

and $\lambda \sim 0.1$ for a strong bond (overlap = 0.8).⁴² The GVB pair lowering, ΔE , is the energetic destabilization realized in replacing the GVB pair ($\sigma^2 - \lambda^2\sigma^{*2}$) by the one configuration (molecular orbital) term (σ^2). A small overlap of the two GVB orbitals indicates large pair lowering energy, and in this case a valence bond description is greatly preferred over the MO description.

In Table II we list these calculational results for the GVB(3/6) wave functions describing the metallacyclopropane and π -complex resonance structures. For comparison, we include the analogous data for the two carbon-carbon bonds in ethylene,⁴³ the carbon-carbon bond in ethane,⁴³ the carbon-carbon bond in cyclopropane,⁴³ the titanium-carbon bond in $\text{Cl}_2\text{Ti}(\text{CH}_3)(\text{H})$,⁴⁴ and the lone pair on Ti in Cl_2Ti .⁴⁵

From these and other data we may generalize that Ti-C bonds are characterized by bond orbitals having an overlap of ~ 0.6 - 0.65 . This is significantly smaller than the overlap of bonding orbitals in a carbon-carbon σ bond (~ 0.8 - 0.85). Also, the inclusion of the second configuration (σ^{*2}) in the molecular wave function is energetically twice as important in the titanium-carbon bond as in the carbon-carbon bond.

Data in Table II indicate that the Ti-C bonds in the metallacyclopropane are quite similar to the "normal" TiC bond in $\text{Cl}_2\text{Ti}(\text{CH}_3)(\text{H})$. Contour plots of the orbitals of this TiC bond are shown in Figure 13. Comparison of these orbitals with the orbitals describing the Ti-C bond in the metallacyclopropane (Figure 2) shows the bent character of the latter bond. Similar plots of the orbitals of the C-C bond in ethane are shown in Figure 14. These two bonding orbitals point directly at one another, unlike the corresponding orbitals of the C-C bond in cyclopropane (Figure 4). Comparison of the two carbon-carbon bonds with the two titanium-carbon bonds shows that there is the same relationship between the two Ti-C bonds as between the two C-C bonds. In this way an evaluation of these GVB wave functions makes the strain in the titanacyclopropane apparent.

The nonpolarity of the Ti-C bonds in both the metallacyclopropane and $\text{Cl}_2\text{Ti}(\text{CH}_3)(\text{H})$ is also apparent from the plots of the GVB orbitals. Note that in each case there is one orbital that

is centered on the metal atom and one orbital centered on the carbon. As a contrasting example, the two GVB orbitals for the Cr-H bond of the d^5 sextet state of CrH ⁴⁶ are shown in Figure 15. This bond is polar ($\text{Cr}^+ \rightarrow \text{H}^-$) because both orbitals (ψ_a and ψ_b) are centered on the hydrogen. Not surprisingly, this polarity also results in a higher overlap (0.77) in this bond than in a typical nonpolar M-H bond (overlap = 0.62 in the Ti-H bond in Cl_2TiH_2).

Finally, we can assess the shape of the titanium bonding orbital in the metallacyclopropane by plotting the amplitude of this orbital in the plane perpendicular to the Ti-C-C ring and along one of the Ti-C bond axes. This plot is shown in Figure 16. From this it is apparent that the Ti bonding orbital is shaped like a d_{z^2} orbital, just as in $\text{Cl}_2\text{Ti}^+-\text{H}$, $\text{Cl}_2\text{Ti}-\text{H}$, Cl_2TiH_2 , $\text{Cl}_2\text{Ti}(\text{CH}_3)(\text{H})$, $\text{Cl}_2\text{Ti}(\text{CH}_2)_3$, $\text{Cl}_2\text{Sc}-\text{H}$, Cl_2ZrH , and Cl_2ZrH_2 .^{10,12,47} The shape of this bonding orbital is critical when evaluating the propensity of this bond to participate in 2 + 2 reactions, as mentioned in the above text. The fact that there is a ring of negative amplitude about the waist of the "dumbbell" of positive amplitude in this orbital means that the $2_s + 2_s$ substrate can approach the reaction bond from any azimuthal direction to form the quadrilateral transition state required for the pericyclic reaction.

The wave function that describes the π -complex form is not surprising. The orbitals in Figure 17 show a doubly occupied d orbital in the singlet state of Cl_2Ti . Comparison of these plots with the corresponding plots for the π -complex form of $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4)$ shows only minor changes. The changes observed in the two carbon-carbon bonds in the C_2H_4 unit, when complexed to the metal, are not surprising. These bond orbitals in the π -complex indicate some distortion from the normal double bond in ethylene (Figure 18), but the ring strain is not nearly as clearly demonstrated here as in the metallacyclopropene form. Furthermore, it is not clear from the π -complex wave function that the ring strain is actually relieved along the 2 + 2 reaction pathway. In this way the ring strain, a *thermodynamic* quantity, can at least qualitatively be related to the *kinetics* of the 2 + 2 migratory insertion reaction.

Registry No. 3, 97391-51-0; 4, 83314-27-6; ethane, 74-84-0; cyclopropane, 75-19-4; ethylene, 74-85-1.

(42) This is the overlap of the two GVB orbitals describing the H-H bond in H_2 .

