Potential Energy Sheets for the nπ* and ππ* Triplet States of α,β-Unsaturated Ketones

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Abstract: The potential energy surfaces of the two triplet states of acrolein have been calculated in a Hartree–Fock SCF formalism. Three motions have been studied: the relaxation of the skeletal bond lengths, the twist of the CH₂ terminal group, and the out-of-plane motion of the hydrogen atom α to the carbonyl group. Using spectroscopic results, more "physically realistic" potential energy sheets have been drawn for acrolein, cyclohexenone, and testosterone acetate. These surfaces provide a better understanding of the spectroscopic properties of α,β-unsaturated ketones and some working hypotheses for their photochemical behavior.

After being vertically excited, a molecule generally undergoes some stabilizing geometrical transformations. For example the ππ* triplet state of ethylene twists 90° around the C–C bond[2a] and the singlet nπ* excited state of formaldehyde becomes pyramidal.[2b] These relaxation processes are generally much more rapid (relaxation time, 10^{-12} sec) than the collisions (collision time, 10^{-10} sec). Then the excited species usually reacts after having reached the absolute minimum, or at least some secondary minimum, of its potential energy surface. The major problem in theoretical organic photochemistry is to correlate the observed photochemical behavior and the electronic configuration of the reacting excited species. This problem appears to be very difficult to solve in the particular case of the cyclic enones. This is due to the great diversity of the possible photoreactions (cycloannelations, isomerizations, hydrogen abstraction, and solvent fixation) as well as to the complexity of the product mixtures occurring in each of these general types of reactions. For example, the photodimerization of isophorone gives[3] head to head (cis-anti-cis or cis-syn-cis) and head to tail (cis-anti-cis and cis-syn-cis) dimers. A further difficulty is our lack of knowledge on the relative localization and on the geometries of the two relaxed nπ* and ππ* triplet states from which most of the photoreactions of enones will proceed. The purpose of this paper is therefore to present the theoretical calculation of the potential energy surfaces of the two triplet states of acrolein, this molecule serving as a convenient model for the cyclic enones. All calculations were carried out within the Nesbet formalism of the *ab initio* SCF theory of symmetry and equivalence restrictions.[4] The program has been written by Stevens.[5] We shall briefly recall that (1) in the case of molecules in their closed-shell ground state, the Nesbet method is identical with that of Roothaan,[6] and the Hamiltonian $\mathcal{H}_{CS}$ is as usual written

$$\mathcal{H}_{CS} = h + \sum_{i}^{occ}(2J_i - K_i) \qquad (1)$$

The monoelectronic term h represents the kinetic energy and the attractive nuclear-electron potential energy operators. The bielectronic terms (summed over all doubly occupied molecular orbitals) take into account the Coulomb (J_i) and exchange (K_i) electron–electron interactions. (2) In the case of an excited open-shell molecule arising from the excitation of an electron out of a filled MO (k) to an empty one (l), a single Hamiltonian is used to calculate both the remaining doubly filled as well as the singly filled molecular orbitals. This Hamiltonian may be written as

$$\mathcal{H}_{OS} = h + \sum_{i \neq k}^{occ}(2J_i - K_i) + $$
$$(J_k - \tfrac{1}{2}K_k) + (J_l - \tfrac{1}{2}K_l) \qquad (2)$$

I. Ground State and Vertical Excited States of Acrolein

Since the purpose of our study is the photochemistry of cyclic enones, the *s-trans*-acrolein is obviously the most appropriate model. The numerical values used for the geometrical description of this model[7] are shown in Figure 1. The geometry of *s-trans*-acrolein being fixed on experimental grounds (and not by minimization of the calculated SCF energy with respect to all independent geometrical parameters), the *ab initio* calculations require only the knowledge of the exponents of the Slater-type atomic orbitals in which the MO's are, as usual, expanded. The exponents of this minimal basis set of atomic wave functions are chosen as 1s (H), 1.2;[8] 1s (C), 5.68; 2s (C) = 2p (C), 1.74; 1s (O), 7.70; 2s (O) = 2p (O), 2.20. Let us first describe the calculation of the ground-state energy of the planar *s-trans*-acrolein.

(a) The first step is the SCF calculation of the closed-shell ground state (A' symmetry); the determinantal wave function ψ_1 and the energy E_1 of this state are given by

$$\psi_1 = | \ldots \pi_1 \bar{\pi}_1 n\bar{n} \pi_2 \bar{\pi}_2 |$$

$$E_1 = -190.185 \text{ au} \qquad (3)$$

Regarding the detailed nature of the molecular orbitals[9]

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(2) (a) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969); (b) G. W. Robinson and V. E. Di Giorgio, *Can. J. Chem.*, **36**, 31 (1958).

(3) O. L. Chapman, P. J. Nelson, R. W. King, D. J. Trecker, and A. A. Griswold, *Rec. Chem. Progr.*, **28**, 167 (1967).

(4) R. K. Nesbet, *Rev. Mod. Phys.*, **33**, 28 (1961); **35**, 552 (1963).

(5) R. M. Stevens, *J. Chem. Phys.*, **52**, 1397 (1970).

(6) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(7) H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 691 (1951).

(8) W. E. Palke and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2384 (1966).

(9) If 1s, s, x, y, z (A) represent the atomic orbitals 1s, 2s, 2p$_x$, 2p$_y$, and 2p$_z$ on atom A then the LCAO developments and eigenvalues ε of the more important MO's are given by $\pi_1 = 0.534z(O) + 0.577z(C_3) + 0.322z(C_2) + 0.210z(C_1)$, $\epsilon_{\pi_1} = -0.460$ au; n = $-0.873y(O) + 0.156y(C_3) - 0.34(1s)(H_4) - 0.252y(C_2) + 0.157x(C_2) + 0.170s(C_2)$, $\epsilon_n = -0.341$ au; $\pi_2 = 0.415z(O) + 0.223z(C_3) - 0.546z(C_2) - 0.595-$

used to construct ψ_1 it is interesting to note that the n orbital is extensively delocalized onto other atoms. This orbital is antibonding between the $C_3 \cdot H_4$ group and the oxygen atom but is strongly bonding between the C_2 and C_3 carbon atoms. The net result is that the n orbital, far from being nonbonding, is slightly below π_2, the highest bonding MO.

