up to $4e_g$. The major effect of the coordination on Br_4^{2-} is the partial depopulation of the σ-antibonding orbitals $3\sigma_u$ and the HOMO $4\sigma_g$ (occupations in the linear model complex are 1.60 and 1.61 e, respectively), therefore stabilizing the Br_4^{2-} ligand, as can be seen in the Br–Br overlap populations (Table IV). Comparison of the extent of electron transfer to a transition metal with that in the alkali metal cation composite discussed above, clearly shows that the transition metal is more efficient in stabilizing the unstable Br_4^{2-} species.

Again, the atomic overlap populations suggest a strong central but a very weak terminal Br–Br bond. Unfortunately, no complexes of Br_4^{2-} are known so far, but this trend is obvious in the bond distances of I_4^{2-} complexes presented in Table IV. These bond distances can be compared to 2.667 and 2.72 Å in I_2 in the solid and in the gas phase[25,32] and to the intermolecular contacts of 3.50 and 3.324 Å in I_2 and $(Te_2)_2I_2$ in the solid state.[24,29,33] All of these data point to a description of the X_4^{2-} species as a central X_2 weakly interacting with two bromide ions. The calculated atomic charges for the central and terminal Br atoms are 0.0 and −0.4, respectively, at the EH computational level. The calculated charge transfer from the Br_4^{2-} ion to the transition-metal fragments is therefore 1.2 e, much larger than that found above for alkali metal cations (0.1–0.2 e), indicating that transition-metal fragments are much more efficient in stabilizing the X_4^{2-} groups than the alkali metal cations.

There is still something puzzling in the I_4^{2-} structures: despite the large HOMO–LUMO gap, the known compounds are not linear. A calculation on our model compound with the experimental distances for Br_4 gives a minimum for the linear molecule, but the energy curve is almost flat (Figure 4). If we let all the Br–Br bond distances be the same, a minimum is found for $\alpha \simeq 120°$. In any case, the energy difference between both structures is rather small and it is controlled by the interactions between the d_{xz} orbitals of the metal and the occupied orbitals of Br_4^{2-}, formally, four-electron repulsions.

In view of the above results we must conclude that X_4^{2-} species should in general be expected to be stable as ligands in transition-metal complexes, and the scarcity of well-characterized examples is only due to the lack of synthetic attempts.

Acknowledgment. We are indebted to CAICYT for financial support (Grant No. 0657/81).

Registry No. Br_4, 12595-73-2; Br_4^{2-}, 12595-74-3; Br_2, 7726-95-6; K^+, 24203-36-9; Cs^+, 18459-37-5.

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Origin of Methyl Conformational Preferences and Rotational Barriers in the Ground States, Excited Triplet States, Radical Cations, and Radical Anions of Molecules Having CH_3–C=X Functionalities

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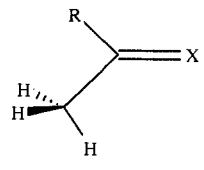
Abstract: Ab initio molecular orbital calculations have been carried out on the ground states, triplet states, radical cations, and radical anions of propene, acetaldehyde, acetaldehyde imine, dimethylbutadiene, and biacetyl. The barrier to methyl group rotation was calculated in each case by geometry optimization with the 3-21G basis set, and, for several cases, subsequent energy calculations were performed with the 6-31G* basis set with inclusion of MP2 correlation energy corrections. It is shown that the conformation about the C(methyl)–C(=X) bond is determined by the relative importance of the repulsion between filled orbitals, which favors "eclipsed" conformations for the ground states (as in ethane), and the overlap between vacant and filled orbitals, which favors eclipsed conformations for ground states and staggered conformations for excited states, and becomes the dominant effect in excited states.

The ground states of propene,[1] acetaldehyde and simple methyl ketones,[2] and acetaldehyde imine derivatives[3] prefer methyl group conformations that have a C–H bond syn or eclipsed with the double bond (**1**). The same conformational preference is exhibited



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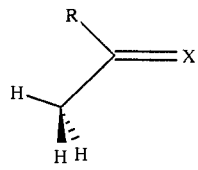

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in conjugated dienes, such as dimethylbutadiene,[4] and in α-dicarbonyl compounds, such as methylglyoxal.[5] Several theoretical calculations have been published that support and provide explanations of the experimental results for simple olefins, aldehydes, and ketones.[6-9] On the other hand, there have been no systematic

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theoretical studies, and, until recently, no experimental information on methyl group conformations in excited electronic states. Recently, the rotational barriers about the C(methyl)–C(carbonyl) bond in the singlet $n\pi^*$ states of acetaldehyde,[10,11] acetone,[10] methylglyoxal,[12] and biacetyl[12] have been measured by fluorescence excitation spectroscopy, and the barriers in the triplet $n\pi^*$ states of methylglyoxal and biacetyl[13] have been determined by the newly developed technique of phosphorescence excitation spectroscopy in supersonic jets.[14] The torsional frequency and tunneling splitting of the methyl group of crystalline toluquinone have been reported for the ground, first excited singlet, and first excited triplet states.[15] In all excited states it is found that the methyl group prefers a staggered conformation of C–H bonds with respect to the carbonyl functionality (**2**).

These recent findings have prompted us to undertake a computational study of the ground and triplet states of molecules having a methyl group attached to a double bond of an alkene, imine, or carbonyl compound, with the goal of understanding the origin of the reversal of the relative stabilities of the two conformers upon excitation. While we were mainly interested in the differences in conformational preference between the ground and triplet states, we have also calculated the rotational barrier in the radical cations and anions. This allowed us to examine the effect of removing an electron from a bonding or nonbonding orbital separately from the effect of adding an electron to an antibonding orbital. Both events occur in the electronic transition from ground state to triplet state. Thus, the ground states, triplet states, radical cations, and radical anions of propene, acetaldehyde imine, acetaldehyde, biacetyl, and dimethylbutadiene have been studied. In the case of the imine, calculations were performed on both the syn isomer—having the N–H bond eclipsed with the C–C bond—and the anti isomer, in which these two bonds are antiperiplanar. The first excited singlet states of acetaldehyde and biacetyl have also been included in our investigation for comparison with the triplets. Taken together, the results provide considerable insight into the origin of the dependence of methyl group conformations and rotational barriers on the electronic state of the molecule.

Results and Discussion

Ab initio calculations[16] have been carried out with geometry optimizations at the Hartree–Fock level (RHF for ground states and UHF for doublets and triplets), using the split-valence 3-21G basis set,[17] on eclipsed and staggered conformers. Single-point energy calculations have been performed on all states of dimethylbutadiene and biacetyl with the 6-31G* basis set,[16] with introduction of correlation energy corrections via second-order Møller–Plesset (MP2) perturbation theory.[18] Energies are not corrected for zero-point vibration, but inclusion of ZPE is known to have little effect on the calculated rotational barrier in ethane.[19]

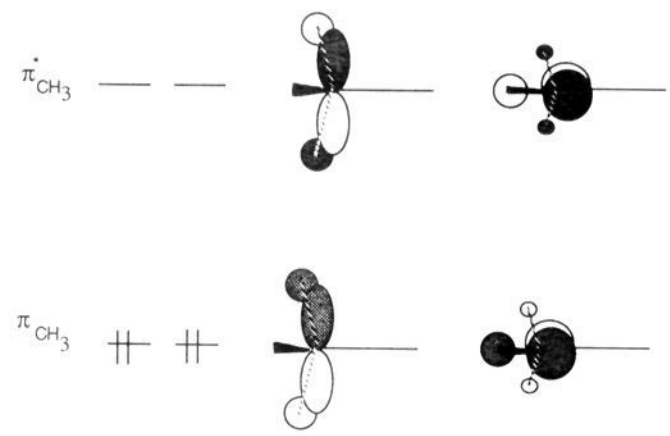

Figure 1. Methyl group orbitals of π symmetry. Each is formed from a carbon p_x or p_y orbital joined in a bonding (π) or antibonding (π^*) fashion with hydrogen 1s orbitals.

Table I. HF/3-21G Relative Energies (E_{rel}, kcal/mol) of Staggered (Relative to Eclipsed) Conformers of S_0, T_1, and the Radical Cation and Anion of Propene[a]

S_0[b]	$T_1(C_s)$	cation	anion
1.78 (2.0)[c]	−1.29	0.85	−0.77

[a] A positive energy means that the staggered conformer is higher in energy than the eclipsed. An experimental barrier is given in parentheses. [b] Reference 8e. [c] Reference 1.