(43) Geometry of this species taken from "Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology. Group II, Volume 7, Structure Data of Free Polyatomic Molecules", K.-H. Hellwege, Ed.; Springer Verlag, Berlin, 1976.

(44) For these model calculations we kept the Cl_2Ti fragment frozen, assigned $r(\text{Ti}-\text{H}) = 1.70 \text{ \AA}$ (ref 12), $r(\text{Ti}-\text{C}) = 2.02 \text{ \AA}$ (ref 10), and $\vartheta(\text{C}-\text{Ti}-\text{H}) = 75^\circ$ (ref 10).

(45) $r(\text{Ti}-\text{Cl}) = 2.328 \text{ \AA}$ and $\vartheta(\text{Cl}-\text{Ti}-\text{Cl}) = 140^\circ$.

(46) The geometry of this diatomic was taken from Huber and Herzberg: K. P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules", Van Nostrand Reinhold Co., New York, 1979. Value $r(\text{Cr}-\text{H}) = 1.655 \text{ \AA}$ was used. See also: S. P. Walch and C. W. Bauschlicher, Jr., *J. Chem. Phys.*, **78**, 4597 (1983).

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Barriers to Rotation Adjacent to Double Bonds

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Abstract: The barriers to internal rotation about C—C single bonds adjacent to C=O or C=C groups have been calculated via ab initio MO theory, and the results are compared with experimental data. With acetaldehyde, acetone, and propene, the calculated barrier is almost independent of basis set, is not significantly affected by correction for electron correlation, and agrees well with the experimental value. On the other hand, the calculated barriers for propanal, 2-butanone, and 1-butene are strongly basis set dependent, and only the 6-31G* set, which includes polarization functions at carbon, gives relative energies which are in reasonable agreement with experiment. Electron correlation has a small effect on the barrier height. The components of the barrier are discussed. The barriers for acetaldehyde, acetone, propene, and 1-butene appear to have the same origin as that for ethane. With propanal and 2-butanone, there are additional terms which arise from a dipole-induced dipole interaction between the carbonyl group and the C—C bond of the ethyl group, and from the overlap of the bond orbitals of these groups.

Our studies of the enthalpies of hydrolysis of acetals, ketals, and ortho esters¹⁻⁴ has led us to investigate the effect of structure

on the energies and conformations of the above, as well as their hydrolysis products, the aldehydes, ketones, and esters. This report

Table I. Energies of Compounds with Threefold Barriers^a

compound	conf	STO-3G	3-21G	6-31G*		
		RHF	RHF	RHF	MP2	MP3
acetaldehyde	e	-150.94599	-152.05525	-152.91596	-153.34456	-153.36034
	s	-150.94421	-152.05344	-152.91427	-153.34296	-153.35870
acetone	ee	-189.53603	-190.88722	-191.96223	-192.52163	-192.54674
	es	-189.53424	-190.88572	-191.96089	-192.52033	-192.54530
	ss	-189.53168	-190.88302	-191.95865	-192.51810	-192.54315
propene	e	-115.66030	-116.42401	-117.07146	-117.45471	-117.48494
	s	-115.65784	-116.42118	-117.06816	-117.45159	-117.48193

^aEnergies are given in hartrees (1 hartree = 627.5 kcal/mol).

Table II. Energy Differences for Compounds with Threefold Barriers (kcal/mol)

compound	conf	STO-3G	3-21G	6-31G*			obsd
		RHF	RHF	RHF	MP2	MP3	
acetaldehyde	e	0.00	0.00	0.00	0.00	0.00	0.00
	s	1.12	1.14	1.06	1.00	1.03	1.17
acetone	ee	0.00	0.00	0.00	0.00	0.00	0.00
	es	1.12	0.94	0.86	0.82	0.90	0.76
	ss	2.73	2.64	2.25	2.22	2.25	
propene	e	0.00	0.00	0.00	0.00	0.00	0.00
	s	1.54	1.78	2.07	1.96	1.89	2.00

will be concerned with the conformations and energies of some simple aldehydes and ketones. In order to provide a basis for comparison, it also includes the corresponding alkenes.

These compounds have received considerable study experimentally,⁵ and theoretically.⁶⁻¹⁰ Our primary interest is with compounds having an ethyl side chain, but we initially studied those having methyl as the substituent, i.e., acetaldehyde, acetone, and propene. Although calculations of the barriers have been reported, we wished to see if there were a significant dependence on the basis set used. The energies of the eclipsed and staggered conformations were calculated by using the STO-3G, 3-21G and 6-31G* basis sets,¹¹ with complete geometry optimization in each case. The energies are given in Table I, the calculated barriers

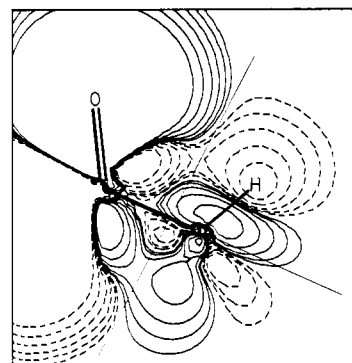


Figure 1. Electron density map for eclipsed acetaldehyde (6-31G*) less than for staggered acetaldehyde formed by 180° rotation about the C-C double bond. The dashed lines represent regions in which the electron density has been depleted in the eclipsed conformer, and the solid lines indicate regions in which electron density has been enhanced.

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


are given in Table II, and the 6-31G* geometries are summarized in Table III. It can be seen that the relative energies are almost basis set independent, and agree with the experimental values.

