Organic and Biological Chemistry

Quantum Organic Photochemistry. I. Intramolecular Potential Energy Surfaces for the Lowest $^3\pi\pi^*$ State of Polyenes[1]

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Abstract: The potential energy surfaces for the lowest $^3\pi\pi^*$ states of polyenes are investigated by *ab initio* (ethylene only), semiempirical SCF–CI, and perturbation molecular orbital theories. The calculated positions of the λ_{max} and 0–0 band positions are in good agreement with available experimental data. The configuration interaction results predict that twisting of one "essentially double" carbon–carbon bond is favorable in polyenes, and indicate a preference for inner, rather than terminal, bond twisting. The barriers to planarity and shapes of the potential curves are rationalized using first-order perturbation theory and the relative stabilities of the biradicals involved.

Until recently, the majority of theoretical calculations reported for the excited states of conjugated molecules have been concerned with the prediction of the λ_{max} band position in singlet–singlet absorption spectra. Thus such calculations deal with the energy difference between the lowest vibrational level of the ground state and an upper vibrational level of the excited state. In contrast, we are concerned in this series of papers with the energetics of the lowest vibrational level of electronically excited states (particularly triplets), since only with such information can intermolecular photochemical reactions in solution be rationalized and predicted.

To this end, molecular orbital calculations at three levels of sophistication—all-electron *ab initio* theory, semiempirical π electron theory with configuration interaction, and independent-electron perturbation techniques—are used to predict the equilibrium bond angles, bond lengths, and bonding energies in low-lying excited states. In the present report, these methods are employed to study the intramolecular energy surface for the lowest $^3\pi\pi^*$ state of ethylene and conjugated polyenes.

Theoretical Methods

(1) *Ab initio* Calculations. The optimum carbon–carbon bond distances in the planar and twisted conformations of ethylene in its $^3\pi\pi^*$ state were evaluated by all-electron, nonempirical SCF-LCAO-MO calculations using a minimal Slater orbital basis set (1s orbitals on H; 1s, 2s, 2p orbitals on C). The closed-shell Hartree–Fock–Roothaan method[2] was used to determine optimum eigenvectors for the ground state, from which the triplet energy was computed by Pople's formula[3]

$$\Delta E = \epsilon_{\pi^*} - \epsilon_\pi - J_{\pi\pi^*}$$

Here ϵ_π and ϵ_{π^*} represent eigenvalues for the π and π^* molecular orbitals, and $J_{\pi\pi^*}$ is the Coulomb repulsion integral between these MOs. All the energy integrals required were evaluated by simulating each Slater-type orbital (STO) as a linear combination of two Gaussian-type orbitals (GTOs) using the STO-2G expansion coefficients and GTO exponents of Hehre, *et al.*[4] The STO exponents employed were those found to be optimum for the ground state at the STO-3G level;[4] *i.e.*, 1.23 for $1s_H$, 5.67 for $1s_C$, and 1.70 for $2s_C$ and $2p_C$ orbitals. Previous experience with such basis sets suggests that accurate bond lengths can be obtained in this manner.[5]

The optimum bond distance R_e for each conformation was determined by calculating the triplet energy for four R values close to the expected R_e value, and then fitting these energies to a cubic equation in R. A twist angle of 89.5° (rather than exactly 90°) was used for twisted ethylene to ensure that both the π and π^* MOs properly reflected the symmetry of the molecule. All the C–H bond lengths were held constant at 1.083 Å, and H–C–H angles of 120° were assumed.

(2) Semiempirical SCF Calculations. The semiempirical SCF π-electron theory used herein is a variant of the NNDO method[6] recently developed in this laboratory, and differs from the usual Pariser–Parr–Pople method in two important respects.

First, both overlap integrals and energy integrals involving differential overlap are *not* neglected in the NNDO method if the two p_π orbitals concerned belong to carbon atoms which are σ bonded to each other. The inclusion of such "bonded overlap" allows one to predict accurate excited-state energies with the same values for the semiempirical parameters as those which yield the most accurate ground-state energies.[6] The inclusion of overlap also avoids the difficulties encoun-

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[2] C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).

[3] J. A. Pople, *Proc. Phys. Soc.*, A68, 81 (1955).

[4] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969).

