl hydrogens. This is comparable to the distance in the CO_2–H_2O complex where π interactions were also found to be absent.[33]

Finally, if pseudoaromaticity were present, there should be a significant difference between the V_1 term of methyl vinyl ether and the V_1 term of vinyl alcohol. The two values are quite similar, and this is true of the entire series of compounds that we have examined. Since the SCF energies adequately describe the conformational preferences, it is also unlikely that a steric or orbital staggering explanation is correct since at the SCF level, the bent bond and σ/π representations are energetically equivalent.

Based on these findings, we believe that the nonbonded pseudoaromatic interaction proposed by Bernardi et al.[5] is insignificant and has no influence on the conformational preference of methyl vinyl ether. As an alternative explanation, we propose that the stabilization of the syn relative to the anti conformation of methyl vinyl ether and many other unsaturated molecules is a result of a reduced molecular dipole moment and conjugative interactions between the oxygen lone pairs and the double bond.

D. Dipole Moment and Molecular Conformation. We believe that electrostatic considerations are an important factor in determining the conformation of these molecules. The idea is not new in that the preferred conformation of methyl formate (**11**) has been attributed to electrostatic effects,[34] but there has been an effort in recent years to look for interpretations in the quantum mechanical wave functions.[35] Houk[36] suggested that electrostatic effects were responsible for the preferred syn conformation of the imine anion, but felt it necessary to provide evidence in support of "this reactionary contention". Wiberg[37] has subsequently offered additional support for the importance of electrostatic effects on the conformational preference of methyl formate. More recently, Houk and Wiberg suggested that changes in electrostatic effects with conformation in esters and ester anions are responsible for the extraordinary acidity of Meldrum's acid.[38] Finally, the importance of electrostatic effects relative to π effects has recently been invoked to explain the greater acidity of carboxylic acids and phenols relative to alcohols.[39]

We have already pointed out that there is a direct relationship between syn–anti energy of these compounds and the electronegativity of the group X. In Figure 6 we show that there is also a direct relationship between the

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(32) Wiberg, K. B. *Tetrahedron* **1968**, *27*, 1083. The values reported here are based on the density matrix in the orthogonal NAO basis set; this improves basis set independence.

(33) Reed, A. E.; Weinhold, F.; Curtiss, L. A.; Pochatko, D. J. *J. Chem. Phys.* **1986**, *84*, 5687.

(34) (a) Wennerstrom, H.; Forsen, S.; Roos, B. *J. Phys. Chem.* **1972**, *76*, 2403. (b) Mark, H. L.; Noe, E. A. *J. Org. Chem.* **1989**, *54*, 1782.

(35) For leading references, see ref 5 and 12.

(36) Houk, K. N.; Strozier, R. W.; Rondan, N. G.; Fraser, R. R.; Chauqui-Offermans, N. *J. Am. Chem. Soc.* **1980**, *110*, 1426.

(37) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935. Cf.: Breneman, C. M.; Wiberg, K. *J. Comput. Chem.*, in press.

(38) Wang, X.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 1870. (b) Wiberg, K.; Laidig, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 1872.

(39) Siggel, M. R.; Thomas, T. D. *J. Am. Chem. Soc.* **1986**, *108*, 4360. For comments on these results, see: Exner, O. *J. Org. Chem.* **1988**, *53*, 1810. Thomas, T. D.; Carroll, T. X.; Siggel, M. R. *Ibid.* **1988**, *53*, 1812. Also: Siggel, M. R. F.; Streitwieser, A., Jr.; Thomas, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 8022. Thomas, T. D.; Siggel, M. R. F.; Streitwieser, A., Jr. *J. Molec. Struct.* **1988**, *165*, 309.

