of van der Waals repulsion for a hydrogen atom to lie at the nucleus, in our 1973 force field we took that center to lie 7.5% of the distance in toward the carbon atom to which the hydrogen is attached. This shift of the repulsion center is based on work by Williams,[18] and has been justified elsewhere. In the cyclodecane molecule, the two pairs of hydrogens which are exerting the severe transannular repulsion come at one another almost head on. Thus, while the internuclear distance between them was 2.15 Å in our 1973 force field, the distance between repulsion centers was 2.25 Å. The repulsion was accordingly a whole lot less than implied in White's paper. When this orientation factor (which is referred to by Bartell as "foreshortening") is taken into account, our 1973 hydrogens were very nearly the same as Schleyer's, in their effective hardness to a head-on approach.

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On Geometries of First Triplet States of Linear Polyenes

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Abstract: A restricted open-shell Nesbet SCF ab initio minimal basis set description of the geometrical changes of the olefinic double bond in the first excited states of linear polyenes is in agreement with experimental evidence on cis-trans isomerization. The allylmethylene triplet form of *s-trans*-butadiene yields the lowest minimum in the first triplet energy surface. There are three close-lying triplet minima corresponding to different triplet forms of *trans,trans*-hexatriene, indicating that cis-trans isomerizations around the central and terminal double bond are competitive. In the first triplet state of the longer polyenes, geometrical changes should take place around the internal double bonds.

Introduction

The properties of the olefinic double bonds in the first excited states (triplet T_1 and singlet S_1) of polyenes have been the subject of numerous theoretical studies. Their motivation ranges from possible interpretation of the vibrational structure of ultraviolet spectra[1,2] to predictions about olefin cis-trans isomerization in photochemical reactions.[3-6] Correspondingly, the use of quantum chemical calculation methods ranges from very elaborate ab initio procedures[2] to semiempirical treatments.[3,4,6]

In this work we investigate the twisting and stretching motion of a linear polyene double bond in the first triplet states as well as, for comparison, in the first singlet excited states. These geometrical changes give rise to "biradicaloids" and particularly to diradicals which are assumed to account for the olefinic photoisomerization mechanism. We seek out the existence of possible minima in the lowest triplet hypersurface because a return through such "diradical" minima in T_1 should be responsible for cis-trans isomerization.

The SCF-minimal basis set STO-3G procedure,[7] using a restricted open-shell Nesbet Hartree-Fock operator and very limited configuration interaction[8] (3 × 3 for singlet and 2 × 2 for triplet states), was applied to all considered geometrical changes on hypersurfaces of the lowest excited states. This admittedly very simplified procedure is used because it mimics well the four-state diradical model,[9] and, therefore, the essential qualitative features of a diradical are reproduced in an acceptable manner.

On the other hand, this simple description, which uses a too limited basis set without diffuse functions and an extremely limited configuration interaction, is evidently inappropriate for determining the electronic structures of the excited states for the ground state and neighboring geometries. Also, the spectroscopic properties are poorly described because a proper simultaneous description of two electronic states is required for the determination of these properties. The inclusion of diffuse functions and an extension of configuration interaction can differently influence different states.[2] Therefore, a method with a minimal or slightly extended basis set can, in general, lead to uncertain predictions of excitation energies. Especially, the values for excitation energies $S_1 - S_0$ and energy differences $S_1 - T_1$ are usually too large because the diffuse functions contribute more to the S_1 than to the S_0 and T_1 state. Nevertheless, such a simple method can be useful for the qualitative investigation of the twisting and stretching motion on *a single energy surface*. The overall qualitative form of the energy surface for a certain state and for certain geometries can be predominantly determined by the valence orbital components of the wave function, mainly when drastic changes of a bond strength are involved.

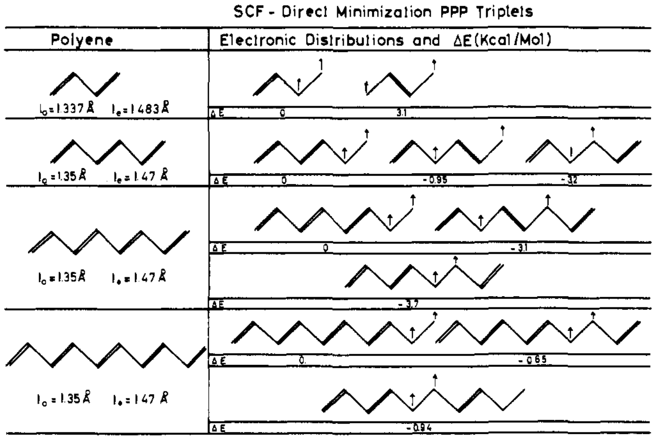
It is remarkable that even the PPP model, when the SCF procedure without symmetry constraints is used, shows the tendency toward a weakening of one double olefinic bond in the first triplet state. Therefore, we use the triplet electronic distributions obtained by the SCF direct minimization procedure[10] as signposts in the search for possible triplet minima.