[5] (a) N. C. Baird, *Chem. Phys. Lett.*, 6, 61 (1970); (b) it is anticipated that the optimum orbital exponents for the triplet state of ethylene should be almost identical with those for the ground state, since this has been established for acetylene by M. G. Griffith and L. Goodman, *J. Chem. Phys.*, 47, 4494 (1967).

[6] N. C. Baird, *Mol. Phys.*, 18, 29 (1970).

tered in deducing excited-state geometries by zero-differential-overlap methods.[7]

Second, the total energy ($\sigma + \pi$) associated with the carbon–carbon bonds is minimized in the NNDO method by using a self-consistent bond order–bond length correlation and a Morse potential for the σ bond energy as in Dewar's methods.[8]

Since the NNDO theory has been described in full elsewhere,[6] only the revisions will be outlined here; the new parameter set yields more accurate bond lengths and heats of formations for ground states than did the original values.

(i) The equilibrium C(sp^2)–C(sp^2) bond energy is increased from 88.0 to 88.8 kcal/mol.

(ii) The two-center component of the resonance integral between bonded carbon atoms separated by distance R (in ångströms) is taken as

$$\beta = -105.202/\exp(1.985R) \qquad (1)$$

(iii) The bond lengths R are now made self-consistent *via* a linear correlation with the bond order matrix P (rather than P') by

$$R_{\text{uv}} = 1.496 - 0.2021P_{\text{uv}} \cos \phi \qquad (2)$$

where ϕ is the twist angle between the pair of bonded p_π orbitals u and v.

For nonplanar polyene geometries, the resonance and overlap integrals are evaluated from the values β^0 and S^0 for parallel p_π orbitals using the cosine of the twist angle

$$\beta = \beta^\circ \cos \phi \qquad (3)$$

$$S = S^\circ \cos \phi \qquad (4)$$

No allowance is made for hyperconjugative interactions between the "localized" σ electrons and the π networks in the nonplanar species, since the magnitude of this effect is very small according to the *ab initio* results.

The optimum, self-consistent field eigenvectors and bond lengths for the lowest $^3\pi\pi^*$ state were determined using Dewar's "half-electron" method,[9] and for the ground state by the usual closed shell procedure.[2] All transition energies and potential surfaces discussed herein are based upon the optimum energies obtained by allowing the basic (lowest energy) configuration to interact with other Slater determinants which result from one-, two-, and three-electron excitations from the three highest bonding π MOs to the three lowest antibonding π MOs. For ethylene and for butadiene, all possible configurations were allowed in the final state wave functions. For the hexatrienes and for octatetraene, the configurations were ordered according to the absolute magnitude of the matrix element connecting the determinant with the basic configuration; at least 10 and up to 20 such configurations were allowed to mix in the final wave function, the cut-off point being determined when the matrix element involved fell below ±0.45 of the largest such interaction.[10] It is interesting to note that the introduction of configuration interaction lowered the S$_0$–T$_1$ transition energies but did not alter the general shapes of the potential surfaces associated with double-bond twisting.[11]

Results and Discussion

Table I. SCF Bond Lengths (in Ångströms) for Polyenes[a]

Hydrocarbon	Bond	Ground state planar[b]	Lowest planar	$\pi\pi^*$ triplet 90° twisted
Ethylene (*ab initio*)	1–2	1.330	1.569	1.519
Ethylene	1–2	1.337	1.537	1.496[c]
trans-Butadiene	1–2	1.342	1.449	1.496[c]
	2–3	1.472	1.373	1.390
	3–4	1.342	1.449	1.390
trans,trans-Hexatriene	1–2	1.343	1.403	1.390
	2–3	1.470	1.387	1.390
	3–4	1.348	1.465	1.496[c]
Isohexatriene	1–2	1.342	1.381	1.367
	2–3	1.473	1.416	1.422
	3–6	1.347	1.474	1.496[c]
trans,trans,trans-Octatetraene	1–2	1.343	1.380	1.390
	2–3	1.469	1.407	1.390
	3–4	1.349	1.445	1.496[c]
	4–5	1.467	1.371	1.366
	5–6	1.349	1.445	1.424
	6–7	1.469	1.407	1.424
	7–8	1.343	1.380	1.366
β-Carotene	1–2	1.343	1.346	1.347
	2–3	1.469	1.461	1.459
	3–4	1.349	1.363	1.367
	4–5	1.466	1.439	1.431
	5–6	1.350	1.387	1.396
	6–7	1.466	1.408	1.397
	7–8	1.351	1.419	1.431
	8–9	1.466	1.379	1.368
	9–10	1.351	1.444	1.458
	10–11	1.466	1.363	1.348
	11–12	1.351	1.453	1.496[c]

[a] Calculated by the NNDO method unless indicated otherwise. [b] Indicates bond distances used for both ground state and for excited state in λ_{max} calculations. [c] Indicates bond twisted by 90°. Results are listed only for the most energetically stable of the twisted forms possible.