Conformational equilibria may involve a contribution from the attractive portion of the interaction between nonbonded atoms. This results from electron correlation, and will not be reproduced by the single determinant (RHF) calculations. In the case of acetaldehyde, it has been found that the correlation energy contributes very little to the rotational barrier.^{6c} We have examined the effect of electron correlation for all three compounds using the 6-31G* basis set and the Møller-Plesset method through the third order (MP3)¹² (Table I). No significant effect was found. Thus, these cases are very much like ethane, for which the rotational barrier is well calculated at any level of theory.¹³

The geometries agree quite well with the observed structures,¹⁴⁻¹⁶ which also are given in Table III. If the 6-31G*

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Table III. Structures of Compounds with Threefold Symmetry (6-31G*)

unit	conformation ^a			
	e	obsd	s(se)	ss
				
$\tau_{3,1,2,5}$	0.00	0.00 ^b	180.00	
$\tau_{3,1,2,6}$	120.88		58.90	
$r_{C=O}$	1.188	1.216	1.189	
$r_{1,2}$	1.505	1.501	1.509	
$r_{1,4}$	1.095	1.114	1.092	
$r_{2,5}$	1.081	1.086	1.082	
$r_{2,6}$	1.087		1.085	
$\angle 2,1,3$	124.27	123.9	123.81	
$\angle 2,1,4$	115.43		116.00	
$\angle 1,2,5$	110.10		111.14	
$\angle 1,2,6$	109.88		109.81	
$\angle 6,2,7$	107.23	108.3	107.70	
				
$\tau_{4,2,1,5}$	0.00	0.00 ^c	0.00	180.00
$\tau_{4,2,3,8}$	0.00	0.00	180.00	180.00
$\tau_{4,2,1,6}$	120.88		121.23	58.67
$\tau_{4,2,3,9}$	120.88		58.93	58.67
$r_{C=O}$	1.192	1.222	1.192	1.193
$r_{1,2}$	1.513	1.507	1.511	1.518
$r_{2,3}$	1.513	1.507	1.518	1.518
$r_{1,5}$	1.081	1.085	1.081	1.083
$r_{3,8}$	1.081		1.082	1.083
$r_{1,6}$	1.087		1.087	1.085
$r_{3,9}$	1.087		1.085	1.085
$\angle 4,2,1$	121.74		122.70	121.00
$\angle 4,2,3$	121.74		121.85	121.00
$\angle 2,1,5$	109.62	108.7	110.61	112.61
$\angle 2,3,8$	109.62		111.84	112.61
$\angle 1,2,3$	116.51	117.2	115.45	118.01
				
$\tau_{1,2,3,7}$	0.00	0.00 ^d	180.00	
$\tau_{1,2,3,9}$	120.53		60.08	
$r_{C=C}$	1.318	1.336	1.317	
$r_{2,3}$	1.503	1.501	1.511	
$r_{1,4}$	1.075	1.081	1.076	
$r_{1,5}$	1.077	1.091	1.078	
$r_{2,6}$	1.079	1.090	1.079	
$r_{3,7}$	1.085	1.085	1.084	
$r_{3,8}$	1.087	1.098	1.086	
$\angle 1,2,3$	124.91	124.3	124.70	
$\angle 2,3,7$	111.32	111.2	111.05	
$\angle 2,1,4$	121.96	121.5	121.93	
$\angle 2,1,5$	121.66	120.5	121.84	
$\angle 1,2,6$	119.16	119.0	118.90	
$\angle 8,3,9$	107.21	106.2	107.73	

^aUnits: Å and deg. ^bReference 14. ^cReference 15. ^dReference 16.

structures are expanded by about 0.7%, the resultant geometries have moments of inertia which agree well with the observed moments obtained via microwave spectroscopy.

What is the origin of the barrier for acetaldehyde, and why does the lower energy conformer have a methyl hydrogen eclipsed with the carbonyl group? It has been suggested that there is a weak covalent bond between the carbonyl oxygen and the eclipsed hydrogen.^{7a} An unambiguous requirement for such a bond is the presence of a bond critical point between the nuclei.¹⁷ No such critical point was found in an analysis of the 6-31G* wave functions. Another suggestion is that there is a hyperconjugative interaction between a methyl group C–H bonding orbital and the π^* orbital of the carbonyl group which favors the eclipsed con-

former.^{6a,e} The methyl tilt angle and the C–H bond lengths have been proposed as sensitive and experimentally accessible probes for the hyperconjugative interaction of a methyl with another group,^{6c} and such interactions are well established in some cases. The available experimental data for acetaldehyde are not adequate to define these geometrical parameters. Thus, we must resort to an examination of the calculated structure (Table III). It can be seen that the gauche/skew hydrogens (H_6 and H_7) have CCH bond angles which are close to tetrahedral in both conformers. In the eclipsed conformer, the CCH angle to H_5 is essentially the same as the other angles, leading to a methyl tilt of only -0.15° which is negligible. Much larger angles are seen in other compounds such as methylamine.^{6c} The small tilt angle found with acetaldehyde provides little support for hyperconjugation as an important interaction. The angle is larger in the staggered conformer (which has a methyl hydrogen eclipsed with the aldehyde hydrogen), but this is also observed with ethane and is probably a repulsive interaction.¹⁸ The calculated CH bond length to H_5 is shorter than that to the other methyl hydrogens, but this may be due to effects other than hyperconjugation.¹⁸