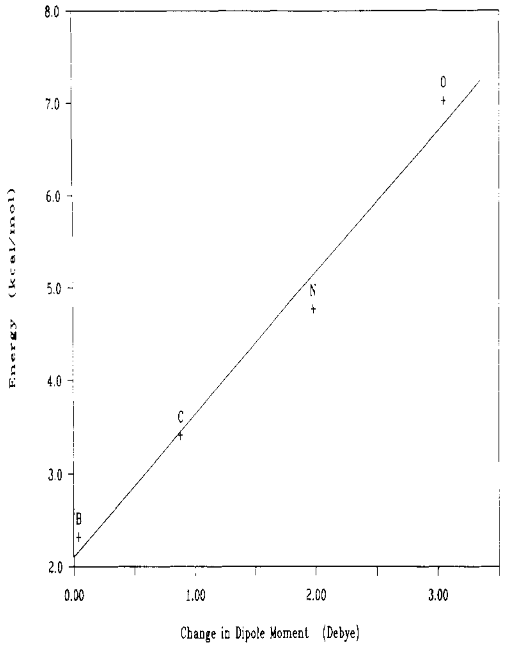


Figure 6. Plot of the difference in dipole moment between the syn and anti conformations vs the energy difference. (The change in dipole moment for compounds 6 and 8 have been averaged.)

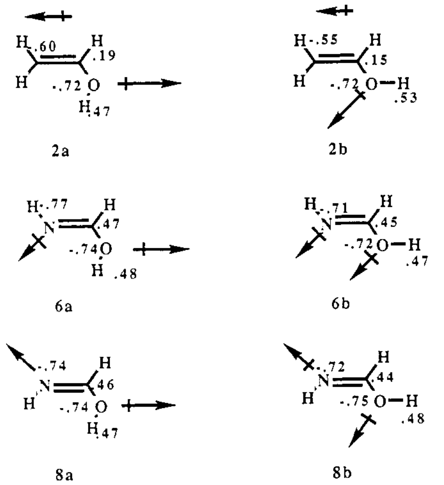


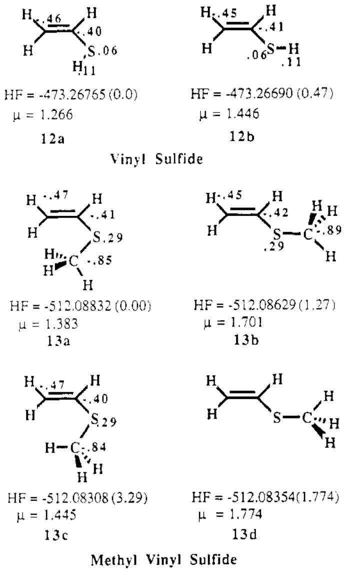
Figure 7. Approximate dipole vectors for the compounds 2, 6, and 8. Natural atomic populations are shown for selected atoms.

difference in dipole moments of the two conformers and the energy difference.

The manner in which the dipole moment is reduced in the syn conformation can be visualized in two different ways, both shown in Figure 7. The first shows that the attraction of heavy atoms having opposite charges is facilitated in the syn conformation. Alternately, sketching approximate component dipole vectors for the molecule shows that the dipoles tend to cancel each other in the syn conformation, but to reinforce one another in the anti. Examination of the component dipole vectors for the related nitrogen compounds provides a qualitative understanding for the large differences for the change in dipole moments observed in compounds **6a**,**b** or **7a**,**b** and **8a**,**b** or **9a**,**b**.

The expectation that the bond polarity would be reversed in methyl vinyl sulfide **13**, which also prefers the syn conformation (**13a**), led Larson et al.[18] to conclude that dipoles are not significant in determining the molecular conformation. The assignment of polarities was based on the population analysis from an STO-3G calculation of vinyl sulfide (**12**).[5] Our 3-21G* calculations for vinyl sulfide and methyl vinyl sulfide (Chart II) confirm the preferred syn conformation as well as uphold the population analysis calculated at lower levels of theory. In contrast, we find that the dipole moment in the syn conformer is lower than that of the anti. This result supports our contention that the dipole moment is important in determining the molecular conformation despite the results of apparent bond polarities based on population analysis.