SCF Direct Minimization PPP Triplets. It is known that the electronic distribution yielding the lowest energy in the Hartree–Fock approximation does not necessarily have the same symmetry as the molecule (so-called "symmetry broken" H–F solutions[11]). In order to reach such symmetry nonadapted Hartree–Fock solutions it is necessary to use a method which does not enforce symmetry constraints on the wave function. In the direct minimization method the SCF solutions are obtained directly by using the variational principle. For this purpose the energy expectation value is minimized with respect to the independent variables in terms of which the coefficients of the one-electron functions in the Slater determinant are expressed (cf. ref 10). Direct minimization procedure, which is a slow alternative to the customary iterative procedure, is valuable for the investigation of hypersurfaces free from symmetry or spin constraints, particularly for hypersurface regions in which the iterative procedure shows convergence difficulties typical of "biradicaloid" geometries.[12] The choice of the starting point in the search for a minimum is arbitrary. A certain distribution of localized double bonds (Kekulé or Dewar structures), as provided by chemical intuition, can be used for this purpose.

The results for the PPP self-consistent triplets[13] are summarized in Table I. For the ground state experimental butadiene geometry, two triplet electronic distributions are obtained using two different starting points in the search for minima (i.e., different starting distributions of localized unpaired spins and double bonds). The asymmetrical electronic distribution yields a very low bond order for one double bond and strongly localized unpaired spins. This asymmetrical solution (symmetry nonadapted) has lower energy than the symmetrical one.

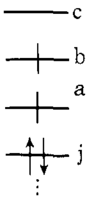
For the single fixed geometry of hexatriene, octatetraene, and decapentaene, use of different starting points in the direct minimization method gave rise to three different electronic distributions, one symmetrical and two asymmetrical, as illustrated in Table I. In the case of hexatriene and decapentaene, the symmetrical electronic distribution yields the lowest energy. It is, of course, not possible to assign direct physical meaning to all these solutions which represent local Hartree–Fock minima for *a single* molecular geometry (nonuniqueness of the Hartree-Fock problem[13,14]). Nevertheless, these results can be used as indication that in the triplet state the nuclei would like to follow the calculated optimal electronic distributions and depart from the geometry of the ground state by stretching and twisting the double bond which has a low bond order in the triplet asymmetrical Hartree–Fock solution.

Table I^a



^{a}The energy ΔE (kcal/mol) is relative to the energy of the asymmetric electronic distribution with weakened one terminal double bond. The arrows indicate high spin density positions. Double and single bonds in the electronic distributions are drawn for large and small values of the bond orders.

Scheme I



Ab Initio Treatment. According to previous theoretical considerations[1-6] and our PPP results, the geometrical changes in the first excited states should considerably weaken or abolish the π character of one olefinic double bond. In this manner, "biradicaloid" geometries are created and, therefore, a proper treatment of open-shell configurations $a\bar{b}$ and $\bar{a}b$ is essential (cf. Scheme I). We use the approximate restricted open-shell Hartree–Fock operator according to Nesbet:

$$\hat{F} = \hat{h} + \sum_{j<a} (2\hat{J}_j - \hat{K}_j) + (\hat{J}_a - \tfrac{1}{2}\hat{K}_a) + (\hat{J}_b - \tfrac{1}{2}\hat{K}_b)$$

where j labels doubly occupied MOs, a and b are singly occupied MOs, and $\hat{h}$, $\hat{J}_j$, $\hat{K}_j$ are usual one-electron Hamiltonian, Coulomb, and exchange operators, respectively. The SCF procedure is performed for the open shell $a\bar{b}$ configuration. For the diradical geometries this configuration yields an electronic distribution with nearly one unpaired electron on each radical site. The configuration $a\bar{b}$ gives a nearly symmetrical electronic distribution, even when the coupling between localized orbitals representing the radical sites is forbidden for symmetry reasons and, consequently, MO's a and b are localized on the radical sites as well. This is the case of the 90° terminally twisted polyenes which are, according to Salem's classification,[9] heterosymmetric diradicals. They are characterized by the localized functions assigned to the radical sites which belong to different irreducible representations of the molecular symmetry group. Similarly, the approximate Nesbet open-shell SCF procedure is appropriate[16] for a treatment of the nonsymmetric diradicals with close lying orbital energies of the two weakly coupled radical sites.

The singlets $S(ab)$, $S(a^2)$, and $S(b^2)$, as well as the triplets $T(ab)$ and $T(ac)$, are built up from the molecular orbitals of the SCF open-shell $a\bar{b}$ configuration. The 3×3 configuration interaction for singlets and 2×2 for triplets is introduced (compare ref 8).

For comparison, we use in several calculations the closed-shell Roothaan procedure where the lowest singlet $S_0(a^2)$ is calculated self-consistently. The configurations $S_1(ab)$, $S_2(b^2)$, as well as $T(ab)$, are constructed from the virtual orbitals of S_0. Clearly, if the molecular orbital a is essentially localized on one of the radical sites the electron distribution resulting from $S_0(a^2)$ would be slightly asymmetrical. Therefore, for hetero- and nonsymmetric diradicals the closed-shell SCF iterative procedure easily yields convergence difficulties.