Since the semiempirical parameters of the NDDO method were evaluated by fitting ground-state properties, it is important to test the ability of the theory to predict accurately geometries and energies for excited triplets. To this end, the total bonding energies for both the ground and lowest $^3\pi\pi^*$ states of several compounds have been calculated (with extensive CI), using in each case a completely planar geometry and bond lengths which are optimum for the *ground* state (see third column of Table I). The energy difference between the two states computed in this manner should correspond to the band of greatest intensity and greatest energy in the S$_0$–T$_1$ absorption spectrum.[9c] For ethylene, *trans*-butadiene, and *trans,trans*-hexatriene, the calculated transition energies of 109.5, 80.5, and 67.5 kcal/mol, respectively (Table II), are 4–8 kcal/mol larger than the λ_{max} positions of 104.6, 74, and 60 kcal/mol assigned by Evans.[12] A recent analysis of the ethylene spectrum by Merer and Mulliken indicates that some of the peaks assigned by Evans to singlet–

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(7) N. C. Baird, *Chem. Commun.*, 199 (1970).

(8) See M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969), and previous papers of the series.

(9) (a) M. J. S. Dewar, J. Hashmall, and C. G. Venier, *ibid.*, **90**, 1953 (1968); (b) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); (c) M. J. S. Dewar and N. Trinajstic, *Chem. Commun.*, 646 (1970).

(10) All CI matrix elements were computed according to the formulas given in R. G. Parr, "The Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N. Y., 1964, Chapter II.

(11) More complete details of the calculations are available from the authors.

(12) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

Table II. Calculated S_0-T_1 Excitation Energies (NNDO Method)

	Transition energy, kcal/mol		
Hydrocarbon	ΔE (λ_{max})	ΔE to best planar conformation	ΔE to best twisted conformation (λ_{0-0})
Ethylene	109.5	77.3	61.7
trans-Butadiene	80.5	57.6	53.3
trans,trans-Hexatriene	67.5	48.1	42.0
Isohexatriene	72.3	55.5	48.2
trans,trans,trans-Octatetraene	63.2	43.6	40.3

singlet absorption are, in fact, due to the triplet, and that a value of ∼108 kcal/mol for λ_{max} is more realistic.[13] Assuming that corrections of this order (∼kcal/mol) should also be applied to the Evans' values for butadiene and for hexatriene, then the calculated λ_{max} energies agree satisfactorily with the spectral values.

From their analysis of the ethylene spectrum, Merer and Mulliken were also able to estimate the optimum carbon–carbon distance in the *planar* triplet and the 0–0 band position of the *twisted* triplet. The calculated planar C=C separations in the triplet of 1.57 Å (*ab initio*) and 1.54 Å (NNDO) agree well with their estimate of 1.58 Å, while the (NNDO) calculated 0–0 energy of 61.7 kcal/mol lies only slightly above their estimate of ∼57 kcal/mol.[13] In summary, comparison of the molecular orbital calculations with the limited amount of spectroscopic information available indicates that transition energies and bond lengths for polyene $^3\pi\pi^*$ states can be predicted to within a few per cent, and thus the potential energy surfaces calculated for polyene triplets by the NNDO method should be sufficiently accurate for chemical purposes.

Conjugation in Polyene Triplets. The equilibrium bond lengths determined for the planar and twisted conformations in the triplet (Table I) indicate the unusual effects of conjugation in the excited state. Both the *ab initio* and NNDO methods predict an equilibrium carbon–carbon distance in the planar ethylene triplet which is significantly *longer* than that for a C(sp^2)–C(sp^2) single bond, whereas that in the twisted triplet is shorter by 0.04–0.05 Å and is close to that expected for a single bond. Further, the best planar geometry for both butadiene and for the unbranched hexatriene also contain one or more rather long bonds (Table I). These unusual effects, and the preference of the triplets for a conformation twisted by 90° about a C=C bond (*vide infra*), can be understood by an extension, using perturbation theory, of Mulliken's theory for the ethylene triplet[14] to polyene systems in general.