Chart II



The data provide additional insights on the question of pseudoaromaticity. The energy change for rotation of the methyl group in the syn conformation from staggered to eclipsed is similar for both methyl vinyl ether and methyl vinyl sulfide (3.16 vs 3.00 kcal/mol, respectively). Yet the difference between the syn and anti conformations (CH_3S rotation vs CH_3O) is only 1.27 kcal/mol as opposed to the 3.41 difference for methyl vinyl ether. If pseudoaromaticity were present in methyl vinyl sulfide, the anti–syn difference should be larger. If not, we would expect a lower value for rotation of the methyl. On the other hand, if our arguments that the energy changes of the methoxyl group are primarily a result of the changes in dipole moments while those of the methyl group are steric, then the results for the methyl vinyl sulfide are consistent. The changes in dipole moment are much smaller in methyl vinyl sulfide than in the ether, and the conformational energy difference should also be smaller, which it is. While the bond lengths in methyl vinyl sulfide are longer, the CSC angle is smaller, giving a steric effect that is similar to that in methyl vinyl ether. Thus we expect a comparable value for methyl rotation, which is also observed.

Vinyl formate is another molecule that illustrates the importance of dipole moments. A six-electron pseudoaromatic attraction is possible for this molecule in the syn–syn conformation (**14a**). This rotamer, however, is a local minimum on the potential surface with the global minimum being the syn–anti conformer (**14b**).[34b] The dipole moments of conformers **14a** and **14b** (1.894 and 1.734, respectively) are significantly lower than those of **14c** and **14d** (4.026 and 4.168, respectively), and this accounts for the significant stabilization of the first two (Chart III). The preference of **14b** over **14a** is likely due to steric considerations. Steric repulsions are at a minimum at **14d**; however, this conformer is 4.58 kcal/mol above the global minimum.

Table VI. Important Hyperconjugative Interactions (kcal/mol) for the Series $H_nX{=}CHOH$

molecule	oxygen in plane lone pair → X=C σ*	oxygen in plane lone pair → CH_g σ*	OR σ → X=C σ*	OR σ → CH_g σ*	XH_t σ → C_2O σ*
HB=CHOH (4)					
syn	6.4	1.9		3.2	
anti		5.4	3.3	0.8	
$H_2C{=}CHOH$ (2)					
syn	5.8	1.6		3.6	10.0
anti	1.0	6.1	3.7	0.6	9.3
$HN{=}CHOCH_3$ (NH anti to oxygen) (6)					
syn	5.6	1.3		4.1	11.6
anti	3.4	5.4	1.7		12.7
HN=CHOCH (NH syn to oxygen) (8)					
syn	8.4	1.6		4.2	29.1[a]
anti	2.7	5.7	1.6		26.4[a]
$O{=}CHOCH_3$, formic acid (10)					
syn	8.2	1.5		4.8	52.1[b]
anti	4.3	5.2	4.3		52.4[b]

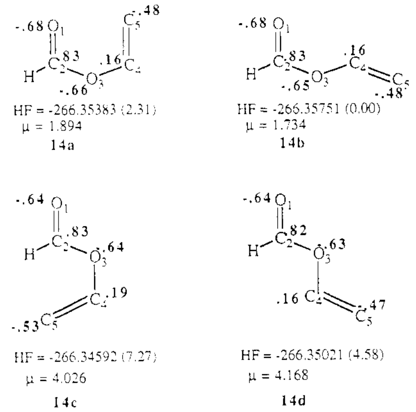
[a] N lone pair → CO σ*. [b] O lone pair → CO σ*.

In all of the systems which we have examined, the lowest energy conformer has had the lowest dipole. The converse is not true, however. Thus it is not possible to rank the stability of a series of conformers using dipole moments exclusively, since steric effects and orbital interactions also play a role. This is particularly true when the dipole moments are similar.

E. Intramolecular Interactions. In addition to the dipole moment, we have found that intramolecular interactions also play a role in determining preferred conformation of a molecule. In this section, we examine those conjugative and hyperconjugative effects which are significant and assess their influence on the relative energies of the syn and anti conformers. The data are summarized in Tables VI and VII. For simplicity, we will confine our discussion to the series ($H_nX{=}CHOH$, Table VII); however, the principles generally apply to both series.