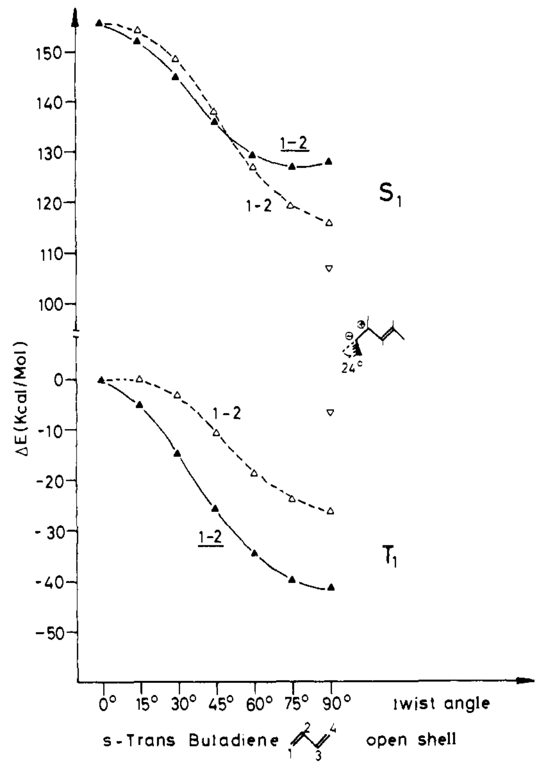


Figure 1. *s-trans*-Butadiene T_1 and S_1 energies relative to the triplet energy of the ground state planar geometry (l_0 = 1.337, l_c = 1.483 Å) (a) for a twisting of the terminal bond 1-2 (△), (b) for a coupled twisting and stretching from l_0 to l_c of the *1-2* bond (▲). For a twist by 15° the length increment of the respective bond is 0.0243 Å. Pyramidalization of CH_2 at the terminally twisted bond with the charge separation is indicated by (▽). Italic numerals in the captions of all figures and in the text correspond to the underlined numerals in the figures.

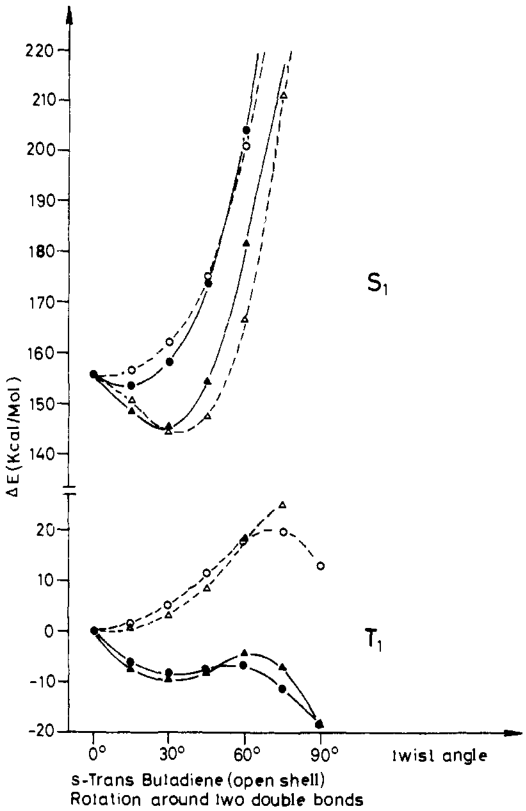


Figure 2. *s-trans*-Butadiene T_1 and S_1 energies for a twisting of two terminal bonds maintaining (a) C_2 symmetry (○), (b) S_2 symmetry (△), and for a simultaneous twisting and stretching from 1.337 to 1.483 Å of both terminal bonds maintaining (c) C_2 symmetry (●), (d) S_2 symmetry (▲). For a twist by 30° the length increment of the respective bonds is 0.0489 Å. All energies are relative to the triplet energy of the ground state planar geometry.

Namely, the large electron density on one radical site causes a high effective potential which forces the electrons to flow toward the other radical site in the next iterative step. These difficulties do not arise if the molecular orbitals a and b are allowed to be delocalized over both radical sites as is the case for homosymmetric diradicals[9] (e.g., the centrally twisted bond of polyenes with $(4n + 2)$ carbon atoms).

From the above qualitative considerations, it is to be expected that the open-shell SCF procedure should yield a better description of the essential diradical features, particularly for hetero- and nonsymmetric diradicals. Therefore, most of the results reported in this work were obtained by using the open-shell Nesbet SCF procedure with the minimal basis set (STO-3G). When the extended basis set (4-31G) or closed-shell SCF method was employed, it is explicitly mentioned.

A. Butadiene. The influence of geometrical changes in the *s-trans*-butadiene terminal double bond on the lowest triplet T_1 and first excited singlet S_1 states is illustrated in Figure 1. The twisting coupled with a stretching (*1-2*) of the terminal bond lowers the triplet energy considerably more than the twisting alone (1-2). The calculations carried out with both basis sets (4-31G and STO-3G) show the same qualitative behavior of the T_1 energy for the terminal bond twisting, but the energy decrease is smaller by 8 kcal/mol when the 4-31G basis set is employed. The twisting of one terminal bond lowers the S_1 energy as well, while a simultaneous elongation of the same bond is not favorable in the regions of fairly loose geometries.[17] The decrease of S_1 in energy for twisting the terminal bond is the same when STO-3G or 4-31G basis set is used.

The 90° terminally twisted butadiene in the S_1 state exhibits a strong sudden polarization effect[18] (i.e., strong charge separation between two diradical centers: methylene and allyl[19]). A 24° pyramidalization of the CH_2 group on the 90° terminally twisted bond in butadiene lowers the S_1 energy by an additional 10 kcal/mol. In contrast, the triplet energy is increased by pyramidalization (cf. Figure 1).