Consider first an acyclic polyene XY twisted by 90° about one bond, r–s, which is a double carbon–carbon linkage in the ground-state representation. If both hyperconjugation effects and nonbonded overlap are neglected, the π MOs of the twisted polyene do not extend along the entire molecule, but are associated with one or the other of the orthogonal π networks X and Y joined at the r–s bond.

Since a double bond is twisted, both X and Y possess odd numbers of p_π orbitals. According to independent electron theory, the π MOs of X and Y are identical with those for the free radicals (XH)· and (YH)·. In particular (see Appendix), the two unpaired electrons singly occupy two "nonbonded" MOs (NBMOs), denoted ϕ_X and ϕ_Y. When XY becomes planar, the two NBMOs combine to yield a more stable bonding orbital, ψ^+, and a less stable antibonding orbital, ψ^- (Figure 1). The first-order relationship between the energy levels ϵ^+ and ϵ^- (of ψ^+ and ψ^-, respectively), and those of ϵ_X and ϵ_Y in the twisted conformation, is given by the 2 × 2 secular determinant

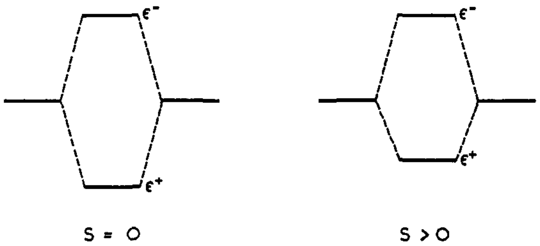

Figure 1. First-order interaction between degenerate nonbonding orbitals, with (a) overlap integrals neglected, and (b) overlap included.

$$\begin{vmatrix} \epsilon_X - \epsilon & \beta_{XY} - \epsilon S_{XY} \\ \beta_{XY} - \epsilon S_{XY} & \epsilon_Y - \epsilon \end{vmatrix} = 0 \qquad (5)$$

Here β_{XY} and S_{XY} represent, respectively, the resonance and overlap integrals between the molecular orbitals ϕ_X and ϕ_Y. Note that eq 5, and subsequent equations, apply regardless of whether X and Y are degenerate or not.

If all overlap integrals between different atomic orbitals are (incorrectly) neglected as in the simple Hückel method, the $S_{XY} = 0$ and the energy levels ϵ^+ and ϵ^- are split equally about the average of ϵ_X and ϵ_Y. However, if overlap integrals are *not* neglected, the antibonding level ϵ^- is destabilized to an extent *greater* than the bonding level ϵ^+ is stabilized; mathematically the eigenvalues are given by

$$\epsilon^{\pm} = (\epsilon_X + \epsilon_Y - 2\beta_{XY}S_{XY} \pm T)/2(1 - S_{XY}^2) \qquad (6)$$

where

$$T^2 = (\epsilon_X - \epsilon_Y)^2 + 4\beta_{XY}^2 + 2\beta_{XY}S_{XY}^2 + 4\epsilon_X\epsilon_Y S_{XY}^2 - 4\beta_{XY}S_{XY}(\epsilon_X + \epsilon_Y) \qquad (7)$$

Since ψ^+, ψ^-, ϕ_X, and ϕ_Y are all singly occupied, the net change $\Delta E'$ in π energy in the planar conformation relative to the twisted

$$\Delta E_\pi = \epsilon^+ + \epsilon^- - \epsilon_X - \epsilon_Y \qquad (8)$$

is given by

$$\Delta E_\pi = -2S_{XY}(\beta_{XY} - \epsilon_0 S_{XY})/(1 - S_{XY}^2) \qquad (9)$$

where ϵ_0 is the arithmetic average of ϵ_X and ϵ_Y, and β_{XY} and S_{XY} represent the "resonance" and overlap integrals between the MOs ϕ_X and ϕ_Y. Note that, in contrast to most bonding interactions, the magnitude of ΔE_π is independent of the difference between ϵ_X and ϵ_Y.