(b) The second step is the calculation (by virtual excitation) of the energies of the low-lying excited singlet states of A' symmetry. The lowest singly excited state arises from the excitation of an electron out of the π_2 bonding orbital to the π_3^* antibonding one.

$$\psi_2 = \frac{1}{\sqrt{2}}\{|\ldots|\pi_2\overline{\pi}_3^*| + |\ldots\pi_3^*\overline{\pi}_2|\} = S_{\pi,\pi^*}$$

$$E_2 = -189.805 \text{ au} \tag{4}$$

The two lowest doubly excited states arise from the excitation of two electrons respectively from π_2 (S_π) and n (S_n) to π_3^*.

$$\psi_3 = |\ldots\pi_1\overline{\pi}_1 n\overline{n}\pi_3^*\overline{\pi}_3^*| = S_\pi$$

$$E_3 = -189.619 \text{ au} \tag{5}$$

$$\psi_4 = |\ldots\pi_1\overline{\pi}_1\pi_2\overline{\pi}_2\pi_3^*\overline{\pi}_3^*| = S_n$$

$$E_4 = -189.561 \text{ au} \tag{6}$$

(c) The final step is the configuration (i.e., mixing) calculation between these four states. The most important matrix element couples ψ_1 and $\psi_3 = S_\pi$ (0.117 au), whereas the other ones are very small (0.013 au between ψ_1 and $\psi_4 = S_n$) or equal to zero (between ψ_1 and $\psi_2 = S_{\pi\pi^*}$ due to the Brillouin's theorem). Therefore the state $\psi_3 = S_\pi$ is the only one which mixes appreciably with ψ_1.[10] The energy of the ground state of the s-trans-acrolein is then lowered to -190.208 au. This value shall be the zero point in our energy scale.

Let us turn now to the triplet states of s-trans-acrolein. Experimentally the (0,0) band of the $^3A''-{}^1A'$ ($^3n\pi^*$) transition has been determined by uv studies[12] and by magnetic rotation spectroscopy.[13] This (0,0)

$z(C_1)$, $\epsilon_{\pi_2} = -0.309$ au; $\pi_3^* = '0.574z(O) - 0.459z(C_3) - 0.464z(C_2) + 0.653z(C_1)$, $\epsilon_{\pi_3*} = 0.219$ au; $\pi_4^* = -0.505z(O) + 0.696z(C_3) - 0.686z(C_2) + 0.476z(C_1)$, $\epsilon_{\pi_4*} = 0.390$ au.

(10) More precisely the 4×4 determinant of the CI problem is given by

	ψ_1	ψ_2	ψ_3	ψ_4	
ψ_1	$-190.185 - E$	0	0.117	0.013	
ψ_2	0	$-189.805 - E$	-0.014	-0.013	
ψ_3	0.117	-0.014	$-189.619 - E$	0.0086	$= 0$
ψ_4	0.013	-0.013	0.0086	$-189.561 - E$	

The complete wave function of the ground state, corresponding to the lowest root $E = -190.208$ au, is represented by $\psi_{GS} = 0.9814\psi_1 - 0.1905\psi_3 - 0.0219\psi_4 - 0.0073\psi_2$. In their calculation on ethylene Kalder and Shavitt[11] have obtained very similar coefficients for the mixing of the ground state with the doubly excited $\pi \to \pi^*$ state, $\psi_{GS} = 0.96928\psi_1 - 0.24594\psi_3$. It also has to be pointed out that the first excited singlet state $S_{\pi\pi^*}$ very slightly mixes with ψ_1 (they both have the same symmetry A') but does not contribute to the energy lowering of the ground state (the matrix element between these two states being equal to zero).

(11) V. Kalder and I. Shavitt, J. Chem. Phys., 48, 191 (1968).

(12) (a) J. C. D. Brand and D. G. Williamson, Discuss. Faraday Soc., 35, 184 (1962); (b) K. Inuzuka, Bull. Chem. Soc. Jap., 34, 729 (1961); (c) A. C. P. Alves, J. Christoffersen, and J. M. Hollas, Mol. Phys., 20, 625 (1971).

(13) (a) W. H. Eberhardt and H. Renner, J. Mol. Spectrosc., 6, 483 (1961); (b) E. J. Bair, W. Goetz, and D. A. Ramsay, Can. J. Phys., 49, 2710 (1971).
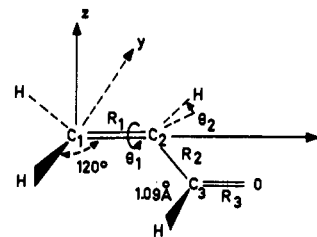
Figure 1. Skeletal structure of s-trans-acrolein.

band appears at 4122 Å (69.3 kcal/mol) and is the strongest band[12c] of the system in perfect agreement with the SCF value of the vertical excitation energy (69.6 kcal/mol) obtained using $\mathcal{K}_{OS}(2)$ with $k = n$ and $l = \pi_3^*$.[14] On the other hand nothing is known experimentally concerning the $^3A'-{}^1A'$ ($^3\pi\pi^*$) transition. The 4060-Å band of the uv spectra of acrolein was tentatively assigned to this transition[15] but this appears to be wrong. (We shall discuss later the assignments of the 4060- and 4322-Å bands.) However, the phosphorescence excitation methods show that in various steroidal enones the $^3n\pi^*$ and $^3\pi\pi^*$ triplet states are nearly degenerate with one another.[16] Since the π electronic structures of the acrolein molecule and the steroidal enones are similar, their spectral properties should be also similar. On this basis the two triplet states of acrolein should be also quasidegenerate. Theoretically (using $\mathcal{K}_{OS}$ with $k = \pi_2$ and $l = \pi_3^*$) the $\pi\pi^*$ triplet state is located 90 kcal/mol above the ground state[17] and appears to be 20 kcal/mol too high.

The vertical excitation energies of the two triplet states being determined, we consider now the effect of various deformations of the geometry of s-trans-acrolein: rotation around the single central bond and around the ethylenic double bond, relaxation of the skeletal bond lengths, and out-of-plane motion of the H_3 hydrogen atom.

II. Rotation around the Single C_2C_3 Bond

The experimental data on positions of zero point levels in torsional vibration potential energy curves in acrolein[13b] are summarized in Figure 2. Two facts have to be pointed out. The first is the existence of a second rotamer of acrolein. This rotamer may be the s-cis form or a gauche form with a small out-of-plane angle. (Such a gauche form has been

(14) The same calculation also gives the vertical energy of the $^1A''-{}^1A'$ ($^1n\pi^*$) transition, 80.9 kcal/mol. The (0,0) band of this transition is located at 3860 Å, i.e., 74 kcal/mol above the ground state of s-trans-acrolein,[12c] and the maximum is located at 29800 cm^{-1} ($\epsilon = 17$), i.e., 85.1 kcal/mol above the ground state.[15]

(15) J. M. Hollas, Spectrochim. Acta, 19, 1425 (1963).

(16) G. Marsh, D. R. Kearns, and K. Schaffner, J. Amer. Chem. Soc., 93, 3129 (1971).

