IONIZATION POTENTIALS AND MO ENERGIES FOR ALKENES

Figure 4.

resolution was measured using the Xe doublet at 12.130 and 13.436 eV and the width at half height was found to be 50 mV. The instrument was calibrated using Xe, He, and CO_2.

Compounds. All compounds were commercial samples or were prepared using standard literature methods. Final purification was effected using gas chromatography and the identity and purity of the compounds was confirmed by NMR spectroscopy.

Calculations. The MO energies were calculated using GAUSSIAN-70[18] and the experimental geometries. The atomic coordinates are listed in the Ph.D. thesis of G.B.E.

References and Notes

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Molecular Structure of Acrolein Electronic States[1a]

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Abstract: The ground and low-lying singlet and triplet states of acrolein, CH_2CHCHO, have been studied with ab initio SCF methods using a double ζ basis set of Gaussian orbitals. The cis and trans ground-state geometries were optimized and vertical excitation energies were determined for n $\rightarrow$ π^* and $\pi \rightarrow \pi^*$ singlet and triplet states. The separation between the cis and trans ground states was found to be 540 cm^{-1}. Optimization of major bond lengths placed the $\pi \rightarrow \pi^*$ states very close energetically to the n $\rightarrow \pi^*$ states. For all excited states, the carbon–oxygen bond length was substantially longer than in the ground state. For the $\pi \rightarrow \pi^*$ singlet and triplet, the single/double bond character of the carbon–carbon bonds is interchanged with respect to the ground state. The ground and lowest excited singlet and triplet states are planar.

Acrolein is isoelectronic with glyoxal and butadiene, but has not received as much experimental attention as glyoxal and has been the subject of fewer theoretical investigations than butadiene. Nonetheless, because of conjugation of the carbon–carbon double bond with a carbon–oxygen bond, acrolein is of unique spectroscopic and electronic structure interest.

Among the early studies of acrolein is that of Walsh, who characterized the vacuum ultraviolet spectrum, identifying a high-energy singlet state.[2] Inuzuka studied the n $\rightarrow$ π^* exci-

tation and placed the 0–0 band for the $^1A' \rightarrow {}^1A''$ transition[3] at 25 851 cm^{-1}. From vibrational analysis of the spectrum, Inuzuka estimated the lengthening of the C=O bond in the $^1A''$ state to be 0.1 Å. Brand and Williamson[4] studied the spectrum under high resolution and derived barrier heights for internal rotation about the two carbon–carbon bonds in the ground state and the excited singlet state and concluded that there was increased π-electron density in the central carbon bond in the excited state. They also determined that the C=O

bond lengthening for the $^1A''$ state was about 0.12 Å. At about the same time, Hollas[5] had studied the acrolein spectrum and proposed possible structures for the excited singlet of acrolein and also of glyoxal. Hollas also made a tentative identification of a singlet to triplet transition with a band origin at about 4060 Å. Brand had identified the 4122-Å band as the n → π* triplet transition.[4] In 1966, Cherniak and Costain[6] provided very accurate information on the trans ground-state structure of acrolein from microwave spectra.

In recent years, the spectrum of acrolein has been of continued interest. Trying to demonstrate cis-trans photoisomerization, Becker, Inuzuka, and King[7] considered cis and trans states arising from not only an n → π* excitation, but also from a π → π* excitation. They used emission spectra and semiempirical calculations to suggest that the π → π* triplet is energetically quite close to the n → π* triplet. They concluded that largely because of potential barriers between cis and trans excited states and internal conversion, photoisomerization did not occur. In 1971, Alves, Christoffersen, and Hollas[8] presented some of the most interesting spectroscopic results of studies on acrolein. Their rotational band contour analysis of the 4060-Å system indicated that it was due to a cis $^1A'$ → $^1A''$ (nπ*) transition. They determined the cis-trans ground-state energy difference to be 700 cm^{-1} and the difference of the $^1A''$ states to be −530 cm^{-1}. The 4120-Å band was confirmed to arise from the trans n → π* triplet transition. The magnetic rotation spectrum was investigated by Bair, Goetz, and Ramsay,[9] who not only reconfirmed the 4120-Å band assignment, but also identified a 4322-Å band to be the corresponding cis transition. They determined the cis-trans energy difference of the $^3A''$ states to be −420 cm^{-1}.