The stabilization of the triplet state with distortion is certainly overestimated owing to the use of a basis set which lacks the diffuse functions, as well as due to the approximate SCF open-shell Nesbet procedure. Both factors contribute to the poor description of closed-shell geometries giving too high energies in the neighborhood of the planar geometry, as discussed in the Introduction (cf. also ref 8).

The T_1 and S_1 energy dependence on the twisting of two double bonds, maintaining C_2 or S_2 symmetry, as well as the energy dependence on the coupled stretching–twisting motion for these bonds, in butadiene is shown in Figure 2 (compare ref 3 and 6).

The torsional barrier to the twisting of both terminal bonds in T_1 is smeared out by their simultaneous elongation. If the C_2 symmetry is maintained, the first excited S_1 state goes through a very shallow minimum for the 15° twist and for both slightly elongated terminal bonds. The S_1 minimum is much deeper when S_2 symmetry is maintained.

The coupled twisting and stretching of one terminal bond is the most energetically favorable distortion of the lowest triplet of butadiene. According to these calculations the alternative simultaneous stretch and twist around both terminal bonds in the triplet state is not energetically that unfavorable.

The calculated dependence of the S_1 energy on geometrical factors can be considered as an indication of the possible nonvertical $S_1 - S_0$ transition in butadiene, analogously to Merer and Mulliken's[1] consideration of V-N transition in

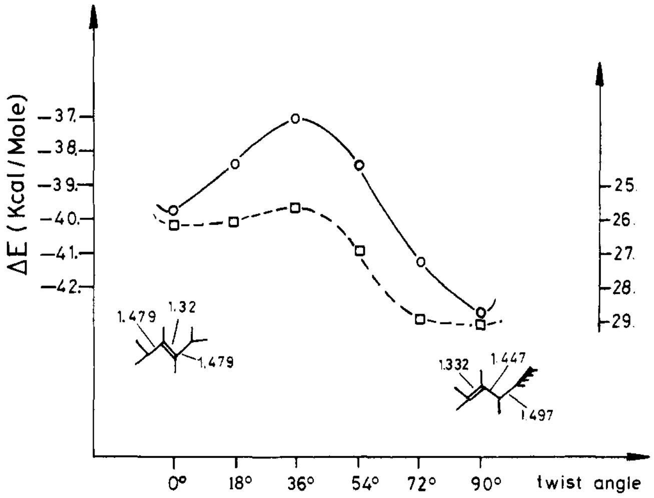


Figure 3. *s-trans*-Butadiene triplet minima relative to the triplet energy of the ground state planar geometry with corresponding forms: relaxed flat 1,4-diradical form(I), left, and methylene-allylic form (II), right. One of the possible pathways from I to II is indicated by (○) when a minimal basis set is used, and by (□) with respect to the right side energy scale, when the 4-31G basis set is used. For a twist by 18° around bond 3-4, the corresponding bond lengths changes are $\Delta l_{12} = -0.0294$, $\Delta l_{23} = 0.0234$, $\Delta l_{34} = 0.0036$.

ethylene. Similar conclusions have been drawn by Shih et al.[2b] from their more elaborate calculations.

Following the signpost of the PPP calculations, the triplet energy minimization using the minimal basis set was performed by a partial geometry optimization (keeping C–H bond lengths and HCH and CCC bond angles constant). Two "minima" with an energy difference of only 3.1 kcal/mol are shown in Figure 3. The lower one corresponds to the methylene–allylic (terminally twisted by 90°) form, and the higher one to the relaxed flat 1,4-diradical form. The neighborhood of each minimum[20] has not been fully investigated, for example, by the gradient method. One of the possible pathways assumed to be energetically most favorable leads from the lower minimum to the higher minimum over a barrier of 5.6 kcal/mol. The calculations with the extended basis set 4-31G yield, for the same pathway, a barrier of only 3.4 kcal/mol and an energy difference of 2.8 kcal/mol between two minima as shown in Figure 3. The experimental work on the benzophenone-sensitized cis-trans photoisomerization of 2,4-hexadienes[21] suggests the allylmethylene description of 1,3-diene triplets which undergo rapid equilibration. The relatively small energy difference between two butadiene triplet minima with a small barrier along a possible reaction path can be taken as an indication that an energetically facile transfer of the distortion from one terminal bond to the other may occur via a flat 1,4-diradical transition state. According to our calculations the nonplanar 1,4-diradical triplet geometry is a less favorable transition state. The doubly 90° twisted 1,4-diradical lies energetically only slightly higher relative to the flat 1,4-diradical but no energetically easy pathway from the flat to the twisted form of 1,4-diradical is found. Also, the pathway from one terminally twisted triplet geometry to another (obtained by mirror image) was investigated by simultaneous twist of both ends so that as allylic resonance is destroyed on one side it is gained on the other. The common nonplanar 1,4-diradical with both ends twisted by 45° (and bond lengths $l_{12} = l_{34} = 1.497$, $l_{23} = 1.31$ Å) is placed at 8.8 and 7.8 kcal/mol relative to the terminally twisted minima, when the limited STO-3G and the extended 4-31G basis set, respectively, was employed.

