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Barriers to Rotation Adjacent to Double Bonds. 5. Remote Substituent Effects on the Syn/Skew Energy Difference for 1-Butene

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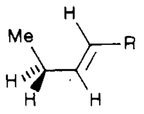
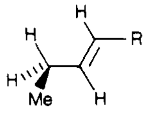
The effect of a trans-1-substituent on the difference in energy between the syn and skew rotamers of 1-butene was estimated by carrying out ab initio molecular orbital calculations using the 6-31G* basis set and then correcting the energies for the effect of electron correlation. Except for R = NH_3^+, the skew rotamer was calculated to have the lower energy, and the proportion of the skew form was found to increase in the order R = CHO, H, Me, F, and NH_2. The effect of the substituents on the calculated structures was examined and suggested that a major part of the change in syn/skew ratio may arise from subtle geometric changes induced by the substituents via steric and rehybridization effects. The conjugation of a carbonyl or amino group with a double bond does not lead to a significant increase in C═C bond lengths, and a rotation which should eliminate resonance effects does not lead to charge shifts in the expected direction. These data indicate that dipolar resonance structures have little importance in the ground states of these molecules.

A recent experimental observation[1] suggested that substituents at the 1-position of a 1-alkene might affect the ratio of alkyl vs hydrogen eclipsed rotamers about the adjacent sp^2–sp^3 bond. Some preliminary ab initio molecular orbital calculations using the 3-21G basis set reproduced a trend suggested by the experimental data. Since conformational issues of this type are frequently encountered in attempts to achieve a stereoselective addition to an unsaturated group, it appeared desirable to examine the problem by using a higher level of theory.

The effect of heteroatom substituents on a hydrocarbon chain generally requires the inclusion of polarization functions at the non-hydrogen atoms (i.e., d orbitals).[2] In addition, we have found that correction for electron correlation is needed if the energy difference is to be calculated correctly.[3] Therefore, we have carried out geometry optimizations for the following compounds using the 6-31G* basis set: where R = H, Me, F, NH_3^+, NH_2, and CHO. The latter two substituents were involved in the initial experimental observations. Although enals prefer a transoid (*s*-trans) conformation, they frequently react in a cisoid (*s*-cis) form. Therefore, both forms of the enals were examined. The fluorine and ammonium groups would provide examples of very electronegative substituents, and the methyl group might give information on possible steric interactions. For example, in the syn rotamer, there may be a repulsive interaction between the terminal methyl group and the syn olefinic hydrogen. A relatively bulky substituent such as R = methyl could change the bond angles at the terminus of the double bond and thereby increase the steric interaction.



syn



skew

The effect of electron correlation was examined by using the Moller–Plesset perturbation method through the third order (MP3).[4] The energies of the compounds are summarized in Table I, and the more interesting relative energies (skew–syn) are given in Table II. The main structural information is summarized in Table III.

Table I. Energies of Substituted 1-Butenes, 6-31G*

R	rotamer	RHF	MP2	MP3
NH_3^+	syn	−211.49289	−212.16607	−212.21301
	skew	−211.49365	−212.16626	−212.21294
CHO (t)	syn	−268.83780	−269.64630	−269.68344
	skew	−268.83863	−269.64668	−269.68361
CHO (c)	syn	−268.83556	−269.64432	−269.68128
	skew	−268.83640	−269.64477	269.68150
H	syn	−156.10498	−156.61940	−156.65909
	skew	−156.10608	−156.62020	−156.65963
Me	syn	−195.14360	195.78957	−195.83832
	skew	−195.14503	−195.79059	−195.83910
F	syn	−254.95365	−255.63548	−255.66980
	skew	−254.95525	−255.63689	−255.67087
NH_2	syn	−211.12831	−211.80619	−211.84898
	skew	−211.13029	−211.80792	211.85039

Table II. Relative Energies of 1-Substituted 1-Butenes (kcal/mol)

R	RHF	MP2	MP3	obsd
NH_3^+	−0.48	−0.12	+0.04	
CHO (t)	−0.52	−0.24	−0.11	
CHO (c)	−0.53	−0.28	−0.14	
H	−0.69	−0.50	−0.33	−0.15[5]
Me	−0.90	−0.64	−0.49	
F	−1.00	−0.88	−0.67	
NH_2	−1.24	−1.09	−0.88	

An experimental energy difference is available only for 1-butene itself, and here it is −0.15 kcal/mol (i.e., the skew rotamer having the lower energy).[5] The calculated MP3 energy difference −0.33 kcal/mol) is in good accord with the observed value. It should be noted that this stands in marked contrast to the corresponding carbonyl compounds where the syn rotamer is favored.[6] The dipole-induced dipole stabilizing interaction present in the carbonyl compounds[7] is missing in the alkenes, and this probably accounts in large measure for the difference in conformational preference.