The magnitude of ΔE_π can be evaluated by expanding ϕ_X and ϕ_Y in terms of atomic orbitals, χ, and by using the extended Hückel theory[15] relationship

$$\beta_{rs} = 1.75\alpha S_{rs} \qquad (10)$$

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[13] A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

[14] (a) R. S. Mulliken, *Phys. Rev.*, **43**, 279 (1933); (b) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, 41, 219 (1947).

[15] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

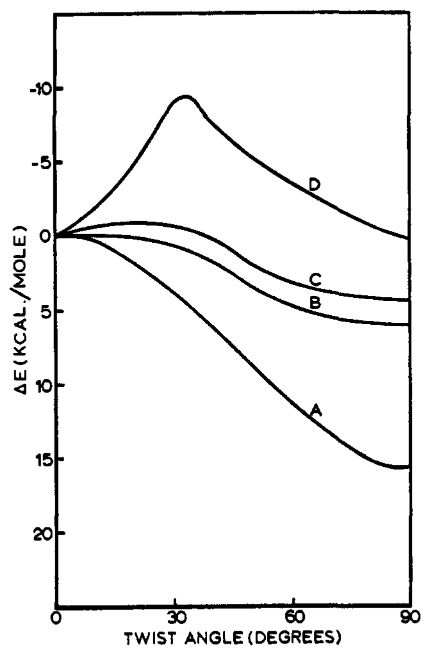

Figure 2. Potential energy curves for C=C bond twisting in polyene triplets: (A) ethylene; (B) 3–4 bond in *trans,trans*-hexatriene; (C) *trans*-butadiene; (D) 1–2 bond in *trans,trans*-hexatriene. All energies are relative to the vibrationally relaxed planar conformation.

where α is the Coulomb integral for a carbon $2p_\pi$ orbital. Since $\epsilon_0 = \alpha$, then from eq 9

$$\Delta E_\pi = -1.5\alpha c_r^2 c_s^2 S_{rs}^2/(1 - c_r^2 c_s^2 S_{rs}^2) \qquad (11)$$

where c_r and c_s represent the NBMO coefficients at the atoms r and s which link X to Y. Since r and s represent "active" positions in an odd alterant radical, c_r and c_s must be nonzero. Thus the conjugation between the two unpaired electrons is *destructive* rather than constructive, since it involves a *loss* in π energy. Assuming that the total energy for the other electrons in XY is independent of twist angle, then first-order perturbation theory predicts the twisted triplet conformation is preferred to the planar, since the π^* electron is more destabilized than the π electron is stabilized in the planar species (Figure 1).

Since ΔE_π is directly proportional to S_{rs}^2, any geometry change which reduces the magnitude of the overlap integral—such as by stretching the r–s bond or by twisting the p_π orbitals away from each other—reduces the destabilization. Thus the carbon–carbon bond length in the planar ethylene triplet should be longer than the single bond length, and relatively long bond distances should be present in conjugated polyenes—all of which is in agreement with the SCF calculations (Table I).

In the case of acyclic alkenes and polyenes, twisting of the p_π orbitals by 90° about one C=C bond is a more efficient method of reducing the destructive conjugation in the lowest triplet than is bond stretching. The barrier to planarity about such a bond can be estimated by eq 11 since the coefficients c_r and c_s in the NBMO can be readily evaluated using the method of Longuet-Higgins.[16] Numerical estimates of the barriers, calculated according to first-order perturbation theory, are given in Table III.[17] Note that the simple perturbation theory predicts that the barrier to planarity should decrease rapidly as the chain length is increased.

Table III. Energy Differences between Planar and Twisted Triplets

Hydrocarbon	Twisted bond	Energy difference, kcal/mol Perturbation theory	NNDO theory
Ethylene	1–2	16.4	15.6
Butadiene	1–2	8.0	4.3
Hexatriene	1–2	5.3	0.3
	3–4	4.0	6.1
Isohexatriene	1–2	8.0	0.9
	3–6	5.3	7.4
Octatetraene	1–2	4.0	−5.4
	3–4	2.7	3.3
Decapentaene	5–6	1.8	
Styrene	7–8	9.2	
Stilbene	7–8	5.2	