The energy change due to the twisting and stretching motion of a double bond was calculated throughout the whole interval of geometrical changes (from ground state to twisted geometry). Even when only those points which correspond to sufficiently "biradicaloid" geometries in the excited state surfaces can be taken with some confidence, the overall form of the calculated energy dependence on the geometrical factors gives qualitative information on the corresponding part of the real energy surface. The stabilization of the diene triplet state with distortion is too large in comparison with experimental observations. In principle, the mentioned lack of accuracy for the regions near the ground state geometries might even give wrong information about barriers in their neighborhood. Concerning these doubts, it is very encouraging that a part of the triplet and singlet excited potential curves for the twisting motion (from 0° to 30°) around both double bonds of butadiene (with maintained C_2 symmetry) calculated by Shih et al. using a large basis set including the diffuse functions and extended CI are very similar to our corresponding potential curves (cf. Figure 2).

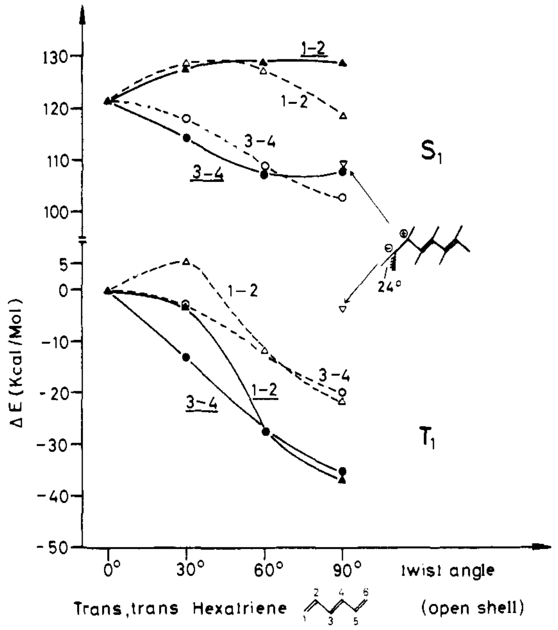


Figure 4. *trans,trans*-Hexatriene T_1 and S_1 energies relative to the triplet energy of "ground state planar geometry" ($l_0 = 1.337$, $l_e = 1.483$) for a twisting of (a) one terminal bond 1-2 (△), (b) the central bond 3-4 (○), and for a coupled twisting and stretching from l_0 to l_e of (c) one terminal bond *l-2* (▲) and (d) the central bond 3-4 (●). For a twist by 30° the length increment of the respective bond is 0.0489. Pyramidalization of CH_2 at the terminally twisted bond with the charge separation is indicated by (▽).

B. Hexatriene. The energy dependence on geometrical changes of central and terminal double bond of *s-trans,-trans*-hexatriene for the lowest triplet and the first excited singlet is shown in Figure 4. For a twisting of the terminal bond (1-2), the triplet energy goes through a barrier which is removed by a simultaneous elongation of this bond (*l-2*). Moreover, the triplet energy of hexatriene with a 90° terminally twisted bond (methylenepentadienyl structure) is slightly lower than the energy of the diallylic structure with the central bond twisted by 90°, whether the respective bonds are simultaneously stretched or not.

In the first excited singlet S_1, only a twisting of the central bond (3-4) could be classified as energetically preferential. On the other hand, the pyramidalization of CH_2 at 90° terminally twisted bond lowers the energy of S_2 (Figure 4). The possible existence of a barrier for twisting the middle bond in the neighborhood of the planar geometry is not excluded, even though it is not revealed by these simple ab initio calculations.

The triplet energy minimization for *trans,trans*-hexatriene

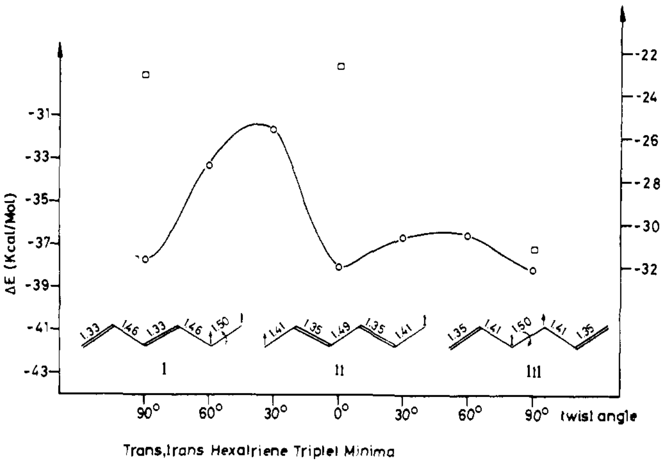


Figure 5. *trans,trans*-Hexatriene triplet minima relative to the triplet energy of the "ground state planar geometry" with corresponding forms: methylenepentadienyl (I), relaxed flat 1,6-diradical (II), and diallyl (III). Possible pathways from II to I and from II to III obtained from open-shell calculations are indicated by (○). The energies obtained from closed-shell calculations with respect to the right side energy scale are indicated by (□). Along the pathway connecting (a) II with I and (b) II with III the bond length changes are (a) $\Delta l_{12} = 0.027$, $\Delta l_{23} = \Delta l_{45} = 0.037$, $\Delta l_{34} = -0.005$, $\Delta l_{56} = 0.03$ for a twist by 30° around the bond 5-6 and (b) $\Delta l_{12} = \Delta l_{56} = -0.02$, $\Delta l_{23} = \Delta l_{45} = 0.02$, $\Delta l_{34} = 0.003$ for a twist by 30° around the bond 3-4.