(17) The singlet $\pi\pi^*$ state is found to be 186.9 kcal/mol above the ground state. The maximum of the $\pi\pi^*$ absorption band being at 1935 Å[18] the theoretical value deviates 40 kcal/mol from the experimental determination. The question may also arise of what state is in fact described by the Hartree-Fock procedure. In the case of ethylene it is now supposed that such a HF calculation does not describe the $\pi\pi^*$ (V) state (7.65 eV) but rather a Rydberg state of the same symmetry at 9.05 eV.[19] The V state would be obtained by using methods of greater sophistication, which would more effectively include the correlation (random phase approximation).[20] It must be pointed out that the acrolein molecule presents two Rydberg states in the vicinity of the $\pi\pi^*$ singlet state (respectively at 163.4 and 178.7 kcal/mol[19]). Is it possible that the HF procedure describes one of these Rydberg states?

(18) A. D. Walsh, Trans. Faraday Soc., 41, 498 (1945).

(19) H. Basch and V. McKoy, J. Chem. Phys., 53, 1628 (1970).

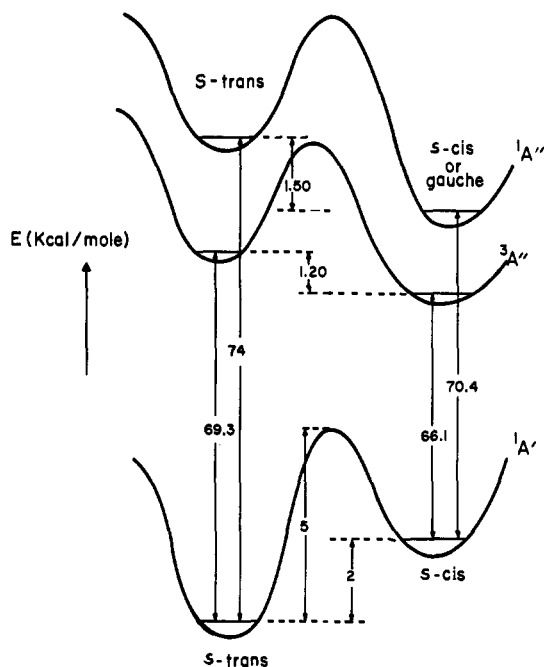(20) T. I. Shibuya and V. McKoy, ibid., 54, 1738 (1971).

Figure 2. Experimental data on positions of *zero-point levels* in torsional vibration potential energy curves. (These data include the relaxation of the bond lengths.)
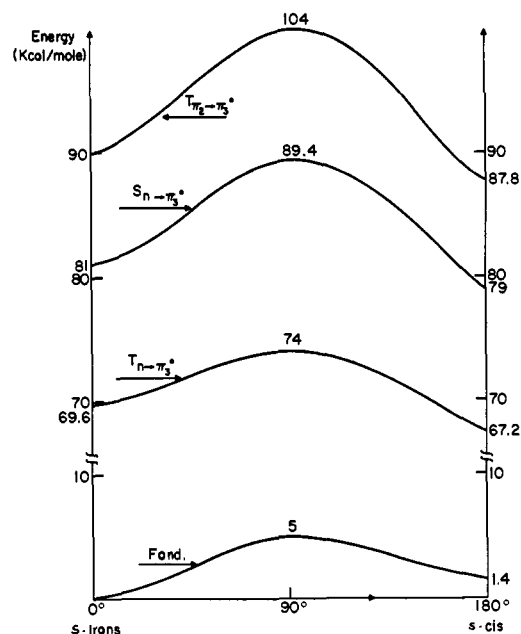

Figure 3. Theoretical potential energy curves for the ground and excited states of acrolein in the rotation around the central single bond. (These curves do not include the possible relaxation of the bond lengths.)

theoretically predicted for butadiene,[21] the angle between the two CH_2CH planes being 20°.) It seems very likely that the second rotamer has the s-cis conformation (indeed, the theoretical potential energy curve does not show such a gauche rotamer). The second point is that the deeper potential well in the singlet or in the triplet $n\pi^*$ excited states corresponds to the s-cis rotamer whereas in the ground state the correspondence is the other way round.[13b] Theoretically the angle ϕ between the two planes CH_2CH and HCO has been varied from 0 to 180° and the potential energy curves are shown in Figure 3. In the ground state the s-cis conformation is 1.4 kcal/mol less stable than the s-trans one (2.3 kcal/mol in the semiempirical calculations of Becker, et al.[22]). Experimentally this energy gap was estimated to be 2 kcal/mol (uv spectroscopy[12c]), 6.4 kcal/mol (microwave spectral studies in the gas phase[23]), and 2.09 kcal/mol (ultrasonic studies of liquid acrolein[24]). The height of the rotational barrier (5 kcal/mol in our calculations, 5.7 kcal/mol in the semiempirical ones[22]) is experimentally 5 kcal/mol[13a] (or 7.02 kcal/mol[24] in the liquid phase). In the two $n\pi^*$ excited states the s-cis rotamer is more stable than the trans one (respectively 2.4 and 2 kcal/mol for the triplet and the singlet state), the corresponding experimental values being 1.2 and 1.5 kcal/mol.[13b] The (0,0) band of the $^1A''-^1A'$ ($^1n\pi^*$) transition of the s-cis rotamer (70.4 kcal/mol) is the 4060-Å absorption band. The (0,0) band of the $^3A''-^1A'$ ($^3n\pi^*$) transition of the s-cis rotamer (66.1 kcal/mol) is the 4322-Å band of the uv spectrum.[13b] Finally the $\pi\pi^*$ triplet state of s-cis-acrolein is predicted

to be more stable (2.2 kcal/mol) than the one of the s-trans rotamer.

The torsional behavior of all these states may be simply explained in terms of the MO's (described in footnote 9). The π_1 and π_3^* molecular orbitals are bonding between C_2 and C_3 and are therefore destabilized. On the other hand π_2 is antibonding between C_2 and C_3 and is then stabilized. (The n molecular orbital remains unaffected.) In the $n\pi^*$ states three electrons are destabilized (in π_1 and π_3^*) whereas two are stabilized (in π_2) and the resulting effect is the destabilization of the states (the heights of the rotational barrier being 4.4 and 7.4 kcal/mol, respectively, in the triplet and the singlet states). For the $\pi\pi^*$ states three electrons are destabilized (in π_1 and π_3^*) whereas only one is stabilized (in π_2). The net destabilization is then bigger than in the $n\pi^*$ case (indeed the $^3\pi\pi^*$ barrier increases to 14 kcal/mol).