Potential Surfaces for Triplets. Although the simple first-order perturbation approach outlined above is useful for qualitative purposes, it neglects many quantum-mechanical effects (particularly configuration interaction and changes in σ bond energy) which may alter in magnitude as the molecule is twisted. Much more realistic potential energy surfaces are obtained using the NNDO-CI approach.[18] The torsional barriers for twisting about one "essentially double" C=C bond in several polyene triplets are illustrated graphically in Figure 2; calculated energy differences between the 0° and 90° conformations are listed in the final column of Table III.[19] Although the shapes of the potential curves and the magnitude of the preference for a 90° twisted conformation are both in semiquantitative agreement with the perturbation theory for ethylene and for *trans*-butadiene, several features of the surfaces for the longer polyenes are in sharp contrast to the predictions of the simple theory. First, the preference for a triplet twisted about an "internal" C=C bond is much greater than expected. Second, the energy gain in twisting a terminal C=C bond is much smaller than anticipated, and becomes negative in long polyenes. Third, intermediate barriers to twisting (peaking at ~30°) are predicted for terminal bond torsion.[20]

These unusual effects obtained in the potential surfaces for the longer polyenes can be understood by considering the bonding character in the systems, which in turn is illuminated by the optimum bond lengths predicted for the vibrationally relaxed planar triplets (Table I). Thus the unbranched hexatriene system is well represented by a structure in which two allylic fragments, each containing one of the two unpaired electrons, are destructively conjugated across a long "single" bond. Since rotation about the central bond does not demand any substantial reorganization of the bonding but does relieve the destructive conjugation, no significant barrier is found, and the 90° twisted

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[16] H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265, 275, 283 (1950). See the appendix of the present paper for a proof that the NBMO coefficients in the Hückel method with overlap included are identical with those for the overlap-neglected Hückel theory.

[17] The extended Hückel theory value for α of 11.4 eV[15] and overlap integral values of 0.2 are assumed.

[18] See also the extended Hückel calculations by R. Hoffmann, *Tetrahedron*, 22, 521 (1966).

[19] See also the calculations by E. M. Evleth, *Chem. Phys. Lett.*, 3, 122 (1969).

[20] The small intermediate barriers (≤1 kcal/mol) for the butadiene torsion and for internal bonds in other systems may well be due to deficiencies in the theoretical method rather than to real effects.

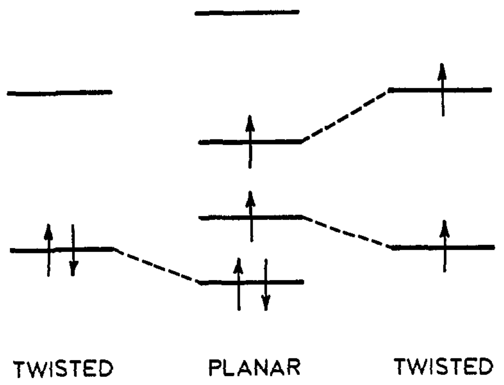
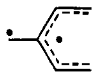


Figure 3. Orbital energy correlation diagram for twisting about the central bond in an otherwise planar butadiene triplet.

form is energetically preferred. In contrast, twisting about the terminal bond does involve significant reorganization of the bonding (and thus leads to an intermediate barrier), from a biallylic form to a "methyl pentadienyl" structure. Finally, the greater inherent stability of two allylic radicals relative to methyl plus pentadienyl of 4–5 kcal/mol effectively nullifies the ~5 kcal/mol reduction in destructive conjugation when the terminal bond is twisted, resulting in a near degeneracy between the planar and 1–2 twisted forms of the hexatriene triplet.[21] In a similar fashion, the potential surfaces for isohexatriene and for octatetraene can be analyzed from the optimum structures predicted for the planar triplets.



In connection with the relevance of the present calculations with regard to experimental studies of isomerization in triplet states, it should be emphasized that the theoretical potential surfaces refer to *vibrationally relaxed* species. Thus if a polyene is sensitized by a species whose triplet energy lies much above the calculated 0–0 band position of the hydrocarbon, sufficient energy may well be available to overcome any of the barriers and stereochemical preferences predicted. Further, the distinct possibility exists that such excess energy can be employed for torsion about more than one bond. For example, an orbital correlation diagram (Figure 3) predicts that twisting about the central single bond in otherwise planar *trans*-butadiene should be energetically unfavorable; our calculations indicate that this process should require ~33 kcal/mol of activation energy (Figure 4). In contrast, torsion about *either* the 2–3 or 3–4 bond in a butadiene species which is already 90° twisted about the 1–2 bond should be similar to that in the allyl free radical, *i.e.*, the barrier is reduced to less than 10 kcal/mol. Thus stereospecificity in triplet isomerization may be observable only with the use of minimal energy sensitizers.[23]