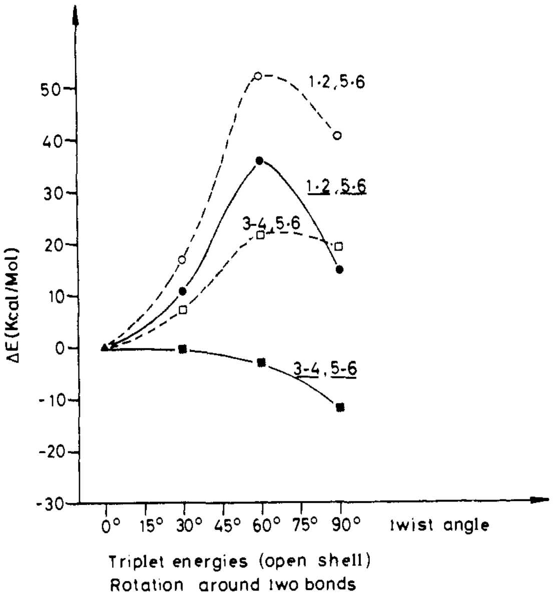
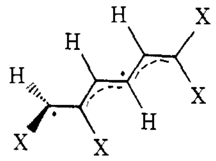


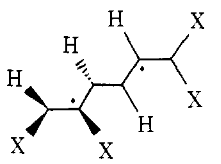
Figure 6. *trans,trans*-Hexatriene T_1 energy relative to the planar "ground state" geometry for a twisting of (a) two terminal bonds with C_2 symmetry (○) (b) one terminal and the central bond (□) and for a coupled twisting and stretching from l_0 to l_e of (c) both terminal bonds maintaining C_2 symmetry (●), (d) one terminal and of the central bond (■). For a twist by 15°, the length increment of two respective bonds is 0.0243 Å.

was performed by again keeping the C–H bond length, as well as the HCH and CCC bond angles, constant. Three minima were found, as shown in Figure 5, lying within ½ kcal/mol from each other, and corresponding to methylenepentadienyl (I), relaxed flat 1,6-diradical (II), and diallylic (III), respectively. The previous semiempirical calculations[4,6] in which the triplet state of hexatriene is best represented by the diallylic form suggested that the isomerization was favored around the central double bond. According to our results all three forms of hexatriene triplets (diallylic, 1,6-diradical, and methylenepentadienyl) are compatible and all of them might be present as intermediates in cis–trans isomerization of conjugated trienes. The methylenepentadienyl structure obtained from "ground state geometry" by coupled stretching and twisting of the terminal bond is even the slightly preferred form of the hexatriene triplet (see Figure 4). Experimental results of Liu and Butt on 2,6-dimethyl-2,4,6-octatriene[22] as well as the results of Padwa, Brodsky, and Clough on the 1,2,6-triphenylhexatriene[23] system are more consistent with preferential isomerization around the terminal double bond. We tested the influence of methyl substitution by performing calculations for the two structures IV and V indicated as possible intermediates by Liu and Butt.[22] The energy difference between the structures IV and V is again negligible (0.4 kcal/mol), similarly as for structures I and III in Figure 5.



IV

X = CH_3



V

The twisting as well as coupled twisting-stretching distortion of the terminal double bond in 3,4-*cis*-hexatriene show almost identical triplet and singlet energy behavior as for *trans,trans*-hexatriene.

The triplet energy dependence on a twisting of both terminal bonds (1-2, 5-6) in *trans,trans*-hexatriene (preserving C_2 symmetry) and the energy dependence on a simultaneous twisting of the central and one terminal bond (3-4, 5-6) is shown in Figure 6. Large barriers, particularly in the first case, can be depicted. Only the lower barrier is removed by performing a coupled elongation and twisting of the central and one terminal bond (*3-4, 5-6*). The singlet excited state energy S_1 is always increased by a simultaneous twist of two double bonds.

For the comparison, the triplet and singlet states of *trans,trans*-hexatriene were studied using the Roothaan closed-shell SCF procedure. The triplet energies were calculated for the *trans,trans*-hexatriene geometries for which the triplet energy minima were obtained using the open-shell Nesbet procedure. The closed-shell method yields a clear preference for the diallylic form as shown in Figure 5.

The calculations using the closed-shell method were carried out for twisting, as well as for a coupled stretching and twisting of *trans,trans*-hexatriene terminal or central bond. A barrier in T_1 is obtained even for a simultaneous elongation and twisting of the terminal bond (*1-2*) (as shown in Figure 7). For a twist angle of 90°, the triplet energy of the methylenepentadienyl form lies always higher than the energy of the diallylic form, independent of whether the simultaneous elongation of the respective bond was performed or not.

As expected from the previous qualitative analysis, the convergence difficulties occur for the 90° terminally twisted hexatriene, which is a heterosymmetric diradical. The nonconvergence can be, of course, avoided if an electron distribution corresponding to the hexatriene geometry with less "biradicaloid" character is appropriately used in the zero step of the iterative SCF procedure.