Table II. Optimized Geometries of S_0, T_1, Radical Cation, and Radical Anion of Propene[a]

	S_0		T_1	
	eclipsed	staggered	eclipsed	staggered
$R(C_1C_2)$	1.316	1.316	1.552	1.548
$R(C_1C_3)$	1.510	1.519	1.505	1.498
$\angle C_2C_1C_3$	124.7	124.2	121.1	118.7
$R(H_4C_1)$	1.076	1.075	1.073	1.071
$\angle H_4C_1C_2$	119.6	119.3	118.5	119.2
$R(H_5C_3)$	1.083	1.082	1.084	1.083
$\angle H_5C_3C_1$	111.2	111.2	111.1	111.7
$R(H_6C_3)$	1.086	1.085	1.088	1.090
$\angle H_6C_3C_1$	110.6	110.9	107.8	108.2
$\omega(H_6C_3C_1H_5)$	120.5	120.0	122.3	122.3
$R(H_7C_2)$	1.074	1.075	1.072	1.072
$\angle H_7C_2C_1$	121.9	122.0	119.6	119.5
$R(H_8C_2)$	1.073	1.073	1.071	1.072
$\angle H_8C_2C_1$	121.8	121.8	120.3	120.7
	cation		anion	
	eclipsed	staggered	eclipsed	staggered
$R(C_1C_2)$	1.409	1.409	1.438	1.431
$R(C_1C_3)$	1.471	1.477	1.510	1.508
$\angle C_2C_1C_3$	124.0	122.6	122.6	121.9
$R(H_4C_1)$	1.076	1.076	1.081	1.079
$\angle H_4C_1C_2$	118.0	117.9	120.3	120.8
$R(H_5C_3)$	1.079	1.078	1.091	1.092
$\angle H_5C_3C_1$	113.8	112.4	109.4	111.3
$R(H_6C_3)$	1.092	1.091	1.104	1.103
$\angle H_6C_3C_1$	109.0	109.7	106.0	106.2
$\omega(H_6C_3C_1H_5)$	123.0	122.0	124.4	124.4
$R(H_7C_2)$	1.073	1.074	1.081	1.081
$\angle H_7C_2C_1$	120.6	120.8	121.5	121.4
$R(H_8C_2)$	1.073	1.073	1.080	1.081
$\angle H_8C_2C_1$	120.8	120.8	121.6	121.8

[a] Distances in angstroms, angles in degrees.

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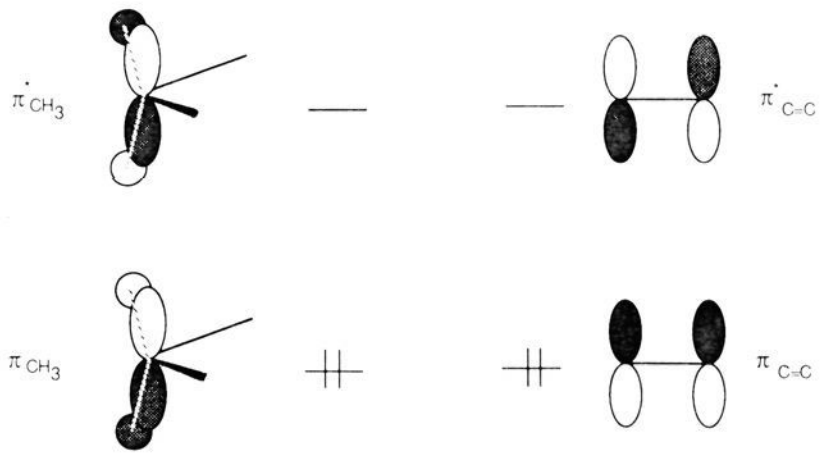

Figure 2. Methyl group and C=C double-bond orbitals of π symmetry.

All calculations were performed with a C_s symmetry constraint, although it is known that simple carbonyl compounds and olefins are not planar in their excited states[20] or radical anion states.[21] The geometries of alkene radical cations may also be nonplanar.[22] However, this C_s symmetry constraint simplifies the analysis of the change in the rotational preference without complications due to effects of nonplanar geometric distortions. We have carried out additional calculations with no symmetry constraints on the triplet $n\pi^*$ conformations of acetaldehyde for the purpose of comparison with the C_s-symmetry species.

Propene. Table I summarizes the results of our calculations on propene. All energies are those of the staggered conformer relative to those of the corresponding eclipsed conformers. Optimized geometries are given in Table II.

The origin of the preferred conformation of a methyl group attached to a C=X group (X = CH_2, NH, O) has been rationalized with perturbation molecular orbital theory for ground-state molecules.[6c,d,23,24] Thus, in propene, the preference for an eclipsed conformation can be explained in terms of the interactions between occupied methyl group orbitals of π symmetry and the π and π^* orbitals of C=X. The origin of the rotational barrier is closely related to that of ethane. As described in detail by Gimarc[25] and Lowe,[23] the overlap of occupied methyl group orbitals of π symmetry (shown in Figure 1) is different in the two conformations of ethane. The overlap of a π_{CH_3} orbital from one methyl with a π_{CH_3} from the other methyl group of ethane is larger in the eclipsed conformation than in the staggered. The interaction between these filled orbitals is repulsive since they are both occupied, and the eclipsed conformation is more destabilized by closed-shell repulsion than the staggered one.[23,25,26] In addition, the overlap of a π_{CH_3} orbital on one methyl group with a $\pi^*_{CH_3}$ orbital on the other is larger for the staggered than the eclipsed conformation. Since this is a stabilizing two-electron interaction, the staggered conformation is more stabilized than the eclipsed. Which of these factors is dominant has been the subject of much debate,[26] but most authors seem to agree with the calculations of Pitzer and co-workers,[27] which indicate that closed-shell repulsion effects dominate in ethane. This effect is likely to be true in nonpolar molecules, in general. On the other hand, Weinhold has argued that the π_{CH_3}–$\pi^*_{CH_3}$ interaction is the dominant factor.[28] In any case, one can most simply summarize the orbital interaction arguments by saying that the eclipsed conformation has some cyclic four-electron, "anti-aromatic" character, and is

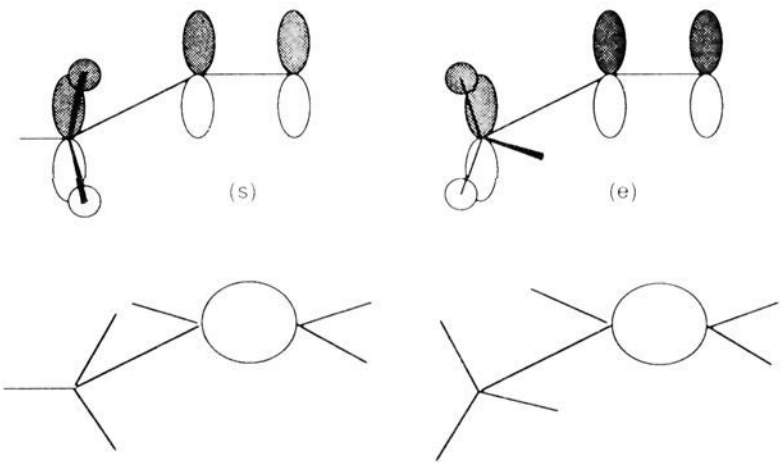

Figure 3. Interaction between the filled $\pi_{C=C}$ and π_{CH_3} orbitals in the staggered (s) and eclipsed (e) conformation of ground-state propene. The corresponding "bent-bond" representations are shown on the lower line.

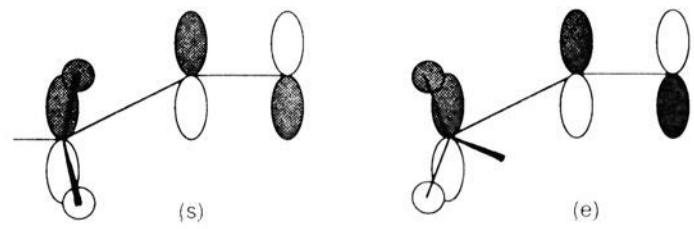

Figure 4. Interaction between the filled π_{CH_3} and vacant $\pi^*_{C=C}$ orbitals in the staggered (s) and eclipsed (e) conformations of ground-state propene.