Theoretical studies of acrolein include the early semiempirical calculations of Inuzuka[10] and Kato and co-workers.[11] The latter authors performed calculations on acrolein, butadiene, and glyoxal. For glyoxal, the vertical excitation energies of the lowest states which they present are in qualitative agreement with recent ab initio calculations.[12] Their calculated vertical excitation energies of acrolein place the n → π* and π → π* triplets very close in energy, less than 0.1 eV. These are shown as the lowest excited states followed by the n → π* singlet and π → π* singlet. The cis set of electronic states were quite similar to the trans.

Ab initio SCF calculations on acrolein were performed by Devaquet and Salem[13] and later by Devaquet.[14] These calculations used a minimum basis set of Slater type orbitals and the reported ground-state energy was −190.185 hartrees.[14] Interest in both studies was centered around the triplet excited states. It was shown that the bond lengths in the triplet states are probably substantially different from the ground state. Unfortunately, the C=C, C-C, and C=O bond lengths were not varied independently so that the molecular structures and relative energies of the states are only qualitatively determined. Four excited states of *trans*-acrolein were studied by Iwata and Morokuma[15] in work on the water–acrolein complex. For all states, the ground-state experimental geometry was assumed. The vertical transition energies they report are 3.40 eV for triplet π → π*, 3.77 eV for triplet n → π*, 4.53 eV for singlet n → π*, and 7.86 eV for singlet π → π*. A diffuse p function was found to be important in the π → π* singlet, which was associated with the high energy state studied by Walsh.[2]

Conjugated C=C and C=O groups can be involved in very interesting chemistry. One exciting example is the thermal ring opening of an oxetene intermediate.[16] A model of the reverse reaction is, of course, ring closure such as in acrolein. This has been studied recently by van der Meer and Mulder using ab initio methods.[17] They predicted a ring closure activation energy of 3.4 eV for the ground state of *cis*-acrolein. An analagous reaction is the formation of cyclobutadiene, which has been studied extensively by Hsu, Buenker, and Peyerim-

hoff[18-20] among others. Another interesting area of acrolein chemistry concerns Diels–Alder reactions. Frontier orbital calculations have been used to investigate such Diels–Alder reactions[21-22] and also regioselectivity in the dimerization of acrolein.[23]

In our recent ab initio SCF study of glyoxal, we predicted the existence of a low-lying biradical triplet state.[12] If an analagous acrolein state exists, its electronic structure could make it quite reactive and potentially important in ring closure and dimerization. Indeed, if it is sufficiently low lying, such an excited state may provide a pathway (for some of the reactions mentioned above) which is competitive with the ground state. But before considering reactions, it is necessary to know the relative energies of the excited states and their geometric structures. This is the primary purpose of this work. It seems clear that, while spectroscopic studies have provided much information on the n → π* states, there is still uncertainty regarding the π → π* states. The existing theoretical studies have not been extensive enough to provide such information. Calculations on acrolein may also help explain the difficulties of the molecules-in-molecules model which proved unsuccessful for glyoxal.[12] This is an important consideration, since it leads to predicting correlation effects in large systems on the basis of more easily studied small systems, e.g., formaldehyde and ethylene.

Theoretical Approach

A double ζ basis set of Dunning-contracted functions,[24-26] C (9s5p/4s2p), O (9s5p/4s2p), and H (4s/2s), was used in the SCF calculations. In the C_s symmetry of planar acrolein, the ground-state occupancy for both cis and trans is 1-13 a$'^2$ 1-2 a$''^2$. π-type orbitals are a$''$ and oxygen n orbitals are a$'$, giving A$''$ n → π* states and A$'$ π → π* states.