III. Rotation around the Ethylenic Double Bond

During the rotation process the n molecular orbital remains almost completely unaffected. Its energy slowly rises from -0.341 ($\theta = 0°$) to -0.327 and its wave function is delocalized onto the other C_2 and C_3 atoms (the major contribution arising here again from the $2p_y$ orbital on the oxygen atom). If the terminal CH_2 group twists 90° there will be two nonbonding symmetry orbitals. The first one (namely y, A' symmetry) is a nearly pure $2p_y$ atomic orbital located on C_1, whereas the second one (namely π', A'' symmetry) is of allylic type with a nodal plane passing near the C_3 carbon atom (Figure 4). The energy of the lowest singlet state may be calculated in two ways. Since the two linear combinations $\pi' + y$ and $\pi' - y$ respectively correlate with the π_2 and π_3^* MO's of the planar molecule, it is possible to use a CI treatment analogous to the one previously used at $\theta = 0°$. The

(21) M. J. S. Dewar and A. J. Harget, *Proc. Roy. Soc., Ser. A*, 315, 443 (1970).

(22) R. S. Becker, K. Inuzuka, and J. King, *J. Chem. Phys.*, 52, 5164 (1970).

(23) E. A. Cherniak and C. C. Costain, *ibid.*, 45, 104 (1966).

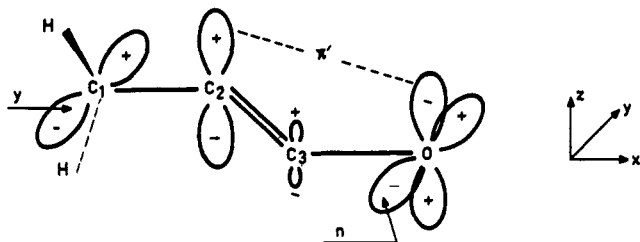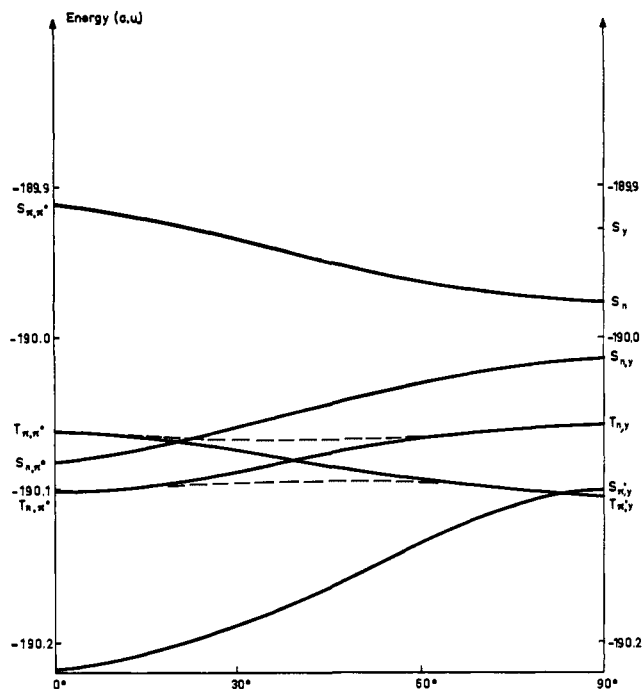(24) M. S. De Groot and J. Lamb, *Proc. Roy. Soc., Ser. A*, 242, 36 (1957).

Figure 4. "Frontier" orbitals in the 90°-twisted acrolein.

Figure 5. Theoretical twisting potentials for the ground and lowest excited states of s-trans-acrolein.

Figure 6. "Real" twisting potentials for the two excited triplet states of s-trans-acrolein.

tion energy of the cis–trans isomerization of dideuterioethylene[26]. During the rotation the $n\pi^*$ triplet state is destabilized (26.4 kcal/mol) whereas the $\pi\pi^*$ one is stabilized (24.5 kcal/mol)[27] (Figure 5). As with ethylene[11] the $\pi'y$ triplet state, lying 1.9 kcal/mol under the corresponding singlet state, is the ground state of the 90° twisted acrolein molecule. For all intermediate values of the twist angle ($0 < \theta_1 < 90°$) the two triplet states have the same symmetry (no symmetry at all) and therefore mix together, the $T_{\pi\pi^*}$ and $T_{n\pi^*}$ correlating respectively with T_{ny} and $T_{\pi'y}$ if $T_{\pi\pi^*} > T_{n\pi^*}$. If the two vertical $n\pi^*$ and $\pi\pi^*$ triplet states are nearly degenerated (Figure 6 with $T_{\pi\pi^*} > T_{n\pi^*}$) then the mixing takes place at very small angles of twist. The $\pi\pi^*$ character increases more and more in the wave function of the $n\pi^*$ triplet state. This admixture may produce a very small barrier in the curve. On the other hand the increasing amount of $n\pi^*$ character in the $\pi\pi^*$ triplet state may produce a very flat minimum in the potential energy curve of the highest triplet state. When the twist is more important the lower triplet is pure $\pi\pi^*$ (and goes down to the $\pi'y$ triplet), whereas the highest level is pure $n\pi^*$ (and goes up to the ny triplet).

IV. Relaxation of the Bond Lengths in s-trans-Acrolein

For each of the six systems of values of the three bond lengths R_1, R_2, R_3 (Table I) the angle of twist has been

mixing of the closed-shell components (7)[25] gives a wave

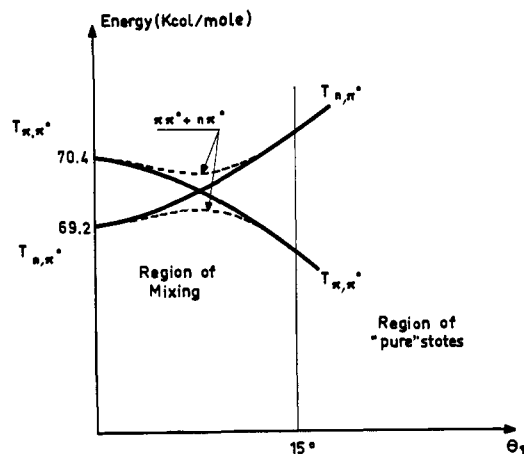$$\psi^+ = |\ldots(\pi' + y)(\overline{\pi' + y})| \text{ and}$$

$$\psi^- = |\ldots(\pi' - y)(\overline{\pi' - y})| \quad (7)$$

function whose spatial part contains a covalent Heitler–London term $\pi'(1)y(2) + \pi'(2)y(1)$ slightly "polluted" by two ionic terms $\pi'(1)\pi'(2)$ and $y(1)y(2)$. The corresponding energy is -190.085 au. The second method, a direct open-shell SCF treatment, removes the ionic terms and gives a purely Heitler–London covalent wave function, therefore slightly improving the energy value, -190.099 au. From this value the rotational barrier is found to be 68.4 kcal/mol. For comparison the corresponding value for ethylene has been determined both theoretically, 83 kcal/mol (by use of an *ab initio* SCF treatment[11]), and experimentally, 61.5 kcal/mol (as the activa-

Table I. Selected Sets of Bond Lengths for R_1, R_2, and R_3

	Geometry						
	(0)	(1)	(2)	(3)	(4)	(5)	(6)
R_1,	1.36	1.37	1.42	1.45	1.48	1.51	1.54
R_2,	1.46	1.42	1.39	1.35	1.32	1.30	1.28
R_3,	1.22	1.25	1.29	1.32	1.34	1.36	1.38

varied from 0 to 90°. The potential energy surfaces of the two triplet states of acrolein are shown in Figure 7 as a function of both R_1, R_2, R_3 and θ_1.