These results confirm the previous conclusion that the closed-shell Roothaan procedure is particularly inappropriate for the description of heterosymmetric diradicals.[24]

C. Octatetraene. The torsional barrier to twisting the terminal bond (1-2) in the triplet state of *all-trans*-octatetraene does not vanish even when a simultaneous stretching of this bond is performed (Figure 8). A preferential geometrical change in the triplet state here should take place along the double bond at position 3 of 1,3,5,7-octatetraene (3-4 or *3-4*). Even though the triplet energy corresponding to the terminal bond twisted by 90° lies lower, the barrier to twisting is too

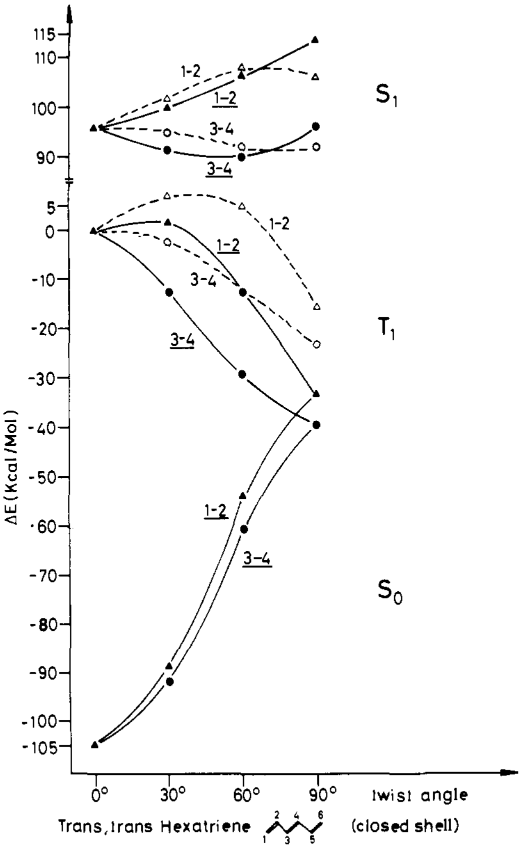


Figure 7. *trans,trans*-Hexatriene S_0, T_1, S_1 energies relative to the triplet energy of the planar "ground state" geometry obtained from *closed-shell calculations* for a twisting of (a) one terminal bond 1-2 (△), (b) the central bond 3-4 (○) and for a coupled twisting and stretching from l_0 to l_c of (c) one terminal bond *1-2* (▲) and (d) the central bond *3-4* (●). For a twist by 30° the length increment of the respective bond is 0.0489 Å.

large to be compensated for. The torsional barriers to twisting the double bonds at the positions 1 and 3, respectively, can be depicted from Figure 8, for the first excited state S_1.

The results for octatetraene indicate that the longer polyenes should follow the trend for a preferred twisted triplet around the internal double bonds. Also the geometrical change of the double bond in the first singlet excited state is no longer energetically favorable.

Conclusions

The description of the lowest excited states of polyenes, obtained by using the restricted open-shell Nesbet Hartree-Fock operator, yields several energetically close-lying triplet forms, which indicate that all of them might play an important role in photochemical isomerizations. The calculated energies of methyleneallylic, and 1,4-diradical flat butadiene triplet forms lie relatively close, but the first structure can be characterized as the more stable. All three triplet forms of hexatriene (methylenepentadienyl (I), flat relaxed 1,6-diradical (II), and diallylic (III)) lie extremely close to each other energetically. These results can be taken with confidence, because the open-shell procedure utilized here should properly describe the triplet states with expressed diradical character which lie on a single energy surface.

A twisting coupled with stretching of the hexatriene terminal bond can compete with the analogous geometrical distortions of the central bond in the triplet state, a fact which is in agreement with photochemical isomerization experiments. Even when the shapes of the energy curves in the neighborhood of the ground state geometries should be taken with caution, it is reasonable to assume that the overall shape of the potential energy curves connecting the ground state and diradical geometries are qualitatively well described.

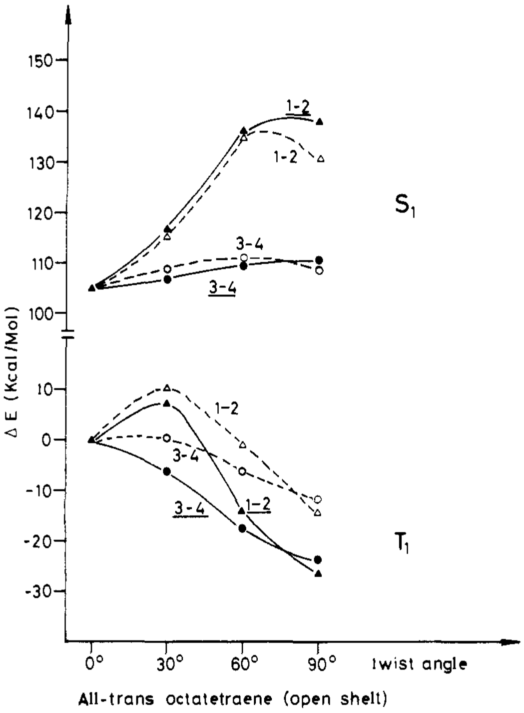


Figure 8. *all-trans*-Octatetraene T_1 and S_1 energies relative to the triplet energy of the planar "ground state" geometry (l_0 = 1.35, l_c = 1.47 Å) for a twisting of (a) one terminal bond 1-2 (△), (b) internal bond at position 3: 3-4 (○) and for a coupled twisting and stretching from l_0 to l_c of (c) one terminal bond *1-2* (▲), (d) the internal bond at position 3: *3-4* (●). For a twist by 30° the length increment of the respective bond is 0.0333 Å.