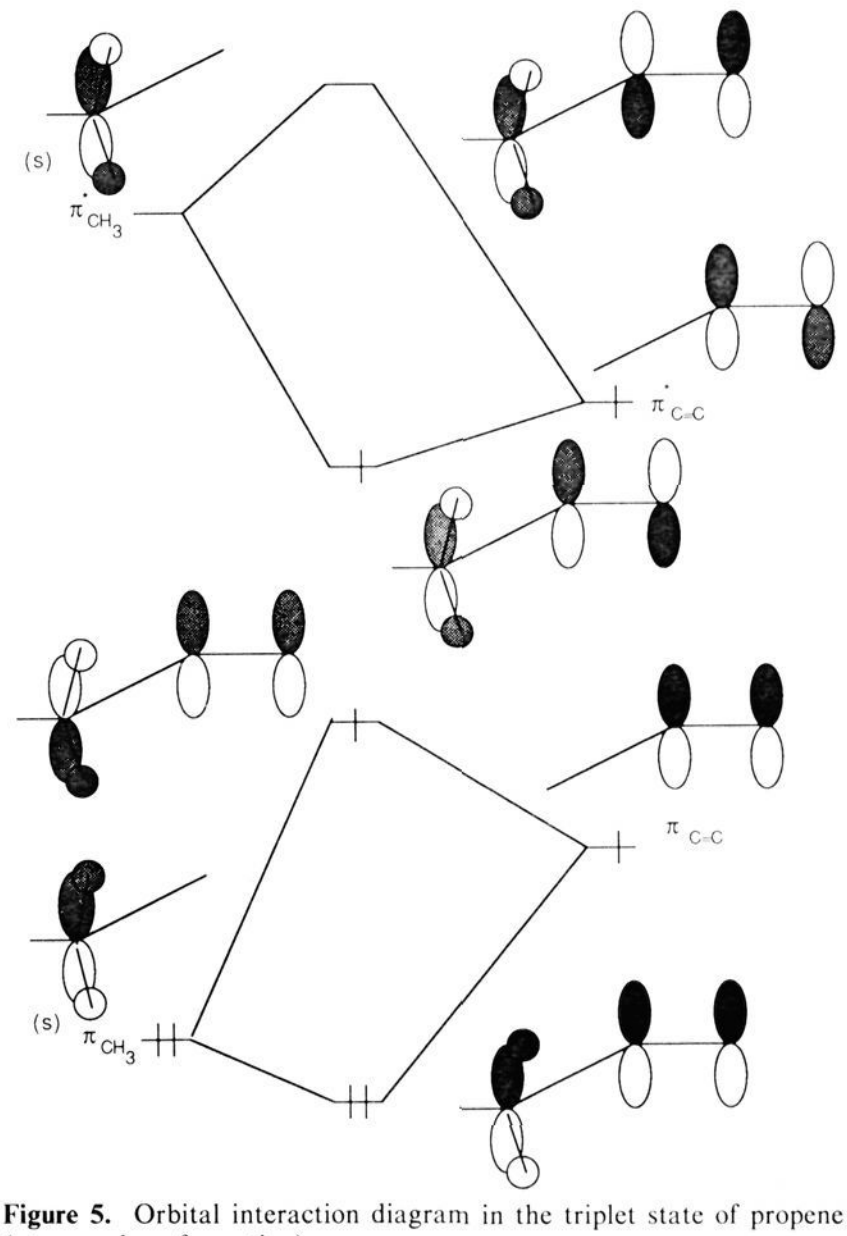

Figure 5. Orbital interaction diagram in the triplet state of propene (staggered conformation).

destabilized with respect to the staggered conformation.

In the case of propene, the analogous orbitals are the π and π^* orbitals of the C=C bond and the π_{CH_3} and $\pi^*_{CH_3}$ orbitals of the methyl group (Figure 2). The overlap between the $\pi_{C=C}$ and π_{CH_3} filled orbitals is larger in the staggered conformation (Figure 3) than the eclipsed, so that closed-shell repulsion is greater for the staggered conformation. In addition, the stabilizing interaction between the filled π_{CH_3} and the vacant $\pi^*_{C=C}$ orbitals is minimized

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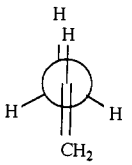
in the staggered conformation (Figure 4), since the two p orbitals of the ethylene π^* orbital have coefficients of opposite signs. The "staggered" and "eclipsed" names of the conformers of propene are really misnomers, since it is the eclipsed conformation of propene that most closely resembles the staggered of ethane and vice versa. For example, using the bent-bond formulation of the double bond of an alkene,[29] the eclipsed conformation has all methyl CH bonds staggered (Figure 3) with both CC bent bonds and a vinylic CH bond. Nevertheless, we will use the conventional nomenclature and refer to conformation **1** as the eclipsed and **2** as the staggered.

We now apply similar perturbational arguments to the analysis of methyl group conformations in the triplet $\pi\pi^*$ state, radical cation, and radical anion of propene. In the ground state, overlap between the filled π_{CH_3} and $\pi_{C=C}$ orbitals is destabilizing, and is most likely the main factor responsible for the preference for the eclipsed (with respect to the C=C bond) methyl group conformation.[8e,23,24] In the triplet $\pi\pi^*$ state, this interaction involves only three electrons (Figure 5). Such interactions are usually stabilizing,[30] so that the staggered conformer is still favored due to greater π_{CH_3}–π_{CC} overlap than in the eclipsed conformation, but they are small, so that this effect should not play a major role in determining the conformational preference. The other relevant three-electron interaction is that between the π_{CH_3} and the half-filled $\pi^*_{C=C}$ orbital. The energy difference between these orbitals is such that little or no stabilization arises from this interaction. Thus both interactions that contribute to stabilization of the ground-state eclipsed conformation are unimportant in the excited state, and in any case will tend to cancel each other because they now favor opposite conformations. On the other hand, overlap between the singly occupied $\pi^*_{C=C}$ orbital and the vacant $\pi^*_{CH_3}$ orbital is stabilizing and large, since these orbitals are close in energy. Overlap and consequently stabilization are greater in the staggered conformation than the eclipsed (Figure 5), because the hydrogens of the methyl $\pi^*_{CH_3}$ group have the same orbital coefficients as the p orbital on the alkene π^* terminus. Thus the 1.3 kcal/mol preference for the staggered conformer in the triplet $\pi\pi^*$ state can be rationalized as due primarily to this effect.

In the radical cation, the interactions to be considered are those between (i) the occupied π_{CH_3} and the half-filled $\pi_{C=C}$ orbitals and (ii) the π_{CH_3} and the vacant $\pi^*_{C=C}$ orbitals. The first, as discussed previously, gives slight stabilization of the staggered conformer, while the π–π^* interaction stabilizes the eclipsed conformer. The largest effect leading to the 0.85 kcal/mol preference for the eclipsed conformation is doubtless the eclipsing of a methyl CH bond with a C_2–H bond in the staggered conformation (**3**). Such an interaction is worth approximately 1 kcal/mol,[31] close to the calculated rotational barrier.



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In the radical anion, there are two factors in opposition. Overlap between the half-filled $\pi^*_{C=C}$ and the vacant $\pi^*_{CH_3}$ favors the staggered conformer, as in the triplet state, while the four-electron interaction between filled π orbitals favors the eclipsed conformation, as in the ground state. If we consider that the anion is derived from the ground state by addition of one electron to $\pi^*_{C=C}$ and that the triplet can be obtained from the cation in the same way, then the change in conformational preference should be similar in going from S_0 to the radical anion as it is in going from the radical cation to T_1. This should lead to a rotational barrier in the anion of (−1.29 − 0.85 + 1.78) = −0.36 kcal/mol. This is about 0.4 kcal/mol in favor of the staggered conformer. This is a very crude argument, but the value predicted by the 3-21G calculation (0.8 kcal/mol) is not far off. Finally, since the carbon atoms in the C=C bond of the anion are expected to be pyramidalized,[21] the barrier in the anion is expected to be greater than what is found when the calculation described above is performed with a C_s symmetry constraint.

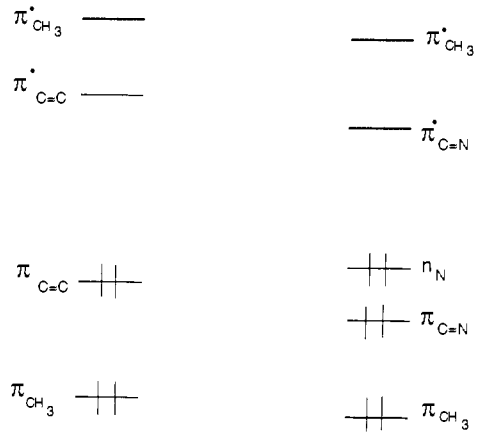


Figure 6. Qualitative comparison of orbital energy levels between propene and acetaldehyde imine in their ground-state electronic configurations.

Table III. HF/3-21G Relative Energies (E_{rel}, kcal/mol) of Staggered (Relative to Eclipsed) Conformers of S_0, T_1, and the Radical Cation and Anion of *anti*- and *syn*-Acetaldehyde Imine[a]

	S_0	$T_1(C_s)$	cation	anion
anti	1.59 (1.64)[b]	−0.93	0.95	0.14
syn	1.14	−1.03	0.99	−0.90

[a] A positive energy means that the staggered conformer is higher in energy than the eclipsed. [b] Experimental value for *N*-methylacetaldehyde imine.[3]

Acetaldehyde Imine. The results of our calculations on the anti and syn isomers of acetaldehyde imine are shown in Table III. Optimized geometries are given in Tables IV. The trend is the same as in propene, with the eclipsed conformers being more stable in the ground state and the staggered ones being more stable in the triplet state. There are, however, significant differences between propene and both isomers of the imine in the magnitude of change in the conformational preference in the series S_0–cation–anion–T_1.

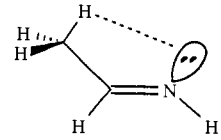
The relevant orbitals to be considered in the interaction diagram are the $\pi_{C=N}$ and π_{CH_3} orbitals, the $\pi^*_{C=N}$ and $\pi^*_{CH_3}$ orbitals, and the nitrogen nonbonding orbital, which lies in the plane of the molecule, orthogonal to the π system. The interactions involved are the same as those discussed for propene (cf. Figures 3 and 4), with the additional effect of the nonbonding orbital. The relative energies of these orbitals and the corresponding orbitals of propene are shown qualitatively in Figure 6. The introduction of the electronegative atom, N, causes the π and π^* orbitals of the imine to be lower in energy than those of propene and also to be polarized, so that N has a larger coefficient than C in the π orbital and N has a smaller coefficient than C in the π^* orbital. In the ground state of either the syn or the anti imine, the eclipsed conformation is favored, but the barrier (1.6 kcal/mol in *N*-methylacetaldehyde imine)[3] is lower than that in propene (2.0 kcal/mol). This is because the coefficient of the carbon atom is smaller in $\pi_{C=N}$ than in $\pi_{C=C}$, so that the difference between the four-electron destabilizing interaction of the staggered and eclipsed conformers is also smaller than in propene.[32] In the syn isomer,

(29) Houk, K. N.; Rondan, N. C.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980. Palke, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 6543.