When the molecule remains in its planar geometry ($\theta_1 = 0°$) the vertical triplets are both stabilized by relaxation of the three bond lengths, the $n\pi^*$ state being

(25) In fact we carried out a 3 × 3 CI calculation including also the singlet state $S = (\pi' + y) \rightarrow (\pi' - y)$; the determinant to be solved is given by

$$\begin{vmatrix} \psi^+ & \psi^- & S \\ \psi^+ & -189.988 - E & 0.113 & 0 \\ \psi^- & 0.113 & -189.954 - E & 0.0218 \\ S & 0 & 0.0218 & -189.866 - E \end{vmatrix} = 0$$

and the wave function corresponding to the lowest root ($E = -190.085$ au) is $\psi = 0.7539\psi^+ - 0.6537\psi^- + 0.0647S$.

(26) B. S. Rabinovitch, J. E. Douglas, and F. S. Looney, *J. Chem. Phys.*, **20**, 1807 (1952).

(27) The $n\pi^*$ singlet state is also destabilized (78.5 kcal/mol), whereas the $\pi\pi^*$ singlet state is stabilized (50.6 kcal/mol).
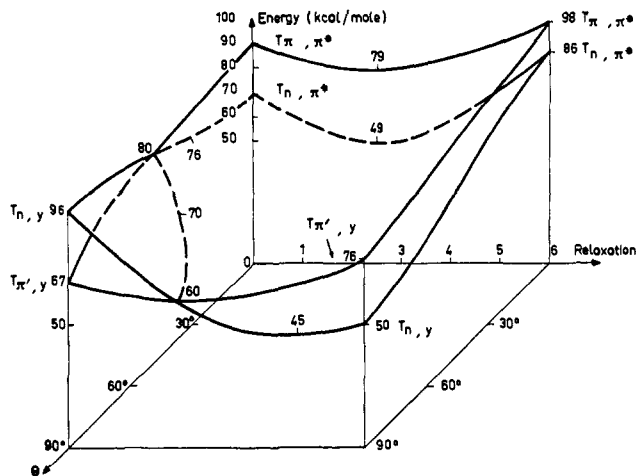
Figure 7. Potential energy surfaces of the two triplet states of acrolein. The origin of the vertical axis is the energy of the s-trans-acrolein in its equilibrium ground state (geometry (0) of Table I).
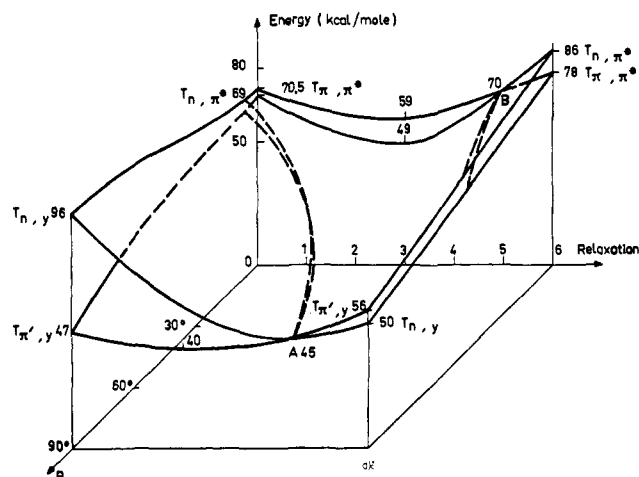

Figure 8. Potential energy sheets of the two triplet states of s-trans-acrolein.

more lowered (20 kcal/mol) than the $\pi\pi^*$ one (11 kcal/mol). The equilibrium geometries are almost the same for these two triplets (as well as for the two singlet states which show the same type of behavior): $R_1 \sim 1.43$ Å, $R_2 \sim 1.37$ Å, $R_3 \sim 1.31$ Å. Concerning first the length of the CO bond (R_3), the detailed analysis of the intensity distribution of the main progression of the $n\pi^*$ absorption band (3860 Å)—this progression being supposed to be due to a pure vibration of the carbonyl group—gives a value of 1.33 Å in the singlet state.[12b] With the same hypothesis the Badger's and Douglas Clark's rules give respectively 1.34 and 1.35 Å.[12a] In a more detailed analysis, taking now into account the three bond lengths, Hollas[15] concludes that the geometry of the $n\pi^*$ singlet state is defined by $R_1 \sim 1.46$ Å, $R_2 \sim 1.35$ Å, $R_3 \sim 1.32$ Å. The angles CCC and CCO which have not been here varied increase to 125°. All these experimental results agree fairly well with our theoretical results.[23] In order to get a qualitatively exact description of the potential energy surfaces of the two triplet states, the $^3\pi\pi^*$ sur-
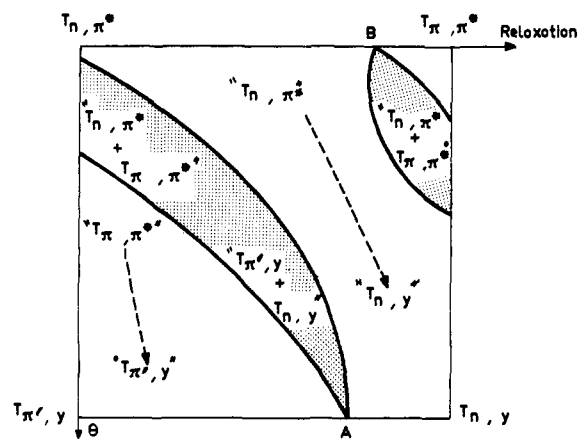

Figure 9. "Orbital nature" of the lowest triplet potential energy sheet of s-trans-acrolein.

face has been lowered by roughly 20 kcal/mol. The two vertical excited states are then nearly degenerate. Even if the absolute excitation energies of the $^3\pi\pi^*$ state are poorly calculated, we expect the relative behavior of the distorted triplet vs. the planar vertical triplet to be sufficiently well described. The CI calculation and this lowering being done we obtain two potential energy sheets (Figure 8) which have only two common points (A and B). In these points the two triplet wave functions, belonging to different irreducible representations (A' and A'') of the symmetry group C_s of the molecule, do not interact.