A third possibility is that the C=O dipole induces a dipole into the C–H bond, leading to an attractive interaction. In terms of orbital interactions, this corresponds to mixing the σ^* CH bond orbital with the σ CH orbital under the influence of the electric field generated by the dipolar carbonyl group. This should be revealed by a change in the electron population of the methyl hydrogens with rotation. A small change was found (Figure 1), but the effect on the nearby hydrogens in the staggered conformation was about half that for the eclipsed hydrogen. Since there are two of the former to one of the latter, the net difference is essentially zero. The inclusion of polarization functions (d orbitals at carbon) increases the polarization of the C–H bonds, but since the effect roughly cancels between the two conformations, there is little effect of basis set on the calculated energy differences.

The simplest view is that the oxygen has little net effect on the rotational barrier, and this is supported by other calculations.^{7d} It seems reasonable to conclude that the barrier in acetaldehyde has the same origin as that for ethane, which is the overlap (exchange) repulsion between the CH bond orbitals.¹³ The same conclusion may be reached for acetone. It is interesting to note that the barrier for acetaldehyde is one-third that for ethane, and that it has one-third as many interactions between C–H bonds as does ethane.

The barrier for propene is considerably larger than for acetaldehyde or acetone. It is, again, well reproduced at any level of theory. Since the carbon–carbon double bond has only a small bond moment, the electron density at the central carbon will be larger than found with the carbonyl compounds. As a result, it is not unreasonable to propose that the exchange terms, which lead to the barrier in ethane,¹³ will be larger with propene than with acetaldehyde. Thus, a larger barrier might be expected. The exchange terms are minimized in the conformer which has the hydrogens staggered and leads to the lower energy conformation having a methyl hydrogen eclipsed with the double bond.

With propanal^{19,20} and 2-butanone,²¹ it is known that the lowest energy conformation has the methyl group eclipsed with the carbonyl, and that the other energy minimum is found with the skew conformation in which the methyl is rotated approximately 120° from the carbonyl. The trans (180°) and gauche ($\sim 60^\circ$) conformations represent maxima. 1-Butene is similar, except that the energies of the eclipsed and skew conformations are now very close.^{22,23}

(18) Using the 6-31G* basis set, staggered ethane has $r_{CC} = 1.527$ Å, $r_{CH} = 1.086$ Å, and $\angle CCH = 111.20^\circ$, whereas eclipsed ethane has $r_{CC} = 1.542$ Å, $r_{CH} = 1.084$ Å, and $\angle CCH = 111.61^\circ$. The CCH angle in the eclipsed conformer is significantly larger than that in the staggered form, and there is a difference in CH bond lengths in the absence of hyperconjugation.

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Table IV. Energies of Ethyl-Substituted Compounds

compound	conf	STO-3G	3-21G	6-31G*/3-21G		
		RHF	RHF	RHF	MP2	MP3
propanal	e	-189.52620	-190.87776	-191.95124	-192.51283	-192.53720
	g	-189.52414	-190.87310	-191.94771	-192.50929	-192.53352
	s	-189.52601	-190.87500	-191.94941	-192.51062	-192.53493
	t	-189.52444	-190.87390	-191.94837	-192.50957	-192.53404
2-butanone	e	-228.11612	-229.70930	-230.99715	-231.68977	
	g	-228.11433	-229.70547	-230.99452	-231.68657	
	s	-228.11487	-229.70565	-230.99428	-231.68684	
	t	-228.11163	-229.70258	-230.99201	-231.68516	
1-butene	e	-154.23876	-155.24193	-156.10471	-156.61900	-156.65872
	g	-153.23693	-155.23948	-156.10162	-156.61626	-156.65593
	s	-154.24022	-155.24315	-156.10586	-156.61964	-156.65912
	t	-154.23761	-155.23983	-156.10238	-156.61615	-156.65595

Table V. Changes in Energy for Ethyl-Substituted Compounds (kcal/mol)

compound	conf	STO-3G	3-21G	6-31G*/3-21G			obsd ^a
		RHF	RHF	RHF	MP2	MP3	
propanal	e	0.00	0.00	0.00	0.00	0.00	0.00 (0.00)
	g	1.29	2.92	2.21	2.22	2.31	2.10 (2.96)
	s	0.12	1.73	1.17	1.41	1.45	0.95 (0.67)
	t	1.10	2.42	1.80	2.04	1.98	1.55 (1.90)
2-butanone	e	0.00	0.00	0.00	0.00		0.00
	g	1.12	2.40	1.65	2.00		
	s	0.78	2.29	1.80	1.83		2.02
	t	2.82	4.21	3.22	2.89		
1-butene	e	0.00	0.00	0.00	0.00	0.00	0.00 (0.00)
	g	1.15	1.54	1.94	1.72	1.75	— (3.19)
	s	-0.92	-0.77	-0.72	-0.40	-0.25	-0.15 (0.43)
	t	0.72	1.32	1.46	1.79	1.74	1.60 (2.12)

^aFor propanal, the barrier estimated via microwave spectroscopy (ref 19) is given first, followed by that estimated via low-frequency infrared spectroscopy (ref 20). For 2-butanone, the data are taken from ref 21. For 1-butene, the barrier estimated via microwave spectroscopy (ref 22) is given first, followed by that estimated via low-frequency infrared spectroscopy (ref 23).