A simple cyclic individual optimization of structure parameters, previously used with ketene[27] and glyoxal,[12,28] was used for eight parameters in the trans ground state. A simple sketch of the molecule is given below (1). For all calculations
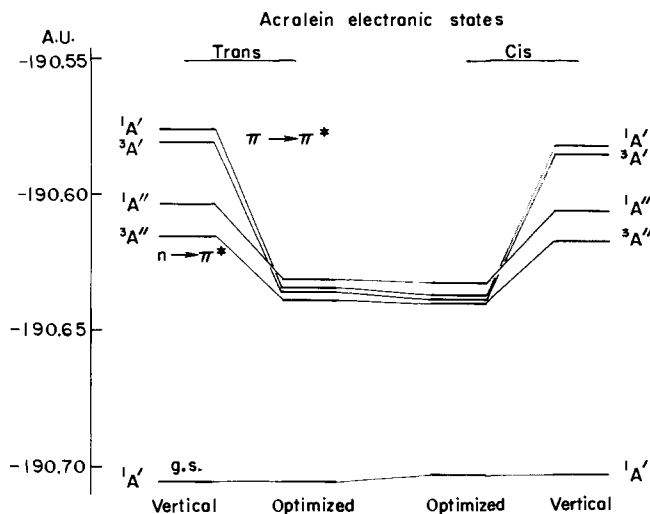

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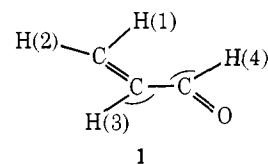
the carbon–hydrogen bond lengths were fixed at 1.075 Å. This distance was chosen on the basis of calculations on other carbonyls done with the same basis set. The methylene H(2)–C–H(1) angle was optimized, but H(1) and H(2) were kept in symmetric positions relative to the C=C bond. As shown in Table I, the bond angles of H(3) and H(4) were not optimized for the cis ground state. Trans values were assumed and the effect of optimization should certainly be small. In the eight excited states, the most important structure parameters, the carbon–carbon and carbon–oxygen bond distances were optimized.

Tests were made to determine if any states were nonplanar. The HCO group was twisted about the central carbon–carbon bond by 6° with other structure parameters fixed at values optimized for the given state. Only one type of symmetry orbitals exist for the nonplanar structures, so that n → π* and π → π* excited states cannot be distinguished by symmetry. Therefore, nonplanar tests on the higher open-shell singlet and triplet states were performed by starting with planar symmetrized orbitals and minimizing mixing of orbitals of different planar symmetries. This forces the Hartree–Fock procedure to converge to a higher root, which should be the desired state. Not surprisingly, these calculations required very many more iterations to converge than the lowest root states.

Table I. Optimized Geometries of Acrolein Electronic States[a]

	State	$R_{C=C}$	R_{C-C}	$R_{C=O}$	$\angle CCC$	$\angle CCO$	$\angle CH_2$	$\angle CCH(3)$	$\angle CCH(4)$
Trans	$^1A'$ gs	1.336	1.477	1.222	123.4	121.4	116.5	116.3	116.2
	$^3A''$ n → π^*	1.344	1.445	1.373					
	$^1A''$	1.347	1.430	1.389					
	$^3A'$ π → π^*	1.465	1.346	1.396					
	$^1A'$	1.467	1.345	1.398					
Cis	$^1A'$ gs	1.336	1.482	1.225	122.6	124.3	117.5		
	$^3A''$ n → π^*	1.350	1.440	1.371					
	$^1A''$	1.354	1.432	1.386					
	$^3A'$ π → π^*	1.466	1.344	1.387					
	$^1A'$	1.469	1.342	1.391					

[a] Bond lengths are in angstroms and angles in degrees. Ground state values were assumed for bond angles not optimized. The $\angle CCH(3)$ and $\angle CCH(4)$ angles, optimized for the trans ground state were used for all other states.