There is a preference for a twist as well as for a coupled twist and stretch of the nonterminal double bond in octatetraene. From these results, we infer the general conclusion that in the longer polyenes the innermost double bonds will twist preferentially in the lowest triplet state.

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1,3 (Nonbonded) Carbon/Carbon Interactions. The Common Cause of Ring Strain, Puckering, and Inward Methylene Rocking in Cyclobutane and of Vertical Nonclassical Stabilization, Pyramidalization, Puckering, and Outward Methylene Rocking in the Cyclobutyl Cation

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Abstract: An analysis of the extensive effects of 1,3 (nonbonded) carbon/carbon interactions in the cyclobutane system is presented. The analysis is based upon MINDO/3 and CNDO/1 and -/2 semiempirical SCF MO calculations in which the specific interactions of interest are zeroed in the Fock matrix. Classical estimates of Baeyer strain (valence strain based upon attenuated overlap) in cyclobutane are found to be in the range 7–11 kcal (as an upper limit), i.e., too small to account for the large (26.4 kcal) experimental cyclobutane strain. On the other hand, the SCF MO calculations yield estimates of 1,3 carbon/carbon repulsions (also termed Dunitz–Shomaker strain) in the range 20–33 kcal, thus suggesting this as the (dominant) companion effect of Baeyer strain in comprising the total strain of cyclobutane. Detailed examination of these 1,3 carbon/carbon repulsions confirm that they should carry over to heats of combustion measurements. The small incremental strain in cyclobutene relative to cyclobutane (2.5 kcal) is also in better accord with the low level of Baeyer strain postulated here, as is the planarity of the cyclobutyl radical. The strain of bicyclo[1.1.0]butane, previously considered anomalously high, is exceptionally well clarified by the concept of Dunitz–Shomaker strain. The variation of the latter type of strain with the pucker and methylene rocking angles provides a unified rationale for both of these additional effects as observed in cyclobutane. Even though puckering shortens the 1,3 carbon/carbon distance, the 1,3 carbon/carbon interaction actually becomes less destabilizing (4.0 kcal) concomitantly with this motion. Dunitz–Shomaker strain in the cyclobutyl cation is 5.1 kcal less than in cyclobutane, in accord with the special stability of this cation. The net interaction between the cationic center and its 1,3 related carbon is now actually bonding. A quantum mechanical basis for both strain relief and vertical nonclassical interactions thus exists. The extensive pyramidalization at the cationic center, as well as methylene rocking in the opposite sense to that in cyclobutane, is also found to be directly and cogently linked to 1,3 carbon/carbon interactions.

In conventional molecular formulas, canonical bonds are used to represent the major interatomic interactions. Generically, these may be designated 1,2 interactions insofar as this implies interactions between directly "bonded" atoms. The interactions between nonbonded atoms are then 1,3 or 1,4 or the like. It can be shown[1] that, of all the nonbonded interactions present in a hydrocarbon molecule, the largest is the 1,3 carbon/carbon interaction. The shortest 1,3 carbon/carbon distances, and therefore potentially the most dramatic manifestations of such interactions, are to be found in the cyclobutane series. Recent studies have documented impressive effects on spin density distributions in cyclobutenoid ion radicals engendered by 1,3 carbon/carbon interactions.[2,3] Significant, though smaller, effects were observed even in molecules with normal valence angles. Other work has implicated 1,3 carbon/carbon repulsions as a component of ring strain in cyclobutane and norbornane.[4] In view of the uniqueness of the 1,3 carbon/carbon interactions within the set of nonbonded interactions and of the cyclobutane series within the aforementioned subset, it appeared fruitful to look for other manifestations of 1,3 carbon/carbon interactions within this series. As will be seen, the catalog of properties which reflect strong and coherent links to the 1,3 carbon/carbon interaction includes virtually all of the exceptional properties of the cyclobutane system.

Ring Strain. More than two decades ago Dunitz and Shomaker reasoned that repulsive 1,3 carbon/carbon interactions must be responsible for a large component of the strain energy of cyclobutane.[5,6] This seemingly attractive theory seems not to have gained widespread acceptance, though without its postulated effect, the near equality of cyclobutane's strain (26.4 kcal/mol) to that of cyclopropane (27.6) still might appear awkward to rationalize. The foregoing assertion perhaps requires amplification. By definition, cyclopropane has no 1,3 (nonbonded) carbon/carbon interactions. Its ring strain therefore must, apart from torsional effects, be engendered by what will here be termed Baeyer strain, i.e., weakened 1,2 carbon/carbon bonding resulting from poor overlap (decreased σ character in the carbon/carbon bonds).[7] The total angular distortion from ideal tetrahedrality in cyclopropane is $3(109 - 60) = 3(49) = 147°$. Notwithstanding the virtually equal experimental strain energies, the total Baeyer distortion in cyclobutane is only $4(109 - 88) = 84°$. Moreover, for small distortions, angle strain is normally assumed to vary as at least