In each case, the energies of the eclipsed, gauche, skew, and trans conformers were obtained by using the STO-3G and 3-21G basis sets with complete geometry optimization. The structures of the eclipsed and trans conformations may be constrained to have C_s symmetry. Thus, energy minimization was easily effected for these conformers. The geometries of the gauche and skew conformers were not as easily obtained since they are not defined by symmetry. Although they represent local minima or maxima, the force exerted by the torsional interaction near a minimum or maximum is so small that the geometry optimization becomes very slow. In these two cases, the optimizations were carried out for structures having approximated the correct torsional angles until the bond lengths and angles no longer varied significantly. Several structures were derived by rigid rotation with torsional angles $\sim \pm 10^\circ$ from the approximate value, and geometry optimization was again effected until bond lengths and angles were essentially constant. The "best" angle was derived from a parabolic fit. The energies are given in Table IV, the barriers are given in Table V, and the geometries are summarized in Table VI. It can be seen that the relative energies obtained by using the STO-3G basis set do not agree with the experimental results. The calculations using the split-valence 3-21G basis set (Table IV) gave considerably improved relative energies. They were still less than satisfactory. It was not practical to carry out a geometry optimization with the 6-31G* basis set for molecules this large and having little symmetry. The 3-21G geometry should be a reasonable approximation, and so the 6-31G* energies were obtained by using these geometries. The relative energies are given in Table V. There clearly is a remarkable difference between the methyl- and ethyl-substituted series, with all basis sets giving essentially the same relative energies in the former case, but with marked differences in relative energy in the latter case. The effect of

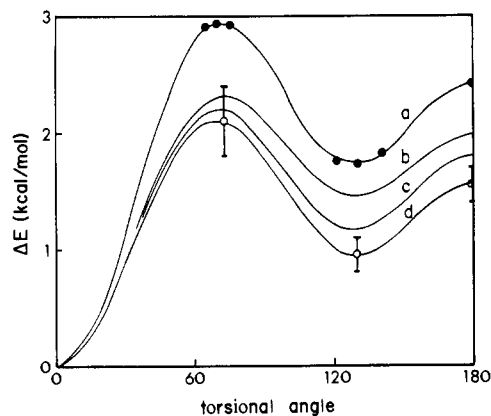


Figure 2. Rotational barrier for propanal. Curve a is for the 3-21G basis set (the solid circles indicate the calculated points); curve b is for the 6-31G*/MP3 energies; curve c is for the 6-31G* energies; curve d is for the experimental data. The open circles give the experimental points (microwave) and the vertical lines indicate the estimated experimental uncertainties.

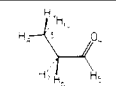
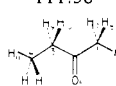
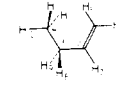
electron correlation also was examined by using the Møller–Plesset method through the third order (MP3) for propanal and 1-butene. This was not practical for 2-butanone because of the long computational times, and only the MP2 energies were obtained. The results for the other two compounds suggest that the difference between the MP2 and MP3 relative energies should be small.

In the case of propanal, the relative energies of the four conformers have been estimated by studying the torsional interactions with use of the microwave spectrum¹⁹ and the low-frequency infrared spectrum.²⁰ The two sets of values are significantly different. The calculated relative energies obtained by using the 6-31G* basis set are in reasonable agreement with the values determined by microwave spectroscopy. The torsional angles for the gauche and skew conformers are well reproduced (calcd 71° , 127° ; obsd $70 \pm 2^\circ$, $122.5 \pm 3^\circ$).¹⁹ Correction for electron

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Table VI. Structures of Ethyl Derivatives (3-21G)^a (3-21G)^a

unit	conformation			
	e	g	s	t
				
$\tau_{4,1,2,3}$	0.00	71	127	180.00
$\tau_{4,1,2,6}$	122.65	192	247	57.64
$r_{C=O}$	1.209	1.210	1.209	1.208
$r_{1,2}$	1.507	1.514	1.508	1.515
$r_{2,3}$	1.534	1.551	1.546	1.535
$\angle_{4,1,2}$	124.55	124.09	125.20	124.19
$\angle_{1,2,3}$	112.52	111.38	110.57	111.94
				
$\tau_{5,2,3,4}$	0.00	75	100	180.00
$\tau_{5,2,3,9}$	122.44	197	219	56.60
$r_{C=O}$	1.211	1.213	1.212	1.213
$r_{1,2}$	1.516	1.515	1.516	1.513
$r_{2,3}$	1.517	1.518	1.518	1.528
$r_{3,4}$	1.534	1.554	1.547	1.536
$\angle_{1,2,3}$	115.74	116.52	116.75	117.89
$\angle_{5,2,3}$	122.07	121.70	121.62	120.07
$\angle_{2,3,4}$	112.50	113.01	113.38	116.02
$\angle_{5,2,1}$	122.19	121.78	121.63	122.04
				
$\tau_{1,2,3,4}$	0.00 ^b	48	119 ^b	180.00
$\tau_{1,2,3,8}$	122.48	169	239	58.51
$r_{1,2}$	1.316(1.34)	1.317	1.316(1.314)	1.316
$r_{2,3}$	1.514(1.51)	1.521	1.508(1.49)	1.521
$r_{3,4}$	1.538(1.54)	1.545	1.545(1.54)	1.542
$\angle_{1,2,3}$	126.43(126.7)	124.43	124.85(125.4)	124.52
$\angle_{2,3,4}$	114.60(114.8)	112.55	112.18(112.1)	112.49

^aUnits: Å and degrees. ^bThe experimental values from ref 22 are given in parentheses.