As pointed out by Larson et al.[18] one of the largest interactions involves the oxygen in-plane lone pair with either the X-C σ* or C-H_g σ* orbitals. Unfortunately, our calculations show that these interactions favor the syn in some compounds and the anti in others. This inconsistency is a result of several factors, of which the most important is the failure of previous analyses to take into account the interaction of the back lobe of the oxygen in-plane lone pair.

Chart III



Vinyl Formate

These back lobe interactions occur with the X-C σ* orbital in the anti conformation and the C-H_g σ* orbital in the syn conformation and are important because the oxygen in-plane lone pair has a significantly higher s character (44% vs 22%) than does the O-H bond orbital and hence has greater electron density in the back than does hydrogen. The interaction with C-H_g σ* orbital is relatively constant for the series of compounds which we examined. As expected, better overlap between this oxygen lone pair and the X-C σ* is obtained when the latter is polarized toward carbon. Thus, compounds **4a,b** show no interaction, while compounds **10a,b** have an energy of 4.3 kcal/mol. In addition, there is a geometric effect that will increase the effectiveness of the overlap. This occurs when the XCO bond angle is increased, bringing the back lobe physically closer to the σ* orbital. When the back lobe interaction is excluded, we find that the interaction as

Table VII. Important Hyperconjugative Interactions (kcal/mol) for the Series $H_nX{=}CHOCH_3$

molecule	oxygen in plane lone pair → X=C σ*	oxygen in plane lone pair → CH_g σ*	OR σ → X=C σ*	OR σ → CH_g σ*	XH_t σ → C_2O σ*
$HB{=}CHOCH_3$ (5)					
syn-eclipsed	7.1	2.3		3.5	
syn-staggered	6.7	2.0		3.2	
anti-eclipsed		6.5	2.9		
anti-staggered		6.2	2.7		
$H_2C{=}CHOCH_3$, methyl vinyl ether (1)					
syn-eclipsed	7.3	2.3		4.5	11.1
syn-staggered	6.7	2.0		4.2	10.5
anti-eclipsed	1.2	7.2	2.3		9.6
anti-staggered	1.1	7.0	2.3		9.4
$HN{=}CHOCH_3$ (NH anti to oxygen) (7)					
syn-eclipsed	7.2	1..9		4.7	12.1 (15.3[a])
syn-staggered	6.6	1.8		4.6	11.6 (15.7[a])
anti-eclipsed	3.9	6.5	1.9		13.2 (15.0[a])
anti-staggered	3.6	6.4	1.8		13.0 (15.0[a])
$HN{=}CHOCH_3$ (NH syn to oxygen) (9)					
syn-eclipsed	9.9	2.2		4.9	30.6[a]
syn-staggered	9.0	1.9		4.7	29.3[a]
anti-eclipsed	3.0	6.7	1.8		27.0[a]
anti-staggered	2.8	6.6	1.7		26.4[a]
$O{=}CHOCH_3$, methyl formate (11)					
syn-eclipsed	9.5	1.9		6.2	50.6[b]
syn-staggered	8.8	1.8		5.2	50.7[b]
anti-eclipsed	4.8	6.2	1.5		52.2[b]
anti-staggered	4.5	6.1	1.5		51.7[b]

[a] Interaction with nitrogen lone pair. [b] Interaction with oxygen lone pair.

Table VIII. Conjugation Energy (kcal/mol) of the Oxygen Out of Plane Lone Pair with the Double Bond and Methyl Group in the Series $H_nX{=}CHOCH_3$

molecule	C=C π^*	CH methyl σ^*	total[a]
$HB{=}CHOCH_3$ (**5**)			
syn-eclipsed	34.6	5.8	46.2
syn-staggered	33.7	7.3	48.3
anti-eclipsed	29.0	6.1	41.2
anti-staggered	27.5	7.4	42.3
$H_2C{=}CHOCH_3$, methyl vinyl ether (**1**)			
syn-eclipsed	49.1	5.5	60.1
syn-staggered	48.4	6.9	62.2
anti-eclipsed	41.1	7.2	55.2
anti-staggered	41.7	7.2	56.1
$HN{=}CHOCH_3$ (NH anti to oxygen) (**7**)			
syn-eclipsed	60.5	4.9	70.3
syn-staggered	59.7	6.1	71.9
anti-eclipsed	53.5	5.7	64.9
anti-staggered	51.7	7.0	65.7
$HN{=}CHOCH_3$ (NH syn to oxygen) (**9**)			
syn-eclipsed	56.0	5.3	66.6
syn-staggered	55.1	6.7	68.5
anti-eclipsed	51.9	5.6	63.1
anti-staggered	50.2	6.8	63.8
$O{=}CHOCH_3$, methyl formate (**11**)			
syn-eclipsed	74.4	4.6	83.6
syn-staggered	73.3	5.7	84.7
anti-eclipsed	68.4	5.3	79.0
anti-staggered	66.7	6.4	79.5