Figure 1. Energies of acrolein electronic states.

Table II. Calculated Acrolein Vertical Excitation Energies

	State	au	cm^{-1}
Trans	$^1A'$ gs	−190.7054	0
	$^3A''$ n → π^*	−190.6154	19 760
	$^1A''$	−190.6036	22 350
	$^3A'$ π → π^*	−190.5805	27 420
	$^1A'$	−190.5760	28 410
Cis	$^1A'$ gs	−190.7030	0
	$^3A''$ n → π^*	−190.6172	18 820
	$^1A''$	−190.6061	21 250
	$^3A'$ π → π^*	−190.5850	25 880
	$^1A'$	−190.5815	26 660

Table III. Acrolein Optimized Electronic State Energies

	State	au	cm^{-1}	Dipole moment, D
Trans	$^1A'$ gs	−190.7054	0.0	4.11
	$^3A''$ n → π^*	−190.6387	14 640	1.72
	$^1A''$	−190.6314	16 250	1.91
	$^3A'$ π → π^*	−190.6356	15 320	3.06
	$^1A'$	−190.6344	15 590	2.96
Cis	$^1A'$ gs	−190.7030	0.0	3.48
	$^3A''$ n → π^*	−190.6393	13 980	1.93
	$^1A''$	−190.6325	15 460	2.05
	$^3A'$ π → π^*	−190.6384	14 170	2.78
	$^1A'$	−190.6369	14 500	2.69

Results and Discussion

Table I gives the optimized molecular geometries. The only experimental values are for the ground state of the trans form. Cherniak and Costain[6] give a C=C bond length of 1.345 Å, about 0.01 Å longer than we have determined, and C–C–C bond angle of 119.8° or 3.6° smaller than our theoretical result. The other structural parameters agree quite well; the experimental C–C bond length was 1.470 Å, the C=O bond length 1.219 Å, C–C–O angle 123.3°, and all hydrogen angles agreed with calculated values to within 2°. The double ζ basis set is sufficient for describing the acrolein ground state and since the excited states being considered are all low-lying valence excitations, we believe the basis is adequate for the excited states as well. Morokuma[15] concluded that some diffuse functions are necessary to account for Rydberg character of the π → π^* singlet. However, we feel that with a sufficiently large basis set, e.g., a double ζ set, the π → π^* singlet is essentially entirely a valence excitation without Rydberg character. This was demonstrated[12] to be the case for glyoxal. We note that the vertical excitation energy of this state which we have determined is much less than the 3G (minimum basis) or 3G + p energies of Morokuma.

The vertical excitation energies are given in Table II. The energies for the n → π^* states are lower than observed 0–0 transition energies. This result, however, is consistent with related theoretical predictions on other systems. In calculations on formaldehyde with the same basis set, the n → π^* vertical transition energies were also too small.[12] This is due to a greater correlation energy correction in the ground state than in the open-shell excited states. The optimized state energies

are presented in Table III. The ordering of excited states is n → π^* triplet, π → π^* triplet, π → π^* singlet, and n → π^* singlet. The geometry optimization lowered the n → π^* state energies by around 5000 cm^{-1} and the π → π^* states by around 12 000 cm^{-1}. The geometries of corresponding cis and trans states are very similar and correlation effects should be nearly identical. Thus, it is reasonable to compare cis–trans state energy differences with experiment.[9] The cis $^3A''$ state lies 120 cm^{-1} below the trans $^3A''$, compared with an experimental value of 420 cm^{-1}. The theoretical energy difference for the $^1A''$ state was 250 cm^{-1} with the cis state lower in energy, while the experimental result was 530 cm^{-1}. The ground states differ by 540 cm^{-1}, with the cis state being higher, compared to a well determined experimental value of 700 cm^{-1}. While the theoretical energy differences are consistently smaller than experiment, the calculations do correctly order the states even with small energy differences of a few hundred wave numbers.