If one compares the calculated structures of the syn and skew rotamers (Table III), it is seen that the angles α_1, α_2,

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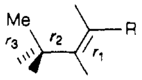
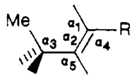
Table III. Structural Data for Substituted 1-Butenes





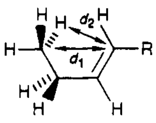
R		r_1	r_2	r_3	α_1	α_2	α_3	α_4	α_5
NH_3^+	syn	1.315	1.505	1.526	126.97	125.48	116.14	120.71	115.34
NH_3^+	skew	1.314	1.503	1.534	126.42	123.93	111.84	121.12	116.28
CHO (t)	syn	1.325	1.503	1.526	123.04	127.49	115.95	120.84	114.64
CHO (t)	skew	1.324	1.501	1.533	122.22	125.80	112.25	121.32	115.71
CHO (c)	syn	1.326	1.502	1.526	122.26	127.34	116.23	121.06	115.63
CHO (c)	skew	1.325	1.500	1.533	121.46	125.62	112.15	121.55	116.71
H	syn	1.319	1.508	1.526	122.74	127.21	115.86	121.11	114.51
H	skew	1.319	1.505	1.532	121.85	125.40	112.51	121.69	115.71
Me	syn	1.320	1.508	1.527	119.82	127.25	116.06	124.75	114.46
Me	skew	1.320	1.505	1.532	118.94	125.37	112.62	125.29	115.66
F	syn	1.311	1.507	1.528	126.88	125.89	115.78	121.46	116.83
F	skew	1.310	1.505	1.532	125.91	123.66	112.55	122.13	118.09
NH_2	syn	1.325	1.510	1.528	120.75	126.22	115.87	126.40	115.37
NH_2	skew	1.325	1.506	1.532	119.79	123.98	113.11	127.04	116.84

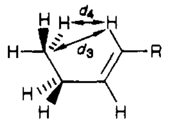
Table IV. Energies and Electron Populations for Acrolein and Vinylamine

	trans (**1a**)	rotated (**1b**)
A. Acrolein, 6-31G*//6-31G*		
energy (H)	−190.76242	−190.74932
E(rel), kcal/mol	0.00	8.22
O	9.320	9.309
C2	4.748	4.748
C3	6.012	6.073
C4	6.059	5.998
H5	0.945	0.956
H6	0.953	0.964
H7	0.965	0.968
H8	0.996	0.985
sum	29.998	30.001

	"planar" (**2a**)	90° (down) (**2b**)	90° (up) (**2c**)
B. Vinylamine, 6-31+G*//6-31G*			
energy (H)	−133.06858	−133.06112	−133.05884
E(rel), kcal/mol	0.00	4.68	6.11
N	8.338	8.237	8.243
C2	5.557	5.580	5.567
C3	5.976	6.016	6.047
H4	0.994	0.955	0.984
H5	0.978	0.979	0.973
H6	0.973	0.997	0.972
H7	0.592	0.618	0.608
H8	0.591	0.618	0.608
sum	23.999	24.000	24.002

Table V. Nonbonded Distances in Syn Rotamers





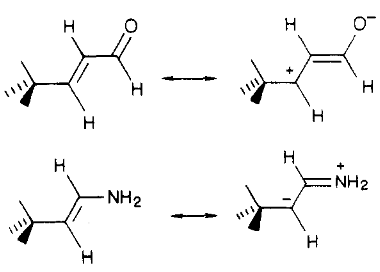
R	d_1	d_2	d_3	d_4
NH_3^+	2.995	2.869	2.715	2.520
CHO (t)	2.995	2.980	2.709	2.507
CHO (c)	2.997	2.984	2.696	2.496
H	2.989	2.971	2.692	2.487
Me	2.995	2.981	2.645	2.448
F	2.956	2.942	2.716	2.509
NH_2	2.975	2.957	2.629	2.429

and α_3 are all significantly larger in the syn rotamer than in the skew form. This change in structure along the carbon chain can only be due to a steric interaction between the methyl and a terminal olefinic hydrogen in the syn form. Therefore, it is not surprizing that the skew rotamer is preferred in most cases.

The one exception is found with R = NH_3^+ where the syn rotamer is predicted to be slightly favored at equilibrium. This substituent is unique in the present group in that it has a very strong inductive effect but does not have the possibility of electron-donation via back-bonding. As a result, it should lead to a relatively large C=C bond dipole which may now interact with the adjacent C—C bond via a dipole-induced dipole interaction. Thus, it appears to be able to help stabilize the syn rotamer in much the same fashion as found for a carbonyl group, although the polarity is opposite to the latter. The calculated stabilization of the syn form by NH_3^+ as compared to CH_3 is 0.5 kcal/mol, about half of the effect of a carbonyl group on an adjacent alkyl group.

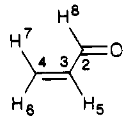
The calculated energy differences suggest that the aldehyde group gives a slightly smaller energy difference than found with the parent and that there is little difference between the cisoid and transoid forms. The latter is predicted to be 1.4 kcal/mol more stable than the former. The other substituents favor the skew form in the order NH_2 > F > Me. The energy changes could be due to structural changes, to electronic effects, or both. The question of structural changes may be explored by examining Table III.