The important consequence is that we can no longer speak of the $n\pi^*$ or $\pi\pi^*$ triplet state but only of the lowest or highest state, the "orbital nature" of each of these states depending on the point of the sheet where it has to be defined. For example, Figure 9 represents the description of the lowest sheet in terms of orbitals. The vertical $n\pi^*$ triplet state allowed to relax its bond lengths (without any twist) remains a $n\pi^*$ triplet state (for very improbable bond lengths, geometry (6), it would be transformed to a $\pi\pi^*$ state). Allowed to twist without changing its bond lengths, geometry (0), this triplet acquires more and more $\pi\pi^*$ character and finally becomes a pure $^3\pi\pi^*$ state. Both twist and relaxation motions transform the $n\pi^*$ triplet slowly into the $n y$ triplet state.

V. Out-of-Plane Motion of H₃

In s-trans-acrolein the relaxation and twist motions were entirely free. When however the enonic group is incorporated to a cycle (cyclohexenone, steroidal enones, ...) the ring strain partly (if, for example, the enonic group belongs to the ring A of steroids) or almost completely (ring B of steroids) prevents these displacements of atoms. The excited specie must imagine less obvious and less efficient ways of stabilizing itself. The out-of-plane motion of H₃ (θ_2) may be such a way because it may help the twisting motion of the CH₂ group. Figure 10, $E(\theta_1,\theta_2)$, shows the effect of this displacement[29] in the case of the $\pi\pi^*$ triplet state.[30] The most stable point always corresponds to θ_1 (twist motion) = 90° and θ_2 (out-of-plane motion) = 0° but

(28) When the CH₂ group is at a 90° twist the two equilibrium geometries are now different. $n y$ triplet state: $R_1 \sim 1.50$ Å, $R_2 \sim 1.31$ Å, $R_3 \sim 1.35$ Å. $\pi' y$ triplet state: $R_1 \sim 1.42$ Å, $R_2 \sim 1.38$ Å, $R_3 \sim 1.30$ Å.

(29) During its out-of-plane motion the hydrogen atom H is supposed here to remain in the bisecting plane of the $C_1C_2C_3$ angle.
(30) This motion does not affect the $n\pi^*$ triplet state which is destabilized by the twisting motion.

the best stabilizing path results from an out-of-plane motion of H_3 in the opposite direction of the twist motion ($\theta_1 > 0$, $\theta_2 < 0$). This motion increases as much as possible the angle between the CH_2 and $C_1C_2H_3$ planes. If then the molecule is not constrained (acrolein) the stabilization process ends at C. If, however, the molecule is strained (cyclohexenone) in such a manner that a twist of no more than 60° is possible, the most stable point will be D, where the out-of-plane motion ($\theta_2 = -40°$) brings an extra stabilization energy of 4 kcal/mol. At that point D (a) the originally pure $2p_z$ atomic orbitals on C_1 and C_2 carbon atoms acquire some $2s$ character; (b) the axis of these new hybrid orbitals are almost perpendicular and such a triplet may be called an "orthogonal" (here πy) triplet state. Finally it must be pointed out that this extra stabilization brought by the out-of-plane motion is maximum in the case of the (0) geometry; when the bond lengths are allowed to relax this effect decreases. It vanishes in the case of the (4) geometry.

VI. Experimental Evaluation of the Stabilization of the Excited States of Unsaturated Ketones

In short the potential energy sheets (Figure 8) tell us that (1) the $n\pi^*$ triplet state remains planar and is lowered (20 kcal/mol) only by the relaxation of the three skeletal bond lengths; (2) the $\pi\pi^*$ triplet state is also lowered by this relaxation process (though to a lesser extent, 11.5 kcal/mol) but is much more efficiently stabilized by the twist of the CH_2 terminal group (23.5 kcal/mol) in the case of an unstrained molecule (acrolein), or by both the twist and the hydrogen out-of-plane motion (22.5 kcal/mol when $\theta_1 = 60°$ and $\theta_2 = -40°$) in the case of a cyclic molecule (cyclohexenone). It is important to compare these results with the available experimental informations. The singlet states stabilization energies may be approximated as the difference between the energies of the Franck–Condon maxima and of the (0,0) band (or sometimes of the onset) of the $n\pi^*$ and $\pi\pi^*$ absorption spectra. Due to the relaxation of the bond lengths, the stabilization energies of the $^1n\pi^*$ state may be estimated to be 11.2, 9.5, and 6.7 kcal/mol in the cases, respectively, of acrolein and monocyclic and polycyclic enones (Table II). The

Table II. Franck–Condon and (0,0) Excitation Energies of the $n\pi^*$ Singlet State of α,β-Unsaturated Ketones[a]

| | Energy | | | |
Substance	Franck–Condon	(0,0)	Stabilization	Ref
Acrolein	85.4	74.2	11.2	15
α-Methylacrolein	86.6	77.3	9.3	b
β-Methylacrolein	86.6	77.3	9.3	b
2-Methylcyclohexenone	87.4	77.5	9.9	c
Isophorone	88	77.7	10.3	c
Cholest-1-en-3-one	83.1	76.4	6.7	c
β-Amyra-1,12-dien-3-one	86.1	79.6	6.5	c

[a] All values in kcal/mol. [b] B. O. Saskena and R. E. Kagarise, *J. Chem. Phys.*, **19**, 994 (1951). [c] R. C. Cookson and S. H. Dandegaonker, *J. Chem. Soc.*, 1651 (1955).

acroleinic value is in poor agreement with the theoretical one, 25.1 kcal/mol (ratio 0.44). Since the $n\pi^*$ singlet and triplet states have similar charge distribution and
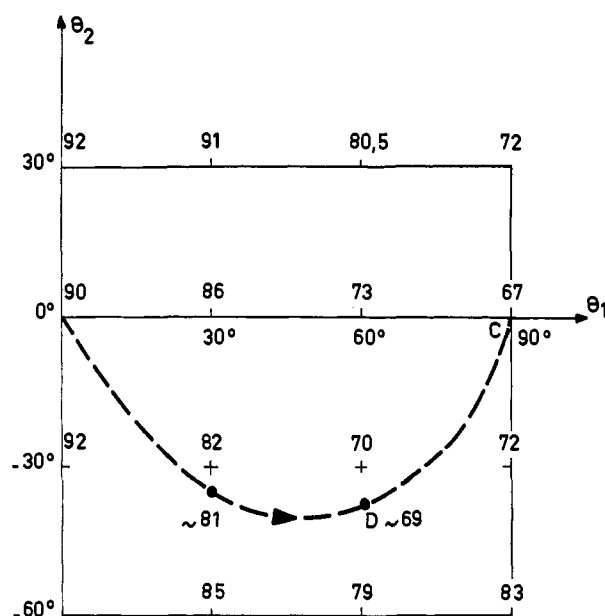

Figure 10. Influence of the out-of-plane motion of the H_3 hydrogen atom in the case of the $\pi\pi^*$ excited triplet state of s-trans-acrolein.