(30) Bernardi, F.; Epiotis, N. D.; Cherry, W.; Schlegel, H. B.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1975**, *97*, 469. Gregory, A. R.; Malatesta, V. *J. Org. Chem.* **1980**, *45*, 122.

(31) Thus, for example, in the series ethane, methylamine, methanol, the staggered conformation is preferred by about 3.0, 2.0, and 1.0 kcal/mol, respectively, that is, by about 1 kcal/mol per pair of eclipsed XH bonds.

the rotational barrier is only 1.14 kcal/mol, most likely a result of destabilization of the eclipsed conformation by NH–CH repulsion and the absence of electrostatic stabilization of the eclipsed conformation by the N-lone pair–eclipsed hydrogen attraction, which may be present in the anti isomer (see **4**).



4

The lowest triplet state of acetaldehyde imine is an $n\pi^*$ state. Since excitation does not involve the $\pi_{C=N}$ electrons, the four-electron repulsive interaction which destabilizes the staggered conformation is maintained in the triplet. The $\pi^*_{CH_3}$–$\pi^*_{C=N}$ interaction stabilizes the staggered conformation, and this effect prevails. Thus, the staggered conformation is favored by 0.9 kcal/mol in the anti isomer and 1.0 kcal/mol in the syn isomer. The *change* in the rotational barrier from S_0 to T_1 is considerably lower than in propene.

The conformational behavior of the radical cations and anions of both isomers are also readily understood. In the radical, ionization takes place from the lone pair, so that the π-orbital repulsion component which favors the eclipsed conformation is essentially unchanged. In the syn isomer, this leads to a barrier (0.99 kcal/mol) that is only slightly smaller than in the ground state. In the anti isomer, there is a reduction of the ground-state barrier to 0.95 kcal/mol, similar to that found in the syn isomer. That there is any reduction at all is probably due to a redistribution of charge following ionization which leaves a formal positive charge on the nitrogen atom. This is in part compensated by polarization of $\pi_{C=N}$ in the direction of nitrogen, which results in a decrease in the $\pi_{C=N}$–π_{CH_3} repulsion.

The radical anion has a very small (0.1 kcal/mol) eclipsed preference in the anti conformer. The four-electron $\pi_{C=N}$–π_{CH_3} repulsion is approximately canceled by the one-electron $\pi^*_{CH_3}$–$\pi^*_{C=N}$ interaction which stabilizes the staggered conformation. In the syn isomer, the staggered isomer is favored, most likely due to the NH–CH repulsion in the eclipsed conformer. Following an argument similar to the one employed in the discussion of the propene anion, the anion barrier should be (−1.03 − 0.99 + 1.14) = −0.88 kcal/mol, in good agreement with the calculated value of −0.90 kcal/mol.

Acetaldehyde. Table V summarizes the results of the calculations on the ground state, $n\pi^*$ triplet, $n\pi^*$ singlet, cation, and anion of acetaldehyde. Optimized geometries for all states are shown in Table VI.

The rotational barrier in the ground state of acetaldehyde (1.14 kcal/mol) is about half that of propene (2.0 kcal/mol). This decrease in barrier is well reproduced by the theoretical calculations. This is mainly due to the decrease in the magnitude of the four-electron destabilizing interaction[8e] between the π_{CH_3} and the $\pi_{C=X}$ filled orbitals in acetaldehyde as compared to propene, caused by the polarization of the $\pi_{C=O}$ orbital. In acetaldehyde, the π orbital coefficient on carbon is smaller than that in propene, thus reducing the repulsion between the π_{CH_3} and π_{CO} orbitals. The possibility that the eclipsed conformer is stabilized by the dipole–induced dipole attraction between O lone pairs and a methyl CH bond has been ruled out by previous calculations.[8e,11] In particular, Baba et al.[11] have performed a very detailed analysis of the factors that affect the rotational barrier in acetaldehyde and conclude that only the hyperconjugative interactions of orbitals of π symmetry are important.

The lowest energy triplet is an $n\pi^*$ state, as in the case of the imine. The orbital interactions are therefore similar, and the staggered conformer is found to be favored to a similar extent. Again, it is the overlap of the singly occupied π^*_{CO} and the vacant $\pi^*_{CH_3}$ orbitals that is primarily responsible for this staggered preference. The magnitude of the barrier in T_1 CH_3CHO (0.7 kcal/mol) is smaller than that in propene (1.29 kcal/mol), which

(32) Pross and Radom[6d] have offered a different explanation for this phenomenon. They suggested, on the basis of STO-3G calculations and analyses of the optimized geometries, that there is a significant interaction between the nitrogen lone-pair and one of the vacant in-plane $\pi^*_{CH_3}$ orbitals in the eclipsed conformer of the anti isomer. This would then lead to an enhanced preference for the eclipsed conformer. However, in our calculations, the population analysis indicates that the methyl hydrogen which is eclipsed with the C=N bond has a higher positive charge than the other two. In the staggered conformer, the reverse is true. This is contrary to what would be expected if the lone pair–π^* interaction were predominant.

Table IV[a]

A. Optimized Geometries of S_0, T_1, Radical Cation, and Radical Anion of *anti*-Acetaldehyde Imine

	S_0		T_1	
	eclipsed	staggered	eclipsed	staggered
$R(C_1N_2)$	1.257	1.257	1.379	1.378
$R(C_1C_3)$	1.505	1.513	1.505	1.502
$\angle N_2C_1C_3$	121.6	121.0	120.2	119.3
$R(H_4C_1)$	1.083	1.082	1.071	1.070
$\angle H_4C_1N_2$	123.5	123.2	116.2	116.4
$R(H_5C_3)$	1.080	1.082	1.083	1.082
$\angle H_5C_3C_1$	109.2	111.2	110.1	109.8
$R(H_6C_3)$	1.086	1.083	1.087	1.088
$\angle H_6C_3C_1$	110.5	109.9	111.7	111.6
$\omega(H_6C_3C_1H_5)$	120.5	120.8	119.7	119.8
$R(H_7N_2)$	1.014	1.014	0.996	0.996
$\angle H_7N_2C_1$	114.7	114.7	141.7	142.0
	cation		anion	
	eclipsed	staggered	eclipsed	staggered
$R(C_1N_2)$	1.252	1.253	1.394	1.388
$R(C_1C_3)$	1.505	1.511	1.511	1.510
$\angle N_2C_1C_3$	124.0	123.5	118.3	118.3
$R(H_4C_1)$	1.083	1.083	1.087	1.086
$\angle H_4C_1N_2$	117.1	116.6	124.7	125.1
$R(H_5C_3)$	1.079	1.078	1.088	1.093
$\angle H_5C_3C_1$	112.0	109.5	106.8	111.0
$R(H_6C_3)$	1.085	1.084	1.103	1.100
$\angle H_6C_3C_1$	108.3	109.7	111.7	111.6
$\omega(H_6C_3C_1H_5)$	120.4	121.1	119.7	119.8
$R(H_7N_2)$	1.011	1.011	1.030	1.030
$\angle H_7N_2C_1$	151.3	150.8	107.4	107.6

B. Optimized Geometries of S_0, T_1, Radical Cation, and Radical Anion of *syn*-Acetaldehyde Imine

	S_0		T_1	
	eclipsed	staggered	eclipsed	staggered
$R(C_1N_2)$	1.257	1.257	1.378	1.377
$R(C_1C_3)$	1.512	1.519	1.510	1.506
$\angle N_2C_1C_3$	127.9	126.8	119.9	118.9
$R(H_4C_1)$	1.077	1.076	1.068	1.067
$\angle H_4C_1N_2$	117.3	117.2	116.7	116.8
$R(H_5C_3)$	1.084	1.081	1.084	1.083
$\angle H_5C_3C_1$	111.4	110.9	110.8	109.5
$R(H_6C_3)$	1.085	1.085	1.087	1.088
$\angle H_6C_3C_1$	110.1	110.6	111.5	111.9
$\omega(H_6C_3C_1H_5)$	120.7	120.2	119.7	119.5
$R(H_7N_2)$	1.016	1.017	0.996	0.996
$\angle H_7N_2C_1$	114.7	114.7	141.6	141.6
	cation		anion	
	eclipsed	staggered	eclipsed	staggered
$R(C_1N_2)$	1.252	1.253	1.393	1.388
$R(C_1C_3)$	1.511	1.517	1.516	1.513
$\angle N_2C_1C_3$	124.5	123.9	126.7	125.6
$R(H_4C_1)$	1.080	1.080	1.082	1.081
$\angle H_4C_1N_2$	116.6	116.1	117.0	117.6
$R(H_5C_3)$	1.079	1.079	1.092	1.093
$\angle H_5C_3C_1$	112.5	109.1	109.3	111.0
$R(H_6C_3)$	1.085	1.084	1.104	1.104
$\angle H_6C_3C_1$	108.1	109.9	111.5	111.9
$\omega(H_6C_3C_1H_5)$	121.6	120.0	119.7	119.5
$R(H_7N_2)$	1.011	1.011	1.033	1.033
$\angle H_7N_2C_1$	151.4	151.8	107.6	107.6

[a] Distances in angstroms, angles in degrees.