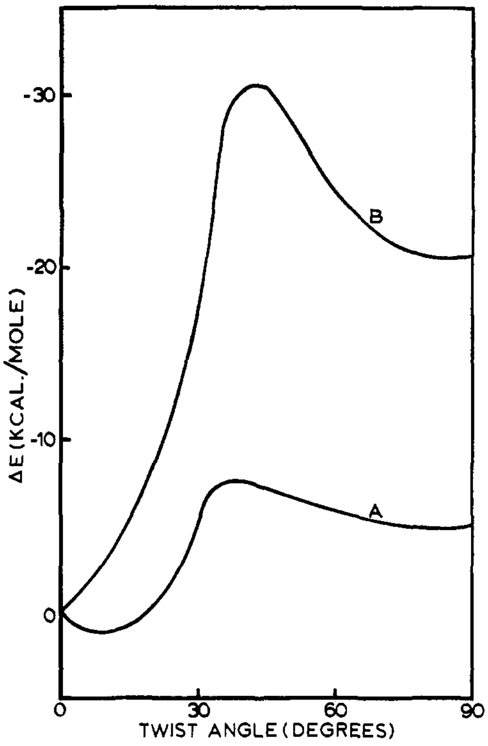


Figure 4. Potential energy curves for 2–3 bond twisting in the *trans*-butadiene triplet: (A) one C=C bond twisted 90°; (B) no C=C bonds twisted.

Energies of Relaxed Triplets. Some comment should be made regarding the magnitude of the 0–0 band positions predicted (Table II), since these values are significantly smaller than the "triplet energies," E_T, usually quoted for these systems. For example, the E_T of ethylene is often quoted as 82 kcal/mol (in comparison with our value of 62) since this corresponds to the lowest energy peak observed by Evans in the S_0–T_1 spectrum.[12] The origin of the discrepancy is likely due to the fact that the 0–0 peak cannot be observed in such systems, due to the extremely low intensity of absorption expected for a transition between two states whose equilibrium geometries are so different. Thus the optimum geometry of the T_1 state of ethylene differs from S_0 by ~0.2 Å in the carbon–carbon bond length and by a full 90° in the dihedral angle between the methylenic groups.

Our low value for E_T of ethylene is supported by (i) the value of ~57 kcal/mol extrapolated by Merer and Mulliken for the S_0–T_1 0–0 band;[13] (ii) the fact that substituted ethylenes can be isomerized using triplet sensitizers whose E_T's lie in the low 60's in energy,[25] and (iii) the fact that the twisted form of the ground state, which should be almost degenerate with the twisted triplet, lies at ~65 kcal/mol.[26]

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[21] Experimental ΔH_f's for the methyl, allyl, and pentadienyl free radicals[22] of 34.4, 41.4, and 52.9 kcal/mol, respectively, indicate that conversion of two allyl radicals into methyl and pentadienyl radicals is endothermic by 4.4 kcal/mol.

[22] See N. C. Baird, *Mol. Photochem.*, 2, 53 (1970).

[23] Isomerization at both double bonds in the 2,4-hexadiene system has been reported[24a,b] The E_T of the sensitizer used (benzophenone) of ~69 kcal/mol[24c] lies well above our calculated E_T of 59 kcal/mol for a butadiene species twisted at both C=C bonds.

[24] (a) H. L. Hyndman, B. M. Monroe, and A. S. Hammond, *J. Amer. Chem. Soc.*, 91, 2852 (1969); (b) J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, 91, 5684 (1969); (c) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 170.

[25] See S. Sato, *Pure Appl. Chem.*, 16, 87 (1968).

[26] J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, 23, 315 (1955).