[a] The conjugation energy between the oxygen lone pair and hydrogen has been doubled when computing the total to account for both hydrogens involved.

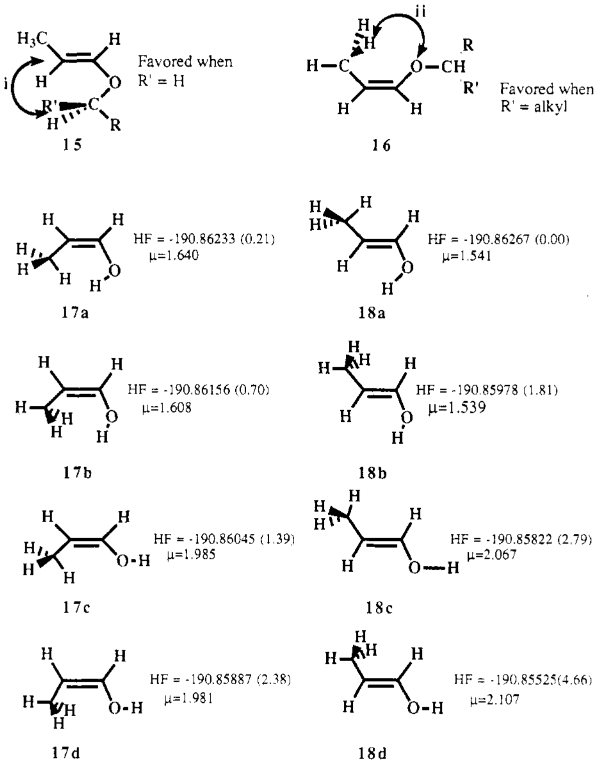
Table IX. Conjugation Energy (kcal/mol) of the Oxygen Out of Plane Lone Pair with the Double Bond in the Series $H_nX{=}CHOH$

molecule	syn	anti
$HB{=}CHOH$ (**4**)	31.6	27.9
$H_2C{=}CHOH$ (**2**)	46.4	42.0
$HN{=}CHOH$ (**6**)	56.7	52.0
$HN{=}CHOH$ (**8**)	54.1	50.3
$O{=}CHOH$ (**10**)	69.6	66.1

proposed by Larson et al. varies from strongly favoring the syn conformer for formic acid (**10**) to having no effect for vinyl alcohol (**2**). The failure of this hyperconjugation to have any significant influence on the conformation of vinyl alcohol can be attributed to the energy of the C–C σ^* orbital being higher than originally estimated.

There are two other interactions of interest. As expected, the lower energy O–R bond does not hyperconjugate as effectively as the lone pair; however, it does make a noticeable contribution that favors the syn conformer for the electronegative elements and tapers off as the polarity of the bond decreases. In addition, there is an interaction favoring the syn conformation that results from a weak overlap of the C-O σ^* orbital with the electron pair on atom X that is anti to the C–O σ bond (the X–H bond in **1**, **2**, **6**, and **7** or the nonbonding electron pair of **8**, **9**, **10**, and **11**) with the latter's σ^*. This interaction is strengthened by increasing the XCO angle, thus moving the antibonding orbital closer to the electron pair. As we have previously noted, this is exactly what happens when the conformation changes from anti to syn.