Table V. HF/3-21G Relative Energies (E_{rel}, kcal/mol) of Staggered (Relative to Eclipsed) Conformers of S_0, $T_1(C_s)$, $T_1(C_1)$, S_1, and the Radical Cation and Anion of Acetaldehyde[a]

S_0[b]	$T_1(C_s)$[c]	$T_1(C_1)$	S_1	cation	anion
1.14 (1.14)[d]	−0.67	−1.49	−0.79 (−1.1)[e]	0.80	−0.26

[a] Experimental values are given in parentheses. [b] References 8e and 19. [c] Reference 19. [d] Reference 2. [e] Reference 10.

Table VI. Optimized Geometries of S_0, $T_1(C_s)$, $T_1(C_1)$, S_1, Radical Cation, and Radical Anion of Acetaldehyde[a]

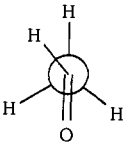
	S_0		$T_1(C_s)$	
	eclipsed	staggered	eclipsed	staggered
$R(C_1O_2)$	1.208	1.209	1.390	1.390
$R(C_1C_3)$	1.507	1.513	1.502	1.498
$\angle O_2C_1C_3$	124.8	123.9	118.4	117.8
$R(H_4C_1)$	1.087	1.086	1.069	1.068
$\angle H_4C_1O_2$	120.9	120.8	115.2	115.2
$R(H_5C_3)$	1.081	1.080	1.083	1.082
$\angle H_5C_3C_1$	109.9	111.2	109.9	109.6
$R(H_6C_3)$	1.086	1.084	1.086	1.086
$\angle H_6C_3C_1$	109.9	109.7	111.3	111.4
$\omega(H_6C_3C_1H_5)$	120.9	121.1	119.7	119.8
	$T_1(C_1)$		S_1	
	eclipsed	staggered	eclipsed	staggered
$R(C_1O_2)$	1.392	1.392	1.404	1.404
$R(C_1C_3)$	1.514	1.508	1.506	1.501
$\angle O_2C_1C_3$	115.7	115.0	118.6	117.9
$R(H_4C_1)$	1.074	1.076	1.072	1.071
$\angle H_4C_1O_2$	112.5	112.2	115.6	115.6
$R(H_5C_3)$	1.083	1.082	1.083	1.082
$\angle H_5C_3C_1$	110.3	109.5	109.9	109.7
$R(H_6C_3)$	1.084	1.083	1.086	1.086
$\angle H_6C_3C_1$	111.0	110.6	111.2	111.2
$\omega(H_6C_3C_1H_5)$	120.1	119.4	120.0	119.8
$\omega(H_4C_1O_2C_3)$	145.4	142.0		
$\omega(H_5C_3C_1O_2)$	7.2	187.4		
$R(H_7C_3)$	1.085	1.087		
$\angle H_7C_3C_1$	110.8	111.5		
$\omega(H_7C_3C_1H_5)$	−119.7	−120.2		
	cation		anion	
	eclipsed	staggered	eclipsed	staggered
$R(C_1O_2)$	1.249	1.249	1.316	1.312
$R(C_1C_3)$	1.489	1.493	1.527	1.525
$\angle O_2C_1C_3$	123.0	122.5	122.8	122.8
$R(H_4C_1)$	1.084	1.084	1.095	1.095
$\angle H_4C_1O_2$	115.0	114.5	122.4	122.7
$R(H_5C_3)$	1.079	1.078	1.088	1.092
$\angle H_5C_3C_1$	112.5	109.9	106.9	110.7
$R(H_6C_3)$	1.089	1.088	1.102	1.099
$\angle H_6C_3C_1$	107.9	109.4	111.3	111.4
$\omega(H_6C_3C_1H_5)$	122.2	121.2	119.7	119.8

[a] Distances in angstroms, angles in degrees.

is the result of differences in orbital occupation and polarization in the two cases. In propene, promotion takes place from a π orbital, whereas in acetaldehyde the π_{CO} orbital is filled even in the triplet, and the four-electron repulsion with π_{CH_3} which favors the eclipsed conformer in S_0 is present even here. The high polarization of the π^*_{CO} orbital leads to a smaller stabilization of the staggered conformer, arising from π^*_{CO}–$\pi^*_{CH_3}$ overlap, than is present in propene (cf. Figure 5). This orbital interaction is the source of the "chemical interaction" used by Clough et al.[15] to model the change in tunneling splitting between S_0 and T_1 toluqinone.

In acetaldehyde, the change in conformational preference is less marked than in the case of the imine. Thus, the calculated barrier is the same for acetaldehyde and the syn imine isomer in the ground state, but in the triplet the staggered conformer is more stable by 1.0 kcal/mol in the imine and by only 0.7 kcal/mol in the aldehyde. The anti imine isomer also has a higher preference for the staggered conformer (0.9 kcal/mol). A possible explanation is that the interaction of the lower lying half-filled $\pi^*_{C=O}$ with the vacant π_{CH_3} (which stabilizes the staggered conformation) is less effective for aldehydes than for imines, since (i) the energy separation between the two orbitals is larger in the aldehyde and (ii) the $\pi^*_{C=O}$ orbital is more polarized than the $\pi^*_{C=N}$ orbital. Similarly, the *difference* between the magnitude of such interactions in staggered and eclipsed acetaldehyde should be smaller than in the imine.

While we assumed a planar geometry for all molecules in these calculations, the triplet states and anions—and possibly the radical cations as well[22]—are pyramidalized, and removing the C_s symmetry constraint will lead to different values of the predicted rotational barriers. Thus, we have reoptimized the triplet state of acetaldehyde with no symmetry constraints. The calculated barrier is now found to be 1.5 kcal/mol. The increase is due to the relief of the eclipsing interaction between the aldehydic proton and one of the hydrogen atoms of the methyl group in the staggered conformer. This interaction vanishes if the carbonyl carbon is allowed to pyramidalize (see **5**).



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One of the most interesting results of the phosphorescence excitation experiment on methylgloxal[13] is that although the S_1 and T_1 states have similar structures, the methyl rotational barrier in the lowest triplet state is significantly lower than in the lowest excited singlet state. Therefore, we addressed this point computationally by performing UHF/3-21G calculations on the excited singlet state of CH_3CHO under the constraint of C_s symmetry. The same interactions present in the triplet determine the magnitude and sign of the barrier. Not surprisingly, this is calculated to be essentially the same in the two states under the C_s symmetry constraint. Attempts at finding the barrier in the nonplanar singlet were unsuccessful, since the HF wave function did not converge without the symmetry constraint. An MCSCF procedure has been used to characterize the singlet excited state, with no geometry optimization.[11]

The rotational barriers caclulated for the cation and anion reflect the same trend established for the imine. Thus, in the cation, the eclipsed conformer is more stable by 0.8 kcal/mol. The decrease from the ground-state barrier is once again caused by an increase in the polarization of $\pi_{C=O}$, which arise from the loss of one electron from the oxygen lone pair. In the anion, the staggered conformer is favored by only 0.3 kcal/mol. The change in conformational preference is smaller than in acetaldehyde imine, where the staggered conformer is favored by 0.8 kcal/mol in the anion. The polarization of the π^*_{CO} orbital causes the $\pi^*_{CH_3}$–π^*_{CO} interaction to just slightly overcome the π_{CH_3}–π_{CO} preference for the eclipsed conformation.

Biacetyl. While it is known that split-valence basis sets with no polarization functions reproduce well the rotational barrier in acetaldehyde, we have found that the introduction of correlation energy corrections (MP2)[18] and polarization functions has a significant effect on the rotational barriers in biacetyl. Table VII shows the calculated barriers at the HF/3-21G level and the HF/6-31G* and MP2[18]/6-31G*//3-21G[17] levels. A HF/3-21G geometry optimization was also performed on the excited singlet $n\pi^*$ state. However, no higher level calculation was performed, since Møller–Plesset perturbation theory is not applicable to the analysis of excited states of the same multiplicity as the ground state. In the calculations shown in Table VII, the O=C—C=O fragment was constrained in an antiperiplanar conformation, which is known to be favored experimentally for α-dicarbonyls.[33]

(33) Glyoxal: Brand, J. C. D. *Trans. Faraday Soc.* **1954**, *50*, 431. Paldus, J.; Ramsay, D. A. *Can. J. Phys.* **1967**, *45*, 1389. Methylglyoxal: Fodor, G.; Mujumdar, R.; Szent-Györgyi, A. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *85*, 4317. Skancke, P. N.; Thomson, C. *J. Mol. Struct.* **1980**, *69*, 241. Biacetyl: Hagen, K.; Hedberg, K. *J. Am. Chem. Soc.* **1973**, *95*, 8266. Tyrrel, J. *J. Am. Chem. Soc.* **1979**, *101*, 3766 and references therein.