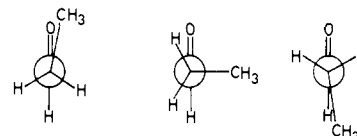
correlation led to a small change in relative energies.

Barriers in compounds of this type are frequently best examined by decomposing them into the onefold, twofold, and threefold terms:

$$V_{\theta} = \sum V_n / 2 (1 - \cos n\theta)$$

The result is shown in Table VII and Figure 2. One may first ask if the barrier may be reasonably represented with just three terms. The values obtained by using the 8 calculated 3-21G energies and just the four values for the minima and maxima were the same, showing that additional terms are not needed. The same twofold and threefold terms were obtained for the 6-31G*/RHF and 6-31G*/MP3 calculated data and for the experimental barrier derived from an analysis of the microwave spectrum. The difference between calculation and experiment appears in the onefold term. The experimental barrier derived from an analysis of the low-frequency infrared modes leads to quite different torsional components, and the threefold component seems unreasonably large. Thus, we suspect that it is less satisfactory than that derived from the microwave spectrum.

The threefold barrier is essentially the same as that for acetaldehyde, indicating that the mechanism operating in the latter case is also found with propanal in unchanged form. This is what one might expect on the basis of other studies.²⁴ The onefold term represents a stabilization at 0°, whereas the twofold term represents stabilization at 0° and 180°. The latter is the dominant term. The twofold barrier has a maximum in energy at 90° where the C—C bond of the ethyl group is orthogonal to the C=O bond: Thus, besides the normal threefold barrier, the principal component represents a stabilizing interaction between the carbonyl group and the ethyl group which is effective at both 0° and 180°. The



V_1	0.0	0.44	0.88
V_2	0.0	1.12	0.00
Sum	0.0	1.56	0.88

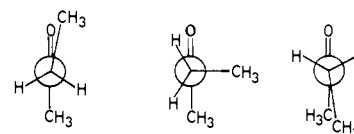
smaller onefold term makes the total stabilization somewhat larger at 0° than at 180°. It is a direct electronic effect, and not a stabilizing nonbonded interaction since electron correlation has only a small effect on the barrier.

The stabilizing interaction leading to a preference for the alkyl group eclipsed with the carbonyl cannot be described as a conventional hyperconjugative interaction since in this conformation the alkyl group is in the nodal plane of the carbonyl π orbital and therefore cannot interact. The simplest explanation for the onefold term in the barrier, and the need for polarization functions at carbon in calculating the magnitude of the barrier, is that the carbonyl dipole induces a dipole in the ethyl group, leading to a stabilizing interaction. The polarization of the ethyl C—C bond is readily seen in Figure 3. Since the polarizability of the ethyl group is large only along the C—C bond, no induced dipole is produced at a 90° angle. The inclusion of d-orbitals at carbon facilitates the polarization of the C—C bond in the presence of the field generated by the carbonyl group. The onefold term might have been larger if it were not for a repulsive steric interaction between the oxygen and the methyl group in the eclipsed conformer which will tend to decrease this component of the barrier. Such an interaction is suggested by the calculated bond angles for propanal, where one finds that the C₁—C₂—C₃ and O—C₁—C₂ angles are significantly larger for the eclipsed than for the trans conformer.

The twofold component of the barrier must arise from an interaction between the C—C bond orbitals of the ethyl group and the C—O bond orbitals of the carbonyl group. The interaction would be at a maximum at 0 and 180°, and would vanish at 90° where the p-components of the bond orbitals would be orthogonal. In this view, the one- and twofold components of the barrier are closely related in origin. The onefold barrier results from mixing of the σ^* C—C bond orbital with the corresponding σ bond orbital in the presence of the field generated by the C=O dipole. The twofold barrier results from mixing the C—C bond orbitals with the C—O bond orbitals.

The barrier for 2-butanone has been less thoroughly studied than that for propanal. The skew conformer lies 2.05 ± 0.10 kcal/mol above the eclipsed conformer in the gas phase, and the torsional angle is about 110°. These features are well reproduced by the calculation at the 6-31G* level. The components of the barrier are given in Table VII and Figure 4. There, the onefold term dominates, and the twofold term is smaller. The threefold term is about the same as found for acetone.