Similarly the predicted E_T for *trans,trans*-hexatriene of 42.0 kcal/mol lies below the last spectroscopic peak observed (at 47 kcal/mol) but is in good agreement with the activation energy of 41.4 kcal/mol required to isomerize thermally a substituted hexatriene about its 3-4 bond.[27] Finally, the E_T of 53.3 kcal/mol for *trans*-butadiene lies about 6 kcal/mol lower than the commonly quoted spectral value; unfortunately no thermal isomerization studies are available for comparison.[28]

One possible deficiency of the NNDO-CI method lies in its prediction that the 0-0 triplet energy of an unbranched polyene decreases only slightly with increasing chain length after hexatriene. Although calculations which include extensive CI are not economically feasible for very long polyenes, the SCF results indicate that the lowest triplet in chains of 14 or more carbons should all lie ~4 kcal/mol lower than that for unbranched octatetraene; *i.e.*, the limiting E_T value is predicted as ~36 kcal/mol. Experimentally, the triplet level of β-carotene lies lower than this limit, at ~25.5 ± 3 kcal/mol.[31] SCF calculations (no configuration interaction) indicate that conformations of the β-carotene triplet in which *one* of the 7-8, 9-10, or 11-12 double bonds is twisted by 90° are essentially isoenergetic with the planar form. Triplet forms of this system in which the 1-3, 3-4, or 5-6 C=C bond is twisted are all less stable than the planar form, the barrier to torsion increasing toward the terminus of the chain. These effects are in agreement with the bond lengths predicted for the planar β-carotene triplet (Table I), which are consistent with a structure in which the ground-state double bond character of the 1-2 and 3-4 links is retained in the excited state, and "bond reversal" occurs only near the chain center. We hope to report on a more detailed potential surface for this interesting system, and for hydrocarbons containing aromatic rings, in later parts of this series.

Appendix

Properties of NBMOs if Bonded Overlap Is Included. According to simple Hückel theory (overlap neglected), each odd alternant free radical has one singly occupied NBMO with $\epsilon_j' = \sigma$ and $m_j = 0$.[32] When bonded overlap is included, the eigenvalues ϵ are related to those of the simple theory by[32]

$$\epsilon_j = \alpha + m_j(\beta - S\alpha)/(1 + m_jS) \qquad (12)$$

Since $m_j = 0$ for an NBMO, then $\epsilon_j = \alpha$ and the level is predicted to be nonbonding even when overlap is included. If only bonded overlap integrals are included, the π electron system in a polyene twisted about a C=C bond is composed of two orthogonal components, each of which is odd alternant in character. Thus the two unpaired electrons singly occupy the orthogonal NBMOs associated with such networks.

The wave functions associated with each NBMO can be derived rather simply. The coefficients of the atomic orbitals are determined from the secular equations

$$\sum_u c_{ju}(H_{uv} - \epsilon_j S_{uv}) = 0 \qquad v = 1, \ldots \qquad (13)$$

For an NBMO, $\epsilon_j = \alpha = H_{uu}$, and since $S_{uu} = 1$, then

$$\sum_{u \neq v} c_{ju}(H_{uv} - \alpha S_{uv}) = 0 \qquad v = 1, \ldots \qquad (14)$$

If χ_u is not bonded to χ_v, then $H_{uv} = S_{uv} = 0$, and the summation can be restricted to orbitals χ_u bonded to χ_v. Further, if for such bonded orbitals both H_{uv} and S_{uv} have standard values β and S

$$(\beta - \alpha S) \sum_{\substack{u \text{ bonded} \\ \text{to } v}} a_u = 0 \qquad (15)$$

Since $\beta > \alpha S$, the coefficients of the NBMO are given by the same formula derived for the conventional Hückel theory,[32] *i.e.*

$$\sum_{\substack{u \text{ bonded} \\ \text{to } v}} a_u = 0 \qquad (16)$$

Since the terminal carbon of a radical is an "active" or "starred" position, its coefficient in the NBMO must be nonzero.

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[27] K. W. Egger and T. L. James, *Trans. Faraday Soc.*, **66**, 410 (1970).

[28] Although Hammond and coworkers[29] have reported the sensitization of substituted butadienes with E_T's as low as 42 kcal/mol, recent experiments indicate the direct energy transfer from the *first* triplet level of the sensitizer is not involved in some low energy cases and perhaps not in any.[30]

[29] R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965), and references therein.

[30] G. S. Hammond, private comunication.

[31] E. J. Land, A. Sykes, and T. A. Truscott, *Chem. Commun.*, 332 (1970).

[32] See A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.