Table VII. HF/3-21G and MP2/6-31G*//3-21G Relative Energies (E_{rel}, kcal/mol) of Distaggered (ss) and Staggered–Eclipsed (se) Conformers of S_0, T_1, S_1, and the Radical Anion of Biacetyl[a]

	S_0(ss)	S_0(se)	T_1(ss)	S_1(ss)	anion(ss)
HF/3-21G	1.26	0.60 (0.80)[b]	−2.20 (−0.66)[c]	−2.38 (−0.67)[d]	−1.34
HF/6-31G*//3-21G	2.30	1.17	−0.85		−0.42
MP2/6-31G*//3-21G	1.90	0.93	−0.87		−0.74

[a] Energies are relative to the dieclipsed (ee) conformation. Experimental values are given in parentheses where available. [b] Rotational barrier in methylglyoxal.[5] [c] Reference 13. [d] Reference 12.

Table VIII. Optimized Geometries of S_0, T_1, Radical Anion, and S_1 of Biacetyl[a]

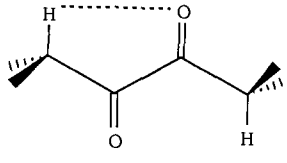
	S_0			T_1	
	eclipsed	staggered	st–ec	eclipsed	staggered
$R(C_1O_2)$	1.210	1.210	1.210	1.239	1.240
$R(C_1C_3)$	1.502	1.505	1.504	1.513	1.514
$\angle O_2C_1C_3$	125.3	124.5	124.9	125.1	122.7
$R(H_4C_3)$	1.080	1.076	1.077	1.080	1.081
$\angle H_4C_3C_1$	109.8	111.1	111.0	110.0	110.0
$R(H_5C_3)$	1.083	1.084	1.084	1.083	1.084
$\angle H_5C_3C_1$	110.0	109.3	109.4	109.3	109.9
$\omega(H_5C_3C_1H_4)$	121.1	121.3	121.3	120.9	120.4
$R(C_1C_6)$	1.525	1.529	1.527	1.480	1.473
$\angle C_6C_1O_2$	119.3	119.4	118.7	119.7	121.2
$R(C_6O_7)$			1.210		
$\angle O_7C_6C_1$			119.9		
$R(C_6C_8)$			1.502		
$\angle C_8C_6O_7$			125.1		
$R(H_9C_8)$			1.080		
$\angle H_9C_8C_6$			109.7		
$R(H_{10}C_8)$			1.083		
$\angle H_{10}C_8C_6$			110.0		
$\omega(H_{10}C_8C_6H_9)$			121.0		

	anion		S_1	
	eclipsed	staggered	eclipsed	staggered
$R(C_1O_2)$	1.278	1.278	1.238	1.239
$R(C_1C_3)$	1.529	1.527	1.516	1.515
$\angle O_2C_1C_3$	120.4	119.6	125.1	122.8
$R(H_4C_3)$	1.085	1.079	1.079	1.081
$\angle H_4C_3C_1$	108.9	109.9	110.0	107.9
$R(H_5C_3)$	1.087	1.089	1.083	1.084
$\angle H_5C_3C_1$	111.2	110.3	109.0	109.7
$\omega(H_5C_3C_1H_4)$	120.5	121.0	121.1	120.5
$R(C_1C_6)$	1.396	1.402	1.487	1.482
$\angle C_6C_1O_2$	123.8	124.5	120.4	121.8

[a] Distances in angstroms, angles in degrees.

Optimized geometries are given in Table VIII.

The ground state of methylglyoxal is known to favor the eclipsed conformer.[5] There are no experimental data on biacetyl, but the barrier is expected to be similar.[12] For methylglyoxal, the experimental barrier to rotation (0.77 kcal/mol)[5] is lower than that of acetaldehyde (1.14 kcal/mol). Our calculations also give a lower barrier (0.93 kcal/mol per methyl group) in biacetyl than in acetaldehyde. This decrease in the preference for the eclipsed conformations can be due to stabilization of the staggered conformations by the interaction of one of the methyl hydrogen atoms with the more remote carbonyl oxygen (**6**). This effect is not present in acetaldehyde and is probably the main factor responsible for reduction of the barriers in biacetyl and methylglyoxal.



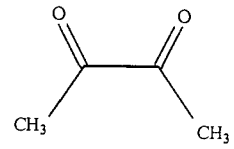
6

That the remote carbonyl is primarily responsible for the observed trends is shown by the calculation of the methyl group rotational barrier in the ground-state s-cis conformer of biacetyl (**7**), in which the two carbonyl groups are constrained to be synperiplanar. The results of our HF/3-21G calculations are shown in Table IX. In this case there can be no interaction between the hydrogen atoms of one half of the molecule with the carbonyl on the other half. We find that in the syn conformer the methyl group shows a marked preference for the ee conformation over the se (1.6 kcal/mol) and the ss conformations (4.4 kcal/mol). The carbonyl π-orbital coefficients are essentially the same as in the anti conformers, so that the exchange interaction between a carbonyl group and the eclipsed hydrogen on an adjacent methyl carbon should be approximately the same. The calculated rotational barrier is in fact somewhat larger than in acetaldehyde, partly due to steric repulsion between the methyl groups.

Table IX. HF/3-21G Relative Energies (E_{rel}, kcal/mol) of Distaggered (ss) and Staggered–Eclipsed (se) Conformers of S_0 Synperiplanar Biacetyl[a]

S_0(se)	S_0(ss)
1.6	4.4

[a] Energies are relative to the dieclipsed (ee) conformation.



7

In the triplet, the distaggered conformation is expected to be favored, owing to the stabilizing interaction between the half-occupied π^*_{CO} orbital and the vacant $\pi^*_{CH_3}$ orbital, as shown in Figure 7. This is the same effect that stabilizes the staggered conformation in acetaldehyde. However, in the case of biacetyl, the preference for the ss conformation (0.4 kcal/mol) is smaller—per methyl group—than for the staggered conformation in acetaldehyde (1.1 kcal/mol), both experimentally[13] and computationally. The overall change in conformational preference ($E_{rel}/(S_0)-E_{rel}(T_1)$) is also smaller (biacetyl, 1.2 kcal/mol per methyl group; acetaldehyde, 1.8 kcal/mol). This is in part due to the decrease in the favorable interaction between a methyl hydrogen atom and the lone pair of the remote oxygen atom (see **6**) upon excitation. This interaction, which stabilizes the ss conformer in S_0, is obviously reduced upon promotion of one of the lone-pair electrons. The very good agreement between the calculated and the experimental rotational barrier in triplet biacetyl supports the experimental value, about which there is some uncertainty.[13]

The se conformer of T_1 biacetyl is expected to be intermediate in stability between the ss and the ee conformer, just as in the ground state. However, the UHF energy of the se conformer is calculated to be about 40 kcal/mol lower than that of the ss and ee conformers. This obviously wrong result arises from the lesser symmetry of the staggered–eclipsed conformer (which has C_s symmetry) as compared to the C_{2v} dieclipsed and distaggered conformers. As shown by Davidson and co-workers,[34] a wave function of lower symmetry is incorrectly favored by an excit-

(34) Nitzsche, L. E.; Davidson, E. R. *Chem. Phys. Lett.* **1978**, *58*, 171. Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783.

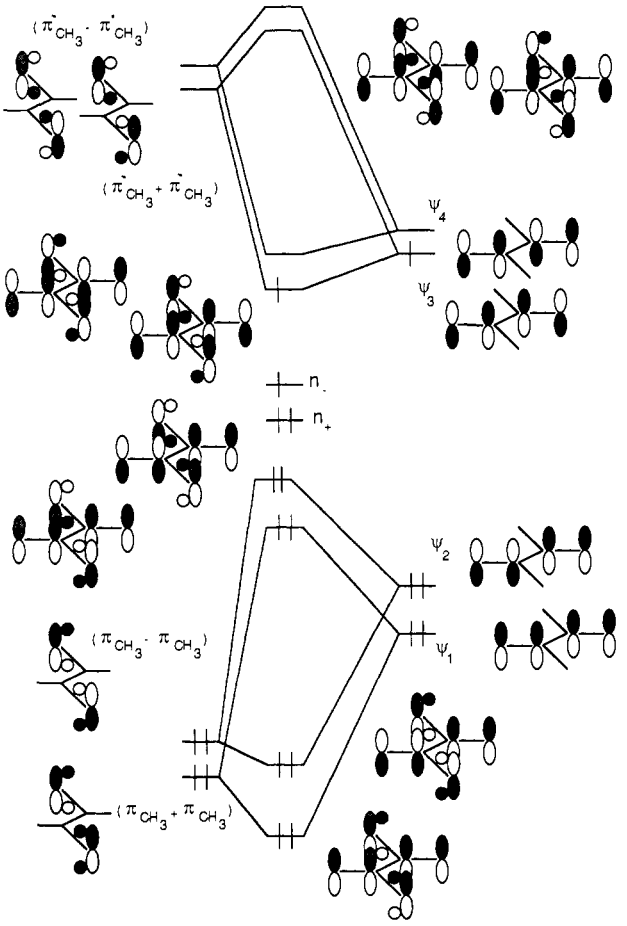


Figure 7. Orbital interaction diagram in the triplet state of biacetyl.

