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Excited-State Properties of Linear Polyenes Studied through a Nonempirical Heisenberg Hamiltonian

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Abstract: The previously derived nonempirical Heinsenberg Hamiltonian for conjugated hydrocarbons is applied to linear polyenes neutral excited states. The vertical transition energies to the lowest triplet (^3B_u) and ^1A_g hidden singlet excited states are studied as functions of the number of carbon atoms. The lowest doublet → doublet transition in odd polyenes is also studied. The relaxed planar triplet and singlet excited-state geometries are given together with their energies and the vertical emission energies. The cis–trans photoisomerization pathway is depicted; for small polyenes the method confirms previous studies of the triplet surfaces and presents new information for the neutral excited singlet surface, which should play a role in the singlet photoisomerization. For large polyenes, extrapolations predict that isomerization becomes impossible around external double bonds and possible around internal double bonds. For large polyenes the lowest triplet in its relaxed geometry is shown to correspond to the soliton pair.

The preceding paper[1] has proposed a nonempirical Heisenberg effective Hamiltonian for the study of π systems. This idea had been suggested in the past from semiempirical grounds by Klein[2] and Ovchinnikov.[3] Our extraction was based on ab initio calculations of the ethylene molecule and took into account bond-length changes and torsion around bonds. It has proved to be very efficient in the ground-state study of all types of compounds (closed shells, radicals or diradicals, alternant or nonalternant, aromatic and nonaromatic, linear, branched, or polycyclic).

The present paper will be devoted to the conformations and energies of neutral *excited* states. Most monoelectronic methods such as SCF calculations give rather reliable results for the ground-state geometries of hydrocarbons, despite nonnegligible configuration interaction (CI) effects. The determination of excited-state geometries and energies is much more difficult since it requires CI descriptions of the excited state. Performing CI calculations requires a large amount of computational effort at both the integral transformation level (which is proportional to N^5, N being the dimension of the atomic orbital basis set) and the CI matrix diagonalization step. Gradient algorithms have speeded the research of ground-state optimal geometries, but they remain very rare at the CI level (see, however, footnote 4) and can hardly be applied for the second states of given symmetry. Our method may give valuable approximations of the