The structure of the excited states is the most important result of the calculations because there are neither complete

Table IV. Calculated Energy Changes due to Twisting[a]

Trans		
	$^1A'$ gs	0.77
	$^3A''$ n → π*	0.11
	$^3A'$ π → π*	−0.30
	$^1A'$ π → π*	0.18
	$^1A''$ n → π*	0.13

[a] Energy change, in millihartrees, from internal rotation about the central C-C bond for the given states at their optimum geometries. The internal rotation angle for the excited states was 6° and for the ground state 10°.

experimental nor theoretical values. For the n → π* states, the central C-C bond is shortened slightly. This is consistent with spectroscopic estimates of Brand and Williamson.[4] The change is also similar to n → π* excited states of glyoxal.[12] Unlike glyoxal, however, the n → π* excitation in acrolein also results in a lengthening of the carbon–oxygen bond by about 0.15 Å, compared with the approximate experimental result of 0.12 Å.[4] The carbon–carbon double bond is lengthened only slightly in these states. Consistent with the large energy change upon optimization, the most dramatic changes in structure occur for π → π* excitations. In these states, the carbon–oxygen bond lengthens at least as much as for the n → π* states. In addition, the two carbon–carbon bond lengths change greatly. The single bond contracts to a distance typical of double bonds, as occurs in glyoxal, while the double bond increases in length by about 0.13 Å.

The structure optimizations were performed with the molecule constrained to be planar. However, tests were made on structures slightly twisted about the central C-C bond and the results are shown in Table IV. It seems likely that most of the states are planar. The $^3A'$ state may, however, have a potential minimum in a gauche form. The probable crossing of the triplets in internal rotation was shown by the potential sheets of Devaquet.[14] Semiempirical calculations of Becker and co-workers[7] gave barriers for internal rotation about the central C-C bond for all states except the higher triplet, where the potential curve was flat. In the reduced symmetry of the non-planar structures, the triplets can mix and, thus, a one-configuration representation of the wave function becomes inappropriate. In glyoxal, C_2 symmetry is maintained in internal rotation, so that the states analagous to acrolein $^3A''$ and $^3A'$ do not have the same symmetry and cannot mix; that is, the crossing is allowed. Furthermore, the reason for the crossing is seen to be a correlation, upon internal rotation, of n → π* states with π → π* states, and the reverse. The lack of symmetry in acrolein means there will be an avoided crossing in the internal rotation potential curves of the triplets. This can be described accurately only with a correlated wave function. Qualitatively, however, this avoided crossing makes it likely that the higher triplet curve may have a minimum between the cis and trans forms or may be nearly flat. The small energy change at the test geometry (see Table IV) and the lack of a CI calculation does not make it possible to confidently predict the true form of the potential. If the mixing were sufficiently large, it could also imply that the π → π* singlet is nonplanar. If there is a minimum for singlet or triplet states, the closeness of the n → π* states, which gives rise to the avoided crossing, means that the effect on total energy of the state is likely to be small. On the other hand, a larger n → π* and π → π* state separation would increase the likelihood of the higher singlet and triplet being nonplanar.

A degree of freedom not considered in this work is rotation around the terminal C=C bond. The calculations of Devaquet[14] show this rotation also results in an avoided crossing between the triplets. With the methylene group perpendicular to the molecular plane, the triplets remain separated by about

the same energy. Becker and co-workers[7] had previously demonstrated this avoided crossing and the approximate flatness of the potential curve of the lowest triplet. The separation of the triplets with the methylene group perpendicular was determined to be much larger than in the planar forms. While their semiempirical calculations did not indicate it, the mixing in the region of the avoided crossing could raise the barrier for the lower state and lower the barrier of the upper state with a similar effect for the singlet states. A more accurate theoretical treatment may be necessary, especially in view of Devaquet's[14] results and the geometry optimization performed here. Nonetheless, the methylene hydrogens are probably in the molecular plane at the equilibrium geometries of the states, due to an overall upward energy shift upon rotation about the terminal C=C bond. Our conclusion on the structures of the excited states is that the lowest triplet and singlet are planar. The higher triplet and singlet may be nonplanar or at least have shallow internal rotation potentials for the central C-C bond.