MO description,[31] this ratio may be used in the triplet case. The stabilization energies of the $^3n\pi^*$ are then *ca.* 9 (acrolein), 7.5 (monocyclic enones), and 5.5 kcal/mol (polycyclic enones).[32] The average stabilization energies of the $\pi\pi^*$ singlet state (due to the twist and out-of-plane motions) are 24.3, 21, and 13.1 kcal/mol in the three cases mentioned above (Table III). The theoretical result for acrolein being 50.6 kcal/mol the one-half ratio holds here again. However, the charge distribution of the $\pi\pi^*$ triplet state has been calculated[31] to be intermediate between the ground and $\pi\pi^*$ singlet states distributions.[33] In addition the singlet state is more "diffuse" than the triplet.[19] If, nevertheless, we keep the same ratio between experimental and calculated stabilization energies, the "real" lowering energies of the triplet $\pi\pi^*$ states are roughly 11.5 (acrolein), 10 (monocyclic enones), and 6.2 kcal/mol (polycyclic and steroidal enones). The $\pi\pi^*$ triplet state is a little more stabilized, by both the twist and out-of-plane motions, than is the $n\pi^*$ triplet state by the relaxation process.

VII. Spectroscopy and Photochemistry of Enones

The spectroscopic behavior of acrolein has been studied by Becker, *et al.*[22] Here we mainly recall their conclusions. The quantum yields of fluorescence and phosphorescence are very low (7 × 10^{-3} and 4 × 10^{-5}, respectively), so one may conclude that 100% of the absorbed quantas are internally converted or photochemically used. A possible photochemical process would be the s-trans–s-cis isomerization by rotation around the central single bond. Our calculations have shown that the rotational barriers in the $n\pi^*$ singlet

(31) H. E. Zimmermann, R. W. Binkly, J. J. McCullough, and G. A. Zimmermann, *J. Amer. Chem. Soc.*, **89**, 6589 (1967).

(32) The lowering of the $^3\pi\pi^*$ due to this relaxation process is guessed to be roughly 3 or 4 kcal/mol.

(33) In the $n\pi^*$ states the C_1 and C_2 carbon atoms bear negative net charges. These two positions in the $\pi\pi^*$ states are electron deficient. In addition it may be added that the C_2 position in the orthogonal $\pi'y$ triplet state is clearly electron deficient, whereas the C_1 net charge is slightly negative.

Table III. Franck–Condon and (Extrapolated) Onset Energies of the $\pi\pi^*$ Singlet State of α,β-Unsaturated Ketones[a]

Substance	Max of band	Onset of band	Stabilization energy	Ref
Acrolein	147	122.7	24.3	18
2-Methyl-5-isopropenyl-Δ^2-cyclohexenone-1 (carvone)	121.5	99.5	22	b
3-Methyl-6-isopropyl-Δ^2-cyclohexenone-1 (piperitone)	121.5	101.5	20	b
4-Isopropyl-Δ^2-cyclohexenone-1 (cryptone)	124.8	102.5	22.3	b
$\Delta^{4,7}$-Ergostadienone-3	119	105.9	13.1	c
Δ^4-Androstenedione-3,17	119	105.6	13.4	d
Testosterone	119	105.6	13.4	d

[a] All values in kcal/mol. [b] R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1408 (1938). [c] F. Wetter and K. Dimroth, *Ber.*, **70**, 1665 (1937). [d] A. Butenandt and D. Peters, *ibid.*, **71**, 2690 (1938).
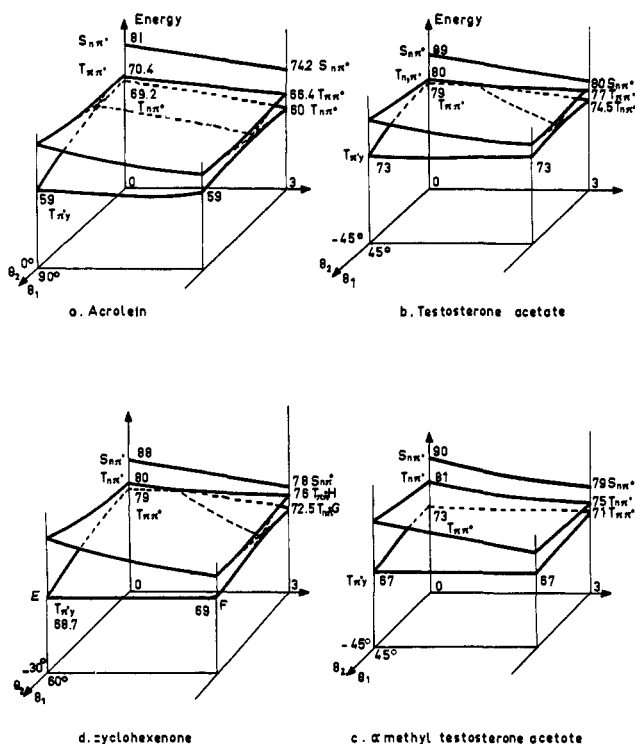

Figure 11. Potential energy sheets for the two triplet states of various enonic compounds.

state (7.4 kcal/mol), in the $n\pi^*$ triplet state (4.4 kcal/mol), and in the $\pi\pi^*$ triplet state (14 kcal/mol) are equal or greater than the ground state barrier (5 kcal/mol). It appears then that no s-trans–s-cis isomerization is expected in acrolein. Indeed there is no change in the intensity and shape of the fluorescence spectrum and no appearance of new bands during the irradiation. Another important mode for loss of quantas would be the twist around the ethylenic double bond. This twisting is indeed a stabilization process of the lowest triplet state (Figure 11a). Near 90°, the lowest $\pi'y$ triplet is nearly degenerate with the ground state and efficient intersystem crossing $T_{\pi'y} \rightarrow S_{\pi'y}$ occurs followed by vibrational relaxation $S_{\pi'y} \rightarrow S_0$. The extremely weak phosphorescence is produced when the molecule is twisted at some intermediate angle.