The small range of calculated C=C bond lengths might first be noted, with R = NH_2 or CHO giving a length only 0.005 Å greater than that for R = Me. This is not what would be expected if the ionic cannonical structures contributed significantly to the ground-state structures: A

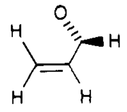


C–C single bond is about 0.2 Å longer than a double bond, and therefore a change of 0.005 Å is negligible and suggests no significant change in double-bond character. Consequently, the conjugative interaction suggested by the above resonance structures is probably unimportant.

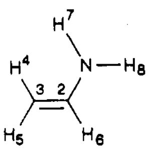
In order to further examine this important question, we have calculated the electron populations for the atoms in acrolein (**1**) and vinylamine (**2**) in both the lower energy and 90° rotated conformers. A 90° rotation should eliminate any possible resonance interaction of the type indicated above, and if the dipolar resonance structures were important in stabilizing the ground states, there should be significant charge shifts on rotation. The electron populations were obtained by integration of the charge density derived from the MO wave functions, making use of the boundary conditions required by Bader's theory of atoms in molecules.[8] The results are shown in Table IV.



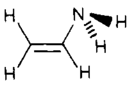
1a



1b



2a



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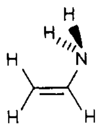

2c

With acrolein, the traditional resonance interpretation would lead to a lower electron population at C4 in the planar structure as opposed to that rotated 90°. The calculated change in population is small and in the *opposite* direction to that which would be anticipated. Vinylamine should have an increased electron population at C3 in the essentially planar form if the dipolar structure were important. Here again, the calculated change in population is small and *opposite* to that required for a resonance interaction.

The interaction between these groups and the double bond might best be considered as a resonance force interaction[9] which involves the correlated motions of the π-electrons in each of the two independent units (double bonds or lone pairs) and also requires coplanarity of the units. This type of interaction is important in most noncyclic conjugated systems such as butadiene and styrene. The rotational barrier in vinylamine is somewhat smaller than that of butadiene (6.6 kcal/mol[10]) and that for acrolein is slightly larger. The origin of the barrier in compounds such as this will be considered in detail at a later time. The reactivity associated with enals and enamines is not mainly a ground-state phenomenon but rather results from the relatively facile polarization of the double bond in the presence of an attacking reagent.

Returning to the geometrical parameters for the substituted 1-butenes, the angle α_4 in Table III reflects steric interactions between the R substituent and the vicinal (vinylic) CH group. In examining the syn rotamers, one finds that the relatively large methyl group leads to a 3.6° increase in angle and amino leads to a 5.3° increase. On the other hand, fluorine and the carboxaldehyde group lead to little change as compared to 1-butene.

The angle α_1 will respond both to changes in α_4 and to the nature of the substituent at the allylic carbon. Both methyl and amino, which provide larger values of α_4, give correspondingly smaller values of α_1 as expected. The largest α_1 values are found with F or NH_3^+ as the substituents. When an electronegative group is attached to a carbon, it will tend to favor a high p component in the carbon orbital, and this will result in increased s character in the bond to the other atoms attached to the carbon and an increased bond angle opposite to the electronegative substituent. Changes in α_1 and α_4 will lead to changes in α_2 and α_5. The remote angle, α_3, does not change significantly through the series of syn rotamers.

It is difficult to consider possible steric interactions by looking at the bond angles, and therefore some nonbonded distances in the syn forms are given in Table IV. Here, the substituents are given in order of increased skew forms. The case where R = NH_3^+ will not be considered since, as discussed above, it appears to have a special interaction which is not present in the other compounds. The smallest d_3 and d_4 distances are found with the NH_2 substituent, and the smallest d_1 and d_2 distances are found with F as the substituent. The largest nonbonded distances are found with R = CHO. Thus the order of substituents is roughly in the order of increasing steric interaction between the methyl group and the double-bond carbon holding the substituent.

It is likely that geometrical changes caused by substituents will have a significant affect on conformational preferences in other systems. It is important to consider such effects before trying to explain conformational preferences in terms of orbital interactions.

Calculations. The calculations were carried out by using GAUSSIAN-82[11] using standard basis sets.[12]

Acknowledgment. This investigation was supported by a grant from the National Institutes of Health. The initial geometry optimizations at the 3-21G level were carried out at Yale using a MicroVax II which was made available via an NSF instrument grant. The 6-31G* geometry optimizations and the post Hartree–Fock calculations were carried out on a Cray computer at the Pittsburgh supercomputer center with the aid of a grant from that center.

Registry No. 1, 107-02-8; 2, 593-67-9; (*E*)-$CH_3CH_2CH{=}CHNH_2{\cdot}H^+$, 112347-84-9; (*E*)-$CH_3CH_2CH{=}CHCHO$, 1576-87-0; (*Z*)-$CH_3CH_2CH{=}CHCHO$, 1576-86-9; $CH_3CH_2CH{=}CH_2$, 106-98-9; (*E*)-$CH_3CH_2CH{=}CHCH_3$, 646-04-8; (*E*)-$CH_3CH_2CH{=}CHF$, 66675-35-2; (*E*)-$CH_3CH_2CH{=}CHNH_2$, 112347-85-0.

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