Electronic Structure. Using the Mulliken populations in Table V and the orbital energies in Table VI, some understanding can be reached concerning the nature of the electronic structure of the states of acrolein. The identification of the 13a′ orbital as an oxygen n orbital is clearly indicated. The 2a″ π orbital has a higher orbital energy than the n orbital and the π* orbital is quite low lying. Interestingly, the two occupied π orbitals are very localized. The 1a″ in the ground state is almost entirely a carbonyl π orbital. The 2a″ is an ethylene π bond. Symmetry restrictions in glyoxal do not allow such localization in glyoxal. Instead, these orbitals correspond to plus and minus combinations of carbonyl π orbitals.

For n → π* excitations, it can be seen that the remaining n electron is completely localized on the oxygen. The 3a″ electron is primarily centered on the carbonyl carbon, which had the greatest positive partial charge in the ground state. As a result of the increased electron density on carbon, the 1a″ orbital changes by shifting electron density back to the oxygen. It becomes a much weaker bonding orbital. The change in 1a″, which is always doubly occupied, probably accounts for the increase of the C=O bond length for the A″ states. This effect is not seen in glyoxal because the orbitals are delocalized. As expected, the n → π* excitation in acrolein reduces the charge on oxygen.

Changes are seen in all the highest filled orbitals for the π → π* excitation. The remaining electron in the 2a″ orbital, which was an ethylene orbital, is shifted to the oxygen. The 1a″ orbital now becomes localized on the central carbons rather than over the carbonyl. The π* orbital is highly localized on the terminal carbon. It is clear that the lenghtening of the C=C bond is due to the change in the 2a″, the lengthening of the C=O bond is due to the change in 1a″ and 13a′, and the central carbon–carbon bond length contraction is the result of an additional C-C bond, specifically the 1a″ orbital. Comparison of the 2a″ orbital in the ground state with the 1a″ orbital in the excited state suggests that the single/double bond character of the carbon–carbon bonds has been interchanged.

The low-lying π → π* triplet of glyoxal is predicted to be a biradical state.[12] This is equally likely for acrolein and, in addition, the π → π* singlet may also be a biradical. For the acrolein π → π* states, the 2a″ is a half-filled orbital localized on oxygen. The electron in the half-filled 3a″ orbital is localized on the methylene carbon. The lack of any delocalization of these orbitals suggests the following representation (2). The
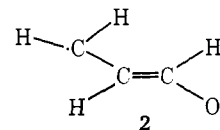

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Table V. Mulliken Populations[a]

MO			¹A′ gs	³A″	Trans ¹A″	³A′	¹A′
13a′	Oxygen	s	0.0	0.0	0.0	0.0	0.0
		p	1.290	0.964	0.968	1.375	1.366
	Carbon₁	s	0.003	0.0	0.0	0.008	0.008
		p	0.130	0.002	0.002	0.167	0.170
	Carbon₂	s	0.016	0.003	0.002	0.0	−0.001
		p	0.221	0.011	0.010	0.148	0.151
	Carbon₃	s	0.0	0.0	0.0	0.001	0.001
		p	0.035	0.001	0.001	0.021	0.021
1a″	Oxygen	p	1.011	1.696	1.762	0.091	0.076
	Carbon₁	p	0.721	0.240	0.163	1.007	1.010
	Carbon₂	p	0.195	0.046	0.046	0.851	0.865
	Carbon₃	p	0.073	0.017	0.019	0.051	0.049
2a″	Oxygen	p	0.321	0.123	0.136	0.871	0.947
	Carbon₁	p	−0.001	0.057	0.096	−0.005	−0.003
	Carbon₂	p	0.827	0.963	0.967	0.066	0.060
	Carbon₃	p	0.852	0.855	0.801	0.067	−0.004
3a″	Oxygen	p		0.074	0.033	0.064	−0.005
	Carbon₁	p		0.764	0.768	0.098	0.089
	Carbon₂	p		−0.006	−0.004	−0.017	−0.017
	Carbon₃	p		0.168	0.204	0.856	0.933
Net	Oxygen		−0.358	−0.209	−0.236	−0.260	−0.256
charge	Carbon₁		0.112	−0.070	−0.041	−0.083	−0.080
	Carbon₂		−0.119	−0.045	−0.048	−0.028	−0.033
	Carbon₃		−0.428	−0.494	−0.492	−0.440	−0.441