Why should the relative importance of the one- and twofold terms be reversed from that found with propanal? The trans conformer has two methyl groups eclipsed, and it is known from studies of *n*-butane that this eclipsed geometry has a considerably higher energy.²⁵ Thus, stabilization is found only at 0°, and 180° is markedly destabilized by a steric effect. The energies, not including the threefold term, are the following:



V_1	0.0	0.95	1.91
V_2	0.0	0.54	0.00
Sum	0.0	1.49	1.91

Table VII. Components of the Rotational Barriers (kcal/mol)

basis set	V_1	V_2	V_3
a. Propanal			
3-21G, all data	0.97	1.41	1.47
3-21G, 4 pts	0.96	1.40	1.46
6-31G*	0.60	1.01	1.20
6-31G*, MP3	0.88	1.12	1.10
exptl (microwave)	0.36	0.99	1.19
exptl (IR)	-0.28	1.19	2.16
b. 2-Butanone			
3-21G, all data	3.00	0.26	1.24
3-21G, 4 pts	2.85	0.23	1.36
6-31G*	2.34	0.08	0.88
6-31G*, MP2	1.90	0.54	0.98
c. 1-Butene			
3-21G, all data	-0.61	-0.46	1.97
3-21G, 4 pts	-0.68	-0.35	2.00
6-31G*	-0.85	-0.11	2.31
6-31G*, MP3	-0.24	-0.09	1.98

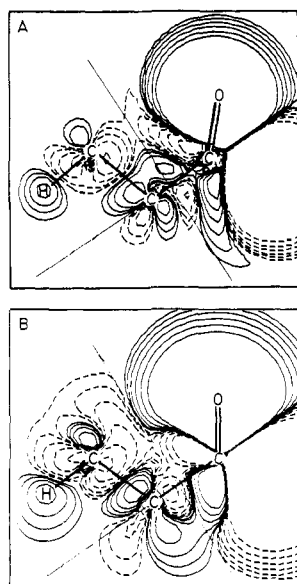


Figure 3. (A) Electron density map for eclipsed propanal less than that for the trans propanal (i.e., rotation of the carbonyl group by 180° around the C-C bond axis) for the ST0-3G basis set. Dashed lines indicate regions of depleted electron density and solid lines indicate enhanced electron density. (B) Electron density as for Figure 2a but using the 6-31G* basis set. Note the increased polarization in the ethyl C-C bond.

Here again, it is interesting to examine the bond angles in the calculated structures. The eclipsed conformer has the largest O-C₂-C₃ angle, just as was found with propanal. The C₂-C₃-C₄ angle is much larger for the trans conformer than for any of the others. Thus, there appears to be a small steric repulsion in the eclipsed conformer, and a large steric repulsion in the trans conformer. This is in agreement with the conclusions which were reached above.

With 1-butene, there are again two sets of data concerning the barrier to rotation. One was derived from an analysis of the microwave spectrum,²¹ and the other was derived from the low-frequency infrared spectrum.²² Both sets of data agree that the eclipsed and skew conformers have approximately the same energy, although they differ in which one has the lower energy. The infrared study found a large barrier between the eclipsed and skew conformers and a smaller barrier between the two skew conformers.

The relative energies of the 1-butene conformers have an order which agrees with the microwave data and reproduce the observed barrier between the two skew conformers (calcd 1.99 kcal/mol; obsd 1.75 kcal/mol). The relative energy of the eclipsed conformer

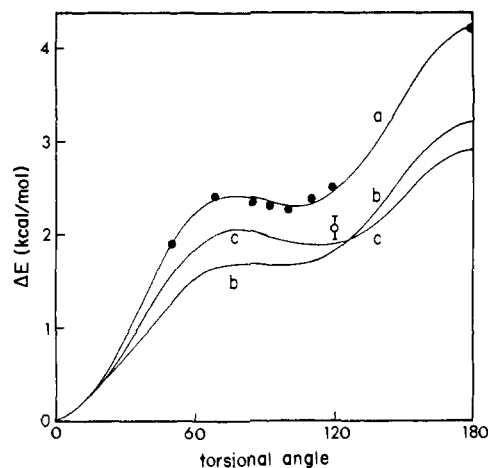


Figure 4. Rotational barrier for 2-butanone. Curve a is for the 3-21G basis set (the solid circles indicate the calculated points); curve b is for the 6-31G* energies; and curve c is for the 6-31G*/MP2 energies. The experimental datum is indicated by an open circle.

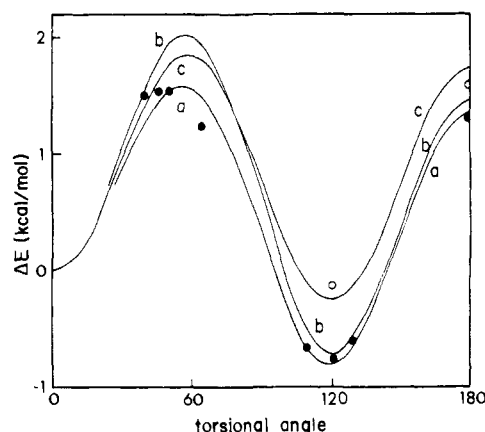


Figure 5. Rotational barrier for 1-butene. Curve a is for the 3-21G basis set (the solid circles indicate the calculated points), curve b is for the 6-31G* energies, and curve c is for the 6-31G*/MP3 energies. The experimental data (microwave) are shown by the open circles.

as calculated by 6-31G* is in good agreement with the microwave results. The bond angles for the eclipsed and skew conformers are well reproduced by the calculation (calcd $\angle C=C-C$ 126.4° (e), 124.9° (s), obsd 126.7° (e), 125.4° (s); calcd $\angle C-C-C$ 114.6° (e), 112.2° (s), obsd 114.8° (e), 112.1° (s)).²² The calculations do not, however, agree with the barrier between the eclipsed and skew conformation as determined from the infrared study. The components of the calculated barrier are shown in Table VII and Figure 5. Although the gauche maximum was found at 48° rather than 60°, leading to some deviation in this region, there is essentially only a threefold barrier with the same magnitude as found with propene. If our model for the barrier in propanal is correct, that is to be expected. No dipole-induced dipole attraction should be found. In view of the agreement in all of the calculations that the gauche and trans forms have similar energies, we are led to conclude that the large gauche-eclipsed energy difference reported in the low-frequency infrared study is incorrect.