Chart IV



Of greatest interest, however, are the differences in the conjugation as the conformation changes. The statement, "as there are no significant differences in the π interactions of the two conformers..."[18] summarizes the common wisdom regarding these systems. As shown in Tables VIII and IX, this assumption is incorrect. The conjugation energy is consistently 5–8 kcal/mol greater in the syn conformation than in the anti.

In the discussion above, it has been noted that the XCO bond angle is larger in the syn conformation than in the anti. In an allyl system, the terminal atoms carry all of the electron density of the nonbonding orbital and have opposite mathematical signs. Thus moving the two lobes of these orbitals apart, as happens when the XCO bond angle is increased, decreases the repulsion and allows an increased occupancy of the orbital. In the unsaturated ethers described here, it is the 3A″ orbital which is most analogous to the allyl nonbonding orbital, and the most visible evidence of the increased conjugation can be seen in the natural atomic populations shown for methyl vinyl ether and vinyl alcohol in Table X. The change for oxygen is minimal, but an increased polarization of the double bond is evident from the data.

The boron compounds **4** and **5** prefer the syn conformation despite the minimal difference between the dipole moments. In these instances, the increased conjugation becomes the major stabilizing force for the syn conformation. For the others, the increased conjugation acts in

Table X. Atom Populations in Methyl Vinyl Ether and Vinyl Alcohol

	Mulliken population analysis			natural population analysis		
molecule	C_1	C_2	O	C_1	C_2	O
methyl vinyl ether (**1**)						
syn-staggered	−0.54	0.18	−0.68	−0.60	0.19	−0.58
anti-staggered	−0.52	0.19	−0.68	−0.54	0.17	−0.58
vinyl alcohol (**2**)						
syn	−0.54	0.16	−0.70	−0.60	0.19	−0.72
anti	−0.51	0.15	−0.70	−0.55	0.15	−0.72

Table XI. Conjugation Energy (kcal/mol) of the Oxygen Out of Plane Lone Pair with the Double Bond as a Function of the CCO Angle for Vinyl Alcohol

bond angle, deg	syn	anti
121	34.50	37.07
123	35.25	37.59
125	35.97	38.07
127	36.66	38.52

concert with the reduced dipole moment to stabilize the syn relative to the anti conformation.

Application

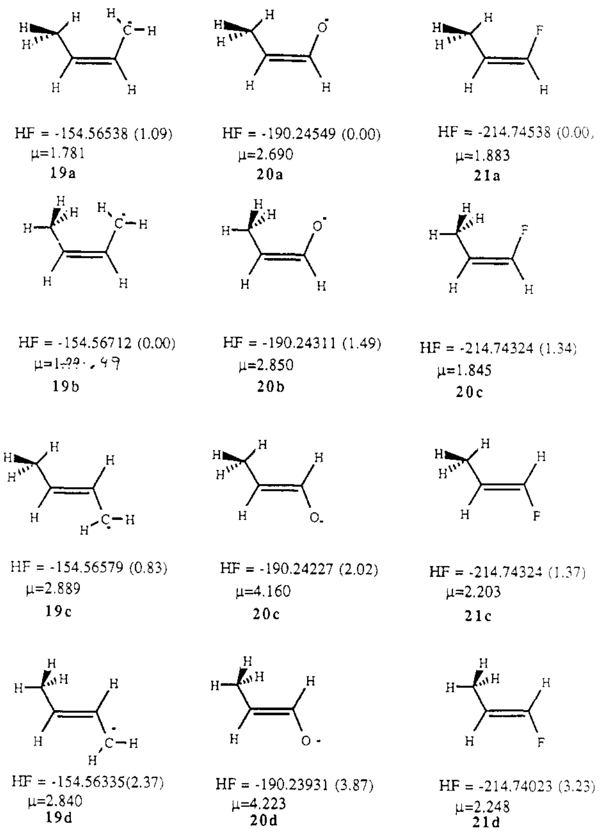
Among the experimental evidence used to support the pseudoaromaticity hypothesis is the study by Okuyama et al.[40] of the relative stabilities of the enol ethers **15** and **16** (Chart IV). The *E* isomer **15** is preferred when R′ is hydrogen; however, for R′ = alkyl, the equilibrium shifts and favors **16**. Bernardi et al.[5] rationalized these results in terms of two pseudoaromatic interactions, i and ii. They reasoned that the preference for **15** when R′ is hydrogen suggested that interaction i was stronger; however, as increasing steric bulk decreased the stability of the syn conformation, the availability of interaction ii in the *Z* isomer shifted the equilibrium toward the right.