ed-state calculation that does not include electron correlation. Such a calculation, in the case of the staggered–eclipsed conformer, yields a structure with very different CO bond lengths and localization of the excitation on only one carbonyl group. Inclusion of configuration interaction is expected to give a lower energy for the C_{2v} structure. Calculations on the triplet state of glyoxal have shown that a C_s structure is favored by UHF theory, but a C_{2v} geometry becomes preferred upon inclusion of electron correlation, either via CI[35] or perturbation theory (MP2).[36] Similarly, we have been unable to obtain meaningful results from UHF calculations on the excited states of methylglyoxal, since this molecule has no element of symmetry other than the molecular plane, and therefore localization of excitation again occurs.[36]

The rotational barrier in the singlet $n\pi^*$ state (1.2 kcal/mol per methyl group) is predicted to be similar to that in the triplet (1.1 kcal/mol per methyl group) at the UHF level of theory. However, the MP2 calculation, which cannot be performed on the excited singlet state, gives a very different value for the barrier in the triplet. Clearly, it will be necessary to perform a calculation which accounts for correlation on the excited singlet in order to obtain a result which addresses the origin of the differences in the experimental values for the S_1 and T_1 states[12,13] in a meaningful way.

The radical cation of biacetyl would be expected to favor the eclipsed conformation, as is found in acetaldehyde. However, we were unable to obtain the rotational barrier, since the radical cation is predicted to dissociate to give the acetyl radical and the acetyl cation.

The radical anion of biacetyl is predicted to favor the staggered conformer by 0.4 kcal/mol per methyl group. The change in conformational preference from the ground state is 1.3 kcal/mol, compared to 1.4 kcal/mol in acetaldehyde. The barrier in the anion of biacetyl is only slightly (0.1 kcal/mol per methyl group) smaller than the one in the triplet. Thus, the stabilization of the staggered conformation in the triplet may be largely due to the presence of an electron in ψ_3, as in the anion, rather than the removal of an electron from ψ_2. If this were the case, then in the cation there should be very little change in the conformational preference for the eclipsed conformer of the ground state. Unfortunately, the lack of computational or experimental data on the cation does not enable us to verify this suggestion.

Dimethylbutadiene. Table X shows the results of our calculations on the ground state, triplet $n\pi^*$ state, radical cation, and radical anion of dimethylbutadiene (DMB). Geometries have been optimized at the HF/3-21G level, and energy calculations on the optimized geometries have been performed at the HF/6-31G* and MP2/6-31G* levels. The effect of a higher quality basis set and correlation energy correction is, in general, less pronounced than in the case of biacetyl. Optimized geometries are given in Table XI.

The calculated barrier per methyl group rotation in DMB (3.2 kcal/mol) is much higher than in propene (1.8 kcal/mol). Experimentally,[4] the barrier is even higher than found by our calculation. This effect is opposite to what takes place in going from acetaldehyde to biacetyl. Although molecular orbital arguments have been suggested to rationalize this increase in the rotational barrier,[4] our calculations indicate that the dominant effect is

Table X. HF/3-21G and MP2/6-31G*//3-21G Relative Energies (E_{rel}, kcal/mol) of Distaggered Conformers of S_0, T_1, and the Radical Cation and Anion of Dimethylbutadiene[a]

	S_0(ss)	T_1(ss)	cation(ss)	anion(ss)
HF/3-21G	6.68 (8.6)[b]	−0.64	2.04	4.32
HF/6-31G*//3-21G	7.37	−0.65	2.15	4.61
MP2/6-31G*//3-21G	6.32	+0.16	2.48	4.94

[a] Energies are relative to the dieclipsed conformer. [b] Experimental value.[4]

Table XI. Optimized Geometries of S_0, T_1, Radical Cation, and Radical Anion of Dimethylbutadiene[a]

	S_0		T_1	
	eclipsed	staggered	eclipsed	staggered
$R(C_1C_2)$	1.324	1.325	1.478	1.481
$R(C_1C_3)$	1.519	1.532	1.525	1.521
$\angle C_2C_1C_3$	120.3	117.4	115.9	122.1
$R(H_4C_3)$	1.082	1.077	1.082	1.078
$\angle H_4C_3C_1$	110.4	113.5	110.7	113.4
$R(H_5C_3)$	1.085	1.084	1.085	1.086
$\angle H_5C_3C_1$	110.8	109.8	111.2	109.7
$\omega(H_5C_3C_1H_4)$	120.0	120.5	119.7	121.0
$R(C_1C_6)$	1.491	1.494	1.335	1.335
$\angle C_6C_1C_2$	122.0	123.0	122.1	123.9
$R(H_7C_2)$	1.073	1.074	1.072	1.073
$\angle H_7C_2C_1$	121.2	120.5	120.1	119.1
$R(H_8C_2)$	1.071	1.069	1.070	1.069
$\angle H_8C_2C_1$	122.9	124.1	121.7	123.1
	cation		anion	
	eclipsed	staggered	eclipsed	staggered
$R(C_1C_2)$	1.394	1.392	1.400	1.401
$R(C_1C_3)$	1.519	1.518	1.527	1.535
$\angle C_2C_1C_3$	115.5	118.6	117.1	113.6
$R(H_4C_3)$	1.075	1.080	1.086	1.080
$\angle H_4C_3C_1$	114.4	110.4	110.9	112.7
$R(H_5C_3)$	1.085	1.084	1.090	1.090
$\angle H_5C_3C_1$	109.1	110.9	111.3	110.5
$\omega(H_5C_3C_1H_4)$	121.1	119.5	120.4	120.7
$R(C_1C_6)$	1.415	1.415	1.404	1.408
$\angle C_6C_1C_2$	120.5	119.4	126.0	127.9
$R(H_7C_2)$	1.073	1.071	1.077	1.078
$\angle H_7C_2C_1$	119.7	120.5	120.8	119.9
$R(H_8C_2)$	1.067	1.070	1.074	1.073
$\angle H_8C_2C_1$	123.6	122.5	122.7	124.0

[a] Distances in angstroms, angles in degrees.

(35) Gaw, J. F.; Schaefer, H. F., III. J. Chem. Phys. 1985, 83, 1741.
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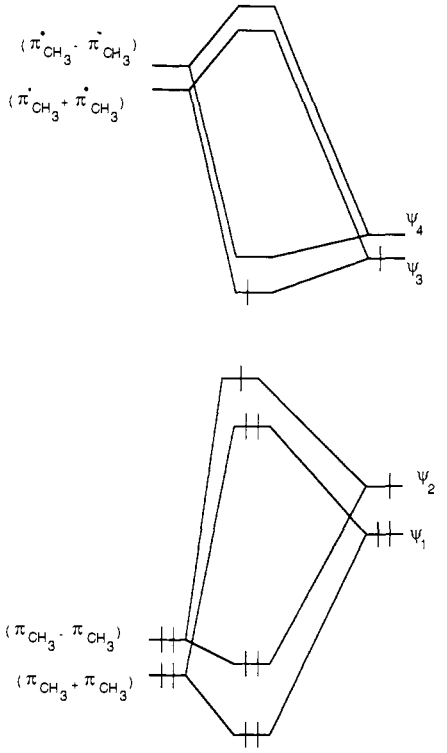


Figure 8. Orbital interaction diagram for the triplet state of dimethylbutadiene.

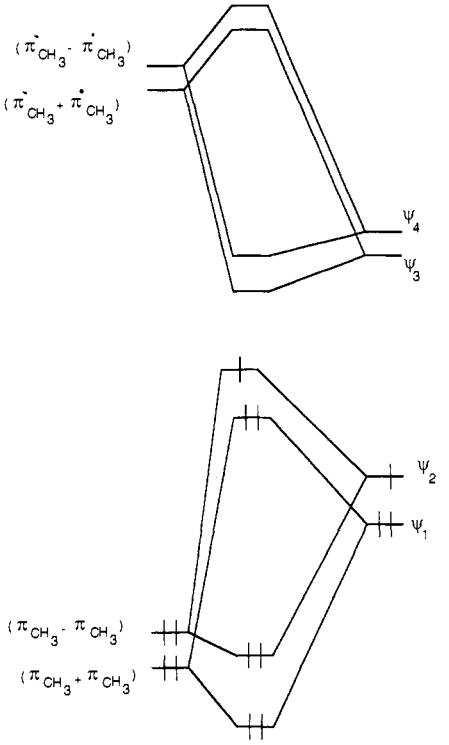
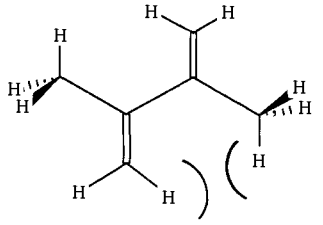


Figure 9. Orbital interaction diagram for the radical cation of dimethylbutadiene.

probably the steric repulsion present in the distaggered (or staggered–eclipsed) conformer, where a hydrogen of the C_2-methyl group is only 1.9 Å away from another hydrogen at C_4 (**8**).