[a] Carbon₁ is the carbon nearest oxygen and carbon₂ is the central carbon. Populations given are sums over all s or p atomic basis functions on each center.

Table VI. Ground State Occupied and Virtual Orbital Energies[a]

	Trans ¹A′ gs	Cis ¹A′ gs
5 a′	−1.4115	−1.4075
6 a′	−1.1000	−1.0875
7 a′	−0.8973	−0.9087
8 a′	−0.8029	−0.7682
9 a′	−0.6831	−0.7152
10 a′	−0.6726	−0.6397
11 a′	−0.6055	−0.6136
12 a′	−0.5642	−0.5512
1 a″	−0.5446	−0.5410
13 a′	−0.4364	−0.4343
2 a″	−0.4009	−0.3946
3 a″	0.0700	0.0632
4 a″	0.1951	0.2165
14 a′	0.2474	0.2534
15 a′	0.2674	0.2781

[a] Energies are in hartrees. The highest four orbitals are unoccupied and their energies were determined from an improved virtual orbital (IVO) calculation.

double bonded central carbons mean that this biradical structure is close to an oxetene structure. The unpaired electrons on the terminal carbon and on oxygen could facilitate ring closure. It seems reasonable, then, that ring opening of an oxetene may proceed quite readily to a $\pi \rightarrow \pi^*$ state. Following the scheme put forth by Becker and co-workers[7] some twisting around the carbon–carbon bonds could then make internal conversion to the ground state efficient. Generally, the discussions of Becker et al.[7] and Devaquet and Salem[13] have shown the importance of internal rotation about the terminal carbon–carbon bond in photochemical reactions and conversion between electronic states. Of significance in this work is the unique biradical electronic structure of only the $\pi \rightarrow \pi^*$ excited states and the substantial geometric structure differences of the various electronic states. These differences may

possibly tend to lessen conversion between states if the molecule were relaxed to the equilibrium structure of an excited state than if it were at a nonequilibrium structure.

The localized nature of the valence molecular orbitals points toward a description of the electronic structure of acrolein as simply ethylene plus formaldehyde. In this model, we could expect the $\pi \rightarrow \pi^*$ states to be higher than the n $\rightarrow \pi^*$ states. As in formaldehyde, SCF calculations predict the n $\rightarrow \pi^*$ states to be too low lying;[12,29] that is, the closed-shell ground state should be lowered relative to these states by adding correlation energy. This would bring excitation energies into agreement with experiment. To the extent of the small carbonyl character of the $\pi \rightarrow \pi^*$ excitations, correlation effects should further separate the ground state and these states, as in formaldehyde.[30] A further upward shift in the $\pi \rightarrow \pi^*$ states would lead to a direct energy correlation of the acrolein excited states with either a formaldehyde or ethylene excitation. However, the conjugation of the double bonds makes the association of the $\pi \rightarrow \pi^*$ states with a pure ethylene excitation inappropriate. In glyoxal, the situation is worse, for n $\rightarrow \pi^*$ excitations are far different from molecules-in-molecules formaldehyde excitations,[12] while for butadiene, the model is successful.[31-32]