We performed 3-21G optimizations of the enols **17a–d** and **18a–d** as models for the enol ethers studied by Okuyama.[35] The results, shown in Chart IV, provide additional evidence for our proposals. It is no surprise that the syn conformation of the enol is the most stable in both **17** and **18**. In either case, the favored conformation of the methyl group has the hydrogen eclipsed against the double bond, the differences in dipole moments are small, and the relative energies show that **18a** is 0.21 kcal more stable than **17a**. It is probable that this preference would be larger for an enol ether than it is for the enol itself. The difference in dipole moments between the four syn conformers of **17** and **18** or between the four anti conformers is small.

As expected, the dipole moments of the anti conformation of the enols are much larger than those of the syn conformation, and this explains the preference for syn conformation and, hence, the *E* isomer. However, when the syn conformer becomes sterically congested, the anti conformation is adopted. In this case, the lower dipole cis isomer **17c** is favored over the trans, **18c**, by 1.40 kcal/mol. It is probable that increased conjugation in **17c** also plays a role in its greater stability. Further the data refute the possibility of a pseudoaromatic interaction because enol **17d** is required for interaction ii proposed by Bernardi et al. However, this conformer is nearly 1 full kcal/mol higher in energy than **17c**, the lowest energy conformer with an anti hydroxyl group.

Chart V shows the 3-21G energies of the crotyl anion (**19**), the propanal enolate anion (**20**), and 1-fluoropropene (**21**), all of which are capable of possessing pseudo-aromatic interactions. The data show the same preference for the *Z* isomer as is shown in the anti conformation of the enol. Furthermore, as the polarity of the substituent increases, the difference in dipole moment increases, and there is a corresponding increase in the relative energies.

Chart V



HF = -154.56538 (1.09)
μ=1.781
19a

HF = -190.24549 (0.00)
μ=2.690
20a

HF = -214.74538 (0.00)
μ=1.883
21a

HF = -154.56712 (0.00)
μ=1[illegible].49
19b

HF = -190.24311 (1.49)
μ=2.850
20b

HF = -214.74324 (1.34)
μ=1.845
20c

HF = -154.56579 (0.83)
μ=2.889
19c

HF = -190.24227 (2.02)
μ=4.160
20c

HF = -214.74324 (1.37)
μ=2.203
21c

HF = -154.56335(2.37)
μ=2.840
19d

HF = -190.23931 (3.87)
μ=4.223
20d

HF = -214.74023 (3.23)
μ=2.248
21d

Rotation of the methyl group induces little change in the dipole moment; there is an increase in energy of 1.34–1.86 kcal/mol as the methyl group moves from eclipsing to staggering the double bond except in the *Z*-crotyl anion.[41] NBO analysis of the wave functions of all three of these compounds confirms recent work supporting the proposal that this stabilization is a result of a larger interaction between the occupied orbitals of π symmetry on the methyl group and the π^* orbitals of the C=C bond in the eclipsed conformation.[12,42]

Schleyer et al.[14] invoked pseudoaromaticity to account for the fact that the *E* isomer is preferred for the crotyl cation and radical, while the anion prefers the *Z* isomer by 4.0 kcal/mol (at 3-21G; the difference increases to 4.7 kcal/mol at MP2/6-31G*//3-21G). NBO analysis of the wave functions of **19–21** again showed that there were no interactions to support such a hypothesis.