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The change in conformational preference from S_0 to T_1 should be smaller than in propene. Figure 8 shows the orbital interaction diagram in T_1 DMB. By analogy with the biacetyl triplet, the interaction between ψ_3 and $\pi^*_{CH_3}$ should be small, and the change in preference per methyl group toward the distaggered conformation should be smaller than in propene. Surprisingly, this is not the case. In triplet DMB, the eclipsed conformation is barely favored (0.1 kcal/mol per methyl group) over the staggered one, and the change in conformational preference from the ground state is equal to $(E_{rel}(S_0) - E_{rel}(T_1)) = 3.1$ kcal/mol per methyl group, which is the same change calculated to take place in propene. A possible rationale for this effect is provided by the calculations on the radical cation and anion of DMB.

In the cation, the preference for the dieclipsed conformer (1.2 kcal/mol per methyl group) is considerably lower than it is in the anion (2.5 kcal/mol). This is confirmed experimentally by the marked decrease in the barrier to methyl group torsion in three Rydberg states of dimethylbutadiene.[37] This is the oppposite of what we find in all other cases, where the anions show a preference for the staggered conformations that is close to that of the triplets. In those cases, the staggered conformers are mainly stabilized by the overlap between a half-filled $\pi^*_{C=X}$ orbital and a vacant $\pi^*_{CH_3}$ orbital. In DMB, this interaction is not very important; in fact, the anion still shows a strong preference for the eclipsed conformation. The difference between DMB and propene in this respect can be explained by considering that (i) ψ_3 in DMB is more strongly polarized than $\pi^*_{C=C}$ in propene (cf. the LUMO of butadiene) and (ii) ψ_3 has one electron delocalized over all four atoms, so that the magnitude of the interaction (per double bond) between this orbital and the vacant π_{*CH_3} orbital is expected to be roughly half that of the π_{*CC}–π_{*CH_3} interaction in propene. These effects result in a much smaller stabilization of the half-occupied ψ_3 orbital in DMB, and since this stabilization is larger for the staggered conformer, even the effect on the relative stability of staggered and eclipsed conformers is expected to be smaller than in propene. On the other hand, the change in conformational preference from S_0 to the cation is about 1.9 kcal/mol, about twice as much as in propene (0.9 kcal/mol). A possible explanation is that the three-electron interaction involving the π_{CH_3} and the half-occupied ψ_2 orbitals (Figure 9) stabilizes the staggered conformer in DMB much more than the eclipsed conformer (Figure 10). In the staggered DMB conformer, the interaction between ψ_2 and π_{CH_3} is similar to the corresponding interaction in propene and leads to some stabilization; however, the eclipsed conformer is stabilized less, because the C_2-methyl hydrogen atoms and the C_3 atom have coefficients of opposite sign (Figure 10). Thus, the effect of π-orbital interactions should lead to a greater preference for the staggered conformer in the DMB cation than in the propene cation. More detailed calculations might be necessary to verify whether other factors are also operating. The DMB cation eclipsed conformer is still more stable than the

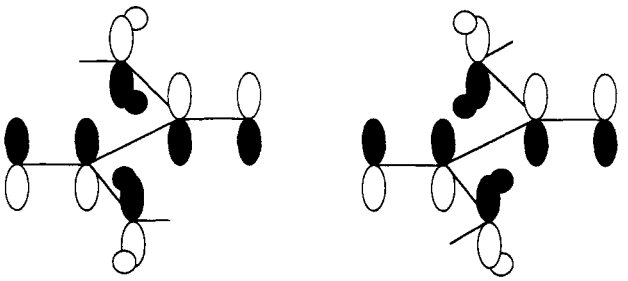

Figure 10. Interaction between the filled π_{CH_3} and half-filled ψ_2 orbitals in the staggered and eclipsed conformations of the radical cation of dimethylbutadiene.

(37) Sabljic, A.; McDiarmid, R. *Chem. Phys. Lett.* **1984**, *106*, 132.

staggered, because of the greater steric crowding of the latter structure, as shown earlier in **8**.

Summary and Conclusions

The ground states, triplet states, cations, and anions of propene, acetaldehyde imine, acetaldehyde, biacetyl, and dimethylbutadiene and the singlet excited states of acetaldehyde and biacetyl have been investigated by ab initio molecular orbital theory. The calculations are in good agreement with the experimental results, where known. In a large number of cases, the preference for one conformation over the other can be explained in terms of simple perturbation theory arguments.

Calculations on the ground states indicate that the rotational barrier is mainly governed by the repulsion between the filled π_{CX} and π_{CH_3} orbitals, but other effects can contribute significantly in specific cases. Our calculations confirm that in the first excited triplet states the staggered or distaggered conformations are generally more stable. This reversal of the ground-state preference is mainly due to the more favorable overlap of the $\pi^*_{C=X}$ orbital with the $\pi^*_{CH_3}$ orbital in the staggered conformation. In agreement with this conclusion, the radical anions of most species show a preference for the staggered conformation, while the cations are always more stable in the eclipsed conformation, but have relatively low barriers.

The experimental study of cases for which predictions have been made is eagerly awaited.

Acknowledgment. We are grateful to the National Science Foundation (Grants CHE-8512785 and CHE-8402996) and the Harris Corp. for financial support of this research.

YCoC: A Simple Organometallic Polymer in the Solid State with Strong Co–C π Bonding

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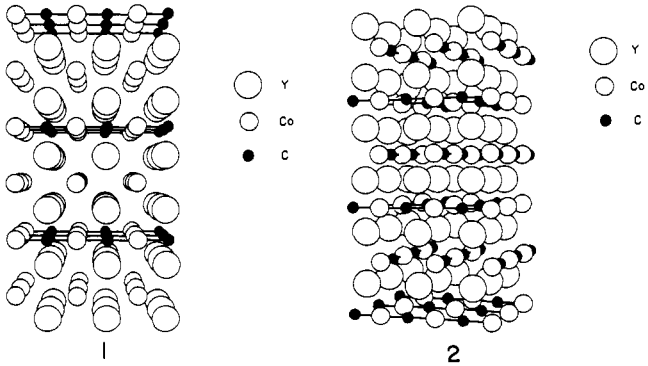
Abstract: Gerss and Jeitschko recently synthesized YCoC, which contains well-isolated infinite linear CoC^{3-} chains, marked by a short Co–C distance. We have examined the bonding in this polymer. It has substantial π character, and that bonding could be strengthened by decreasing the electron count or oxidation. We think the chains should be magnetic.

Gerss and Jeitschko recently synthesized a series of ternary lanthanide carbides, LnCoC, with a new, simple structure.[1] These molecules contain an extraordinary organometallic chain, whose electronic structure is the subject of this paper.

Two views of the $P4_2/mmc$ structure of YCoC are shown in **1** and **2**. Note the striking (–Co–C–Co–C–) infinite linear chains, well separated from each other. The Co–C distance in one of



1 2

these chains is a short 1.825 Å. That is a little shorter than typical metal–carbon distances in bulk transition-metal carbides (1.871 Å in Co_2C),[2] discrete cluster carbides (≥1.90 Å in $[Co_8C(CO)_{18}]^{2-}$ and $[Co_6C(CO)_{14}]^-$),[3] or even Co–carbene (1.905 Å in CpCo(SPh)CR_2)[4] complexes. Transitional-metal carbonyls have comparable distances (1.82 Å in $Co(CO)_4^-$),[5] shorter in other carbonyls. The extended structure before us clearly has well-defined organometallic chains characterized by some metal–carbon multiple bonding. If yttrium is taken as 3+, then formally we have CoC^{3-}. There are interesting conducting and magnetic possibilities for this chain.

Figure 1 shows an extended Hückel band structure of a one-dimensional CoC chain. The computational details are in the Appendix. This is a textbook example of orbital interaction in an extended material, and indeed it has been analyzed in detail by Burdett[6] and by Whangbo.[7] But it has one surprise.

Symmetry-adapted linear combinations of the four carbon valence orbitals and the metal d block are shown in **3** at Γ (same sign in each unit cell) and X (change sign between unit cells). It is clear that the δ M($x^2 - y^2$,xy) set does not interact with any C orbitals and will by itself form a narrow band. Metal (xz,yz) does not mix with C(x,y) at Γ, but it does so at X. This π bonding will push up M(xz,yz) toward X and push C(x,y) down. That is what the band structure shows.

Metal z^2 carries a surprise. At Γ it mixes with C s, at X with C z. Since C z is much closer in energy to M z^2 than C s, we would expect the z^2 band to rise in energy as one goes from Γ to X. But as the figure shows, z^2 is remarkably flat. It goes up from Γ to X, but imperceptibly so.

Why this unusual behavior? Certainly the mixing with C s and z analyzed above is there—see for instance the mirror image trend

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