It can be seen that our calculations are self-consistent and are in good agreement with the experimental barriers as determined by microwave spectroscopy or the temperature dependence of the infrared spectrum. They also are in good agreement with the observed structural data. With acetaldehyde, acetone, propene, and 1-butene, the barrier to rotation has the same origin as that for ethane. The barriers for propanal and 2-butanone have additional terms which result from a dipole-induced dipole interaction between the carbonyl group and the C-C bond of the alkyl

group in addition to the interaction between the C=O and C—C bond orbitals.

Calculations. The geometry optimizations were carried out with the program GAMESS,²⁶ and the MP2-MP3 calculations were carried out with GAUSSIAN-82.²⁷

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Acknowledgment. This investigation was supported by the Division of Basic Energy Sciences, Department of Energy.

Registry No. Acetaldehyde, 75-07-0; acetone, 67-64-1; propene, 115-07-1; propanal, 123-38-6; 2-butanone, 78-93-3; 1-butene, 106-98-9.

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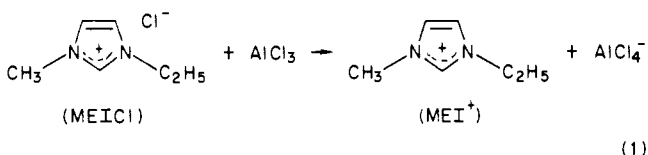
MNDO Calculations of Ions in Chloroaluminate Molten Salts

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Abstract: We have performed MNDO calculations on the anions in molten chloroaluminate salts. Calculated geometries for AlCl_4^- and Al_2Cl_7^- agree in most respects with available data. The vibrational spectrum of Al_2Cl_7^- calculated by MNDO is consistent with the observed IR spectrum and leads to assignment of C_2 symmetry for this ion. The ^{27}Al NMR exchange reaction between the two anions was also studied. The calculated energy of activation in the most realistic model used was 13 kcal mol⁻¹ compared to the experimental value of 10 kcal mol⁻¹.

Mixtures of 1-methyl-3-ethylimidazolium chloride (MEICl) and AlCl_3 are molten salts at and well below room temperatures.¹ The reaction forming this ionic liquid from the two substituents, which are solids at room temperature, is analogous to the reaction forming relatively low-melting inorganic chloroaluminate salts, such as NaAlCl_4 , from NaCl and AlCl_3 :



When AlCl_3 is added in less than stoichiometric amounts (i.e., the apparent mole fraction of AlCl_3 , N , in the melts is less than 0.5), the anions in the melt are AlCl_4^- and the excess Cl^- . Such melts are basic because Cl^- acts as a Lewis base in the melts. When $N > 0.5$, the process

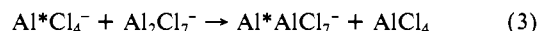


occurs, and the anions present are AlCl_4^- and Al_2Cl_7^- . Since Al_2Cl_7^- acts as a Lewis acid in the melts, such melts are acidic. Plots of the anion fractions of the anions as a function of N over the range $0 < N < 0.67$ are shown in Figure 1. These dependencies are calculated by using the well-justified assumption that the equilibrium constants for eq 1 and 2 are very large.² Further support of this assumption comes from the fact that large equilibrium constants have been deduced from the Raman spectra of similar room-temperature melts of 1-butylpyridinium chloride and AlCl_3 .³

MEICl/ AlCl_3 melts with compositions in the range $0.30 < N < 0.70$ are liquid below room temperature.¹ Properties of these melts, such as density, viscosity, and conductivity, have been reported for the range $0.30 < N < 0.70$.^{4,5} Analysis of the dependence of these properties on N indicates that the coordination number of the MEI^+ in the melts is 2. NMR spectroscopy of the

melts⁵ also supports the model in which each MEI^+ is closely associated with two anions, one above and one below the plane of its ring. Thus the overall structure may best be described as a collection of stacks of varying numbers of MEI^+ -anion pairs, a model which would also explain the almost polymeric properties of the melts at lower temperatures.⁵ Further support for this model comes from the results of Monte Carlo calculations in which the MEI^+ was represented by an oblate spheroid or plate and the anions were taken to be spherical.⁶ These calculations predicted that the plates would tend to stack up with their planes parallel and with the spherical anions alternating between them. Thus in the range $0.50 < N < 0.67$, the MEI^+ ions are probably associated with AlCl_4^- and Al_2Cl_7^- ions as shown in Figure 2. Each stack shown is expected to extend indefinitely as suggested by the dotted lines.

NMR spectroscopy⁷ has also been used to study the exchange reaction occurring in acidic melts between Al_2Cl_7^- and AlCl_4^- :



This reaction can be pictured as occurring between AlCl_4^- and Al_2Cl_7^- ions in adjacent stacks, as suggested by the double arrows in Figure 2. Reaction 3 has been observed in the ^{27}Al NMR peaks of the Al^* in the AlCl_4^- and Al_2Cl_7^- environments in $N = 0.60$ melts, in which the two anions are in equal concentration. Use of the Bloch equation to simulate the ^{27}Al NMR line shapes at

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