Summary

The $\pi \rightarrow \pi^*$ triplet and singlet states of acrolein are quite low lying and, depending on correlation effects, may be very close to the n $\rightarrow \pi^*$ singlet and triplet states. The manifold of excited states shows only minor differences between the cis and trans forms. The structure of the n $\rightarrow \pi^*$ states has as its primary feature a lengthened carbon–oxygen bond. For the $\pi \rightarrow \pi^*$ states, the single and double bonds between the carbons are interchanged relative to the ground state. The higher triplet and singlet states may be gauche forms, but, if so, the potential minimum should be only slightly below the energy of the planar forms. The $\pi \rightarrow \pi^*$ states are biradicals and it is possible that the cis forms of these states are involved with oxetene ring opening. Finally, the localized valence orbital nature of the

electronic states suggests that to some extent, correlation effects may be estimated from formaldehyde and ethylene. That is, the relative energy of the ground state should be shifted downward, while the $\pi \rightarrow \pi^*$ states should be shifted at least slightly upward.

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Thieno[3,4-c]thiophenes. Electronic Structure[1a]

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Abstract: Both the ground-state multiplicity, π stability ("aromaticity"), and ordering and energies of electronically excited and ionic states of the parent thieno[3,4-c]thiophene are studied theoretically in conjunction with a photoelectron spectral study of tetraphenyl[3,4-c]thienothiophene. It is shown that the thienothiophene system is "aromatic" like thiophene, but, nonetheless, unstable due to its particular HOMO structure and energy and the high reactivity resulting therefrom. Its characteristic properties, i.e., its particularly low first ionization energy (high HOMO orbital energy), low-energy first uv transition, strong charge transfer from sulfur to the carbon skeleton, and high 1,3-reactivity are rationalized on localized orbital interaction schemes.

The nature of bonding in the "nonclassical" condensed thiophenes remains a matter of some controversy.[2] With the aim of clarifying this situation we undertook a theoretical study of thieno[3,4-c]thiophene (**1**) and photoelectron (PE) spectral study of tetraphenylthieno[3,4-c]thiophene (**2**).

Theoretical and Experimental Results

Using an unrestricted version of the extended[3] CNDO/S method[4] the ground state of **1** emerges as a triplet which is 1.4 kcal/mol more stable than the closed-shell singlet state.[5,6] The situation is, however, more than reversed when configuration interaction (taking account of all singly and doubly excited configurations up to a perturbative limit of 0.002 eV) is included. In this case, the lowest singlet is 31.8 kcal/mol more stable than the lowest triplet state. Accordingly, the ground state of **1** is anticipated to be a singlet state, in accord with what is found experimentally for **2**.[7]

A very important question concerns the "aromaticity" of thienothiophenes. We provide an answer on the basis of a method which recently[8] proved very satisfactory for that purpose. It consists here of calculating the total energy of **1**
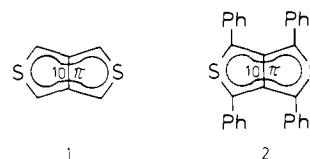
with and without sulfur π bonding and comparing the energy change with that obtained for thiophene. All calculations are done on an sp and spd basis by use of the CNDO/S procedure.[3] The conjugative stabilization energy is 94 (sp) and 138 (spd) kcal/mol for **1**, whereas 33 (sp) and 49 (spd) kcal/mol were predicted for thiophene.[8b] It is interesting to note that, accordingly, **1** is expected to be more "aromatic" than two thiophene molecules. A corresponding effect is detected in the magnitude of charge transfer from the two sulfur atoms to the carbon skeleton. It amounts to 0.72 (sp) and 0.66 e (spd) and is thus appreciably higher than for two thiophenes molecules (for one molecule: 0.22 (sp) and 0.16 e (spd)[8b]). From these data it appears that the d AO's in **1** play, just as in thiophene, no important role (as far as the ground state is concerned). The