Let us now turn to the case of polycyclic α,β-unsaturated enones, for example, the testosterone acetate. The work of Marsh, Kearns, and Schaffner[34,35] has

(34) G. Marsh, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **51**, 1890 (1968).

established that the (0,0) band of the $n\pi^*$ triplet state absorption band and the beginning of the $\pi\pi^*$ phosphorescence emission are very close respectively at 74.5 and 73 kcal/mol. The stabilizations of these states being respectively equal roughly to 5.5 and 6.2 kcal/mol, we expect the vertical excited triplet states to lie at 80 ($n\pi^*$ triplet) and 79 kcal/mol ($\pi\pi^*$ triplet). The potential energy sheets of these two triplets are shown in Figure 11b, where the twist motion has been limited to $\theta_2 = 45°$ and the out-of-plane motion to $\theta_2 = -45°$. The two vertical excited states are almost degenerate and they are strongly interacting. The diffuseness of the $S_0 \rightarrow T_{n\pi^*}$ absorption band is attributed to this strong $n\pi^*$ and $\pi\pi^*$ mixing[34] (*cf.* Figure 6). In addition, whereas the $n\pi^*$ triplet remains planar the $\pi\pi^*$ triplet changes its geometry to a nonplanar configuration resulting from both the twist and out-of-plane motions. The diffuseness of the $\pi\pi^*$ phosphorescence emission is attributed to this nonplanar configuration.[34]

In order to understand the photochemistry of monocyclic enones we must have a description of the potential energy sheets of the two triplet states of cyclohexenone. Since lack of experimental data would otherwise make drawing impossible, we make the reasonable hypothesis that the two vertical excited states of cyclohexenone have respective locations similar to those of the testosterone acetate. Here, however, the stabilization energies are increased due to the less hindered motions ($\sim$10 kcal/mol for the twisted $\pi\pi^*$ triplet and 7.5 kcal/mol for the relaxed $n\pi^*$ triplet). The lower potential energy sheet presents a more or less flat valley of minimum energy. This valley (Figure 11d) starts at the orthogonal triplet state $\pi'y$ (E, 68.7 kcal/mol) and, passing through the relaxed and twisted $n y$ triplet (F, 69 kcal/mol), goes up to the planar relaxed $n\pi^*$ triplet (G, 72.5 kcal/mol). The excited species most likely to react are then either the $n\pi^*$ (G) or the $\pi'y$ (E) triplet states.[36]

It is generally admitted that in the photoadditions of olefins to cyclic enones the oxetane adduct is formed in the $^3n\pi^*$ state.[37] If the polarity of the medium increases, the vertical $n\pi^*$ or $\pi\pi^*$ triplet states are destabilized or stabilized, respectively.[33] Therefore the

(35) D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968).

(36) In addition the point G may act also as a reservoir of excited species which may be thermally promoted to the planar relaxed $\pi\pi^*$ triplet state (the point H of the higher potential energy sheet, in Figure 11d, is only 3.5 kcal/mol higher than G).

(37) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

(38) When a nonpolar solvent (n-hexane) is replaced by a polar one (ethanol), the vertical energy of the $n\pi^*$ singlet is increased[39] (the average increase is 3.8 kcal/mol). The difference in electron distribution be-

populations of G or E decrease or increase, respectively. For example, in the photoaddition of 1,1-dimethoxyethylene to isophorone[41] the oxetane adduct is the major product in n-hexane (42%), is observed in benzene (13%), and is not formed in *tert*-butyl alcohol.

If the absolute minimum of the lowest triplet is at 68.7 kcal/mol (the so called "orthogonal" triplet state), this result is in good agreement with the experimental conclusions. de Mayo has shown[42] that the triplet which reacts in photoannelation and the lowest triplet of cyclohexenone are close together, if they are not identical, in the region of 66.68 kcal/mol. The photoannelation with cyclohexene is, for example, sensitized by the p-trifluoromethylacetophenone which has a triplet energy ($E_T = 70.8$ kcal/mol) greater than the energy of the orthogonal triplet, but smaller than that of the vertical spectroscopic state ($\sim$78 kcal/mol). It appears here necessary to postulate a nonvertical (non-Franck–Condon) sensitization process of the flexible cyclohexenone.[43] The photocycloaddition of olefins (characterized by the two MO's, π and π^*) to cyclohexenone is a very easy process if the excited cyclohexenone reacts in its orthogonal triplet. The orbital interactions ($\pi' + y$ with π and $\pi' - y$ with π^*) strongly favor the formation of the trans adduct (*cf.* Figure 4) and one may wonder if the trans adduct is not the only primary product. The

cis adduct would arise from the opening of a cyclobutenic bond. The resulting equilibrium, trans adduct $\rightleftarrows$ cis adduct, would have two limiting cases: the addition of tetramethylene (no cis adduct formed) and of dichloroethylene (no trans adduct). More generally, Eaton has found[44] that in most of the cases olefins bearing electron-withdrawing groups did not form trans-fused products. Such groups may, for example, favor the breaking of one of the two newly formed cyclobutane bonds or of the CH bond α to the carbonyl group. It would be of great interest to test experimentally this working hypothesis.

Concerning finally the substitution effects, the α methylation of cyclohexenone stabilizes both the $\pi\pi^*$ vertical triplet and the $\pi'y$ orthogonal triplet[45] (these two states have electron deficient α positions, see footnote 33). If we *suppose* that the intersystem crossing to the twisted ground state $T_{\pi'y} \rightarrow S_0$ is enhanced by this 6 kcal/mol energy lowering, we may explain why the 2-methyl substitution greatly diminishes the rate of the photoreaction relative to that of 2-cyclohexenone. If the enone is β substituted the $\pi\pi^*$ vertical triplet (which has an electron-deficient β position) is stabilized here again, but the "orthogonal" triplet (which has a slightly negative net charge in the β position) is not affected. The fact that the intersystem crossing would be unmodified could explain why the substitution of a 3-methyl group in place of a hydrogen does not cause significant rate retardation.[46]

tween the $n\pi^*$ singlet and triplet states is presumably small, and the $n\pi^*$ triplet will exhibit the same behavior. In the same conditions the vertical $\pi\pi^*$ singlet state energy decreases[40] (the average value of lowering is 3.9 kcal/mol). As we have already seen, the electronic distribution of the $\pi\pi^*$ triplet is intermediate between those of the ground state and of the $\pi\pi^*$ singlet state. The $\pi\pi^*$ triplet state also would be lowered though to a lesser extent ($\sim$2 kcal/mol?).

(39) E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3261 (1958).
(40) R. B. Woodward, *ibid.*, **63**, 1123 (1941).
(41) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *ibid.*, **90**, 1657 (1968).
(42) P. de Mayo, A. A. Nicholson, and M. F. Tchir, *Can. J. Chem.*, **48**, 225 (1970).
(43) G. S. Hammond and J. Saltiel, *J. Amer. Chem.*, **85**, 2816 (1963).
(44) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).
(45) The α methylation of testosterone acetate lowers the onset and the maximum of the phosphorescence band by respectively 6.1 and 6.6 kcal/mol[34] (see, for example, Figure 11c).
(46) E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).