We do note, however, that there is a large difference in dipole[43] between the *Z* (**19b**) and *E* (**19c**) isomers of the crotyl anion (0.49 and 2.89 D, respectively), and corresponding differences for the others, giving additional support to our proposal that the dipole moments play a significant role in determining the preferred isomer. Unlike other systems reported here, the global minimum of the crotyl anion has the methyl group staggering the double bond as would be required for the pseudoaromaticity instead of eclipsing it. Further, the trans crotyl anion has the eclipsed methyl as is normal. This is the only exception to the double bond eclipsing rule that we have found and has been rationalized[44] on the basis of electrostatic attractions between the positive methyl hydrogens

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[43] Dipole moments for the charged compounds reported here are defined relative to the center of mass. We have assumed that this center is approximately the same for methyl rotamers. This assumption will not be true for the geometric isomers **19b** and **19c**. Because of this, the dipole computed for **19c** is smaller than it would be if calculated on the same basis as **19b**; hence, our conclusions should still be valid.

[44] Schleyer, P. v. R.; Kaneti, J.; Wu, Y. D.; Chandrasekar, J., manuscript in preparation.

and the anion. The carbanion is a much more effective donor than either the fluoro or oxyanion, and the methyl group rotates from the normal eclipsed, which offers only one acceptor hydrogen, to the staggered, which offers two acceptor hydrogens.

The preference of the aforementioned compounds for the cis isomer parallels the behavior of the dihaloethenes[45] and the halopropenes.[46] The phenomena has been termed the "cis effect",[47] and Crumb has invoked interactions involving permanent dipoles to account for this behavior.[48]

Conclusions

In this paper, we have examined the energies, structures, and intramolecular interactions in X=COR compounds. The calculated conformational preferences are in accord with experiment, where these are known. The decrease in bond angles that occurs when the conformations change from syn to anti have been rationalized in terms of orbital repulsions. In addition, these angle changes give rise to an increased lone pair–double bond conjugation in the syn conformation. While we find $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ interactions to be significant in magnitude, they are unimportant in determining the preferred conformations.

The six-electron pseudoaromatic interaction previously suggested as being responsible for the preferred conformation of methyl vinyl ether and related molecules either is absent or is insignificant. Instead, we propose intramolecular electrostatic interactions to be the most significant factor in determining the preferred conformation. This rationalization has been employed to explain both computational and experimental data for a wide variety of compounds, including vinyl sulfide, methyl vinyl sulfide, vinyl formate, the crotyl anion, and the halopropenes. Taken together with other reports in the literature,[36-38,44,45] the electrostatic effects appear to make a significant contribution in determining the preferred molecular conformation.

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Supplementary Material Available: Absolute energies and geometries of all species calculated here in GAUSSIAN 82 Archive Format (5 pages). Ordering information is given on any current masthead page.

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"Mixed Staffanes" as Intermediate-Length Staffs for Molecular-Size Tinkertoys. Parent Hydrocarbons and Terminal Diiodides Combining Bicyclo[1.1.1]pentane with Cubane or Bicyclo[2.2.2]octane Units

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Photochemically induced addition of [1.1.1]propellane across one or both of the C–I bonds in the 1,4-diiodocubane and 1,4-diiodobicyclo[2.2.2]octane yields doubly terminally functionalized straight molecules ("mixed staffanes") whose length is intermediate between those of the parent [*n*]staffanes differing by one in the value of *n*. Conversion to terminal dilithio derivatives and to the parent hydrocarbons is described, and a single-crystal X-ray structure of 1,4-bis(bicyclo[1.1.1]pent-1-yl)cubane is presented.

[*n*]Staffanes **[*n*]1**, the oligomers of [1.1.1]propellane 1,[1,2] have been proposed as building block units for a molecular-size "Tinkertoy" construction set.[3,4] The facile synthesis, thermal stability, chemical inertness, transparency, straight linear geometry, and short-length increment of only $\sim 3^1/_3$ Å are the main advantages of these molecules. However, it is desirable to have staffs with intermediate lengths and otherwise similar properties. A way to achieve this would be to dope the staffs with rigid straight polycyclic units other than bicyclo[1.1.1]pentane. Inspired by the successful photochemical insertion of 1 into a variety of C–I bonds,[3,5] and particularly that of 1,3-diiodo[1]staffane, 2, which yields 3,3′-diiodo[2]staffane, 3, the photochemical reactions of 1,4-diiodocubane (4) and 1,4-diiodobicyclo[2.2.2]octane (5) with 1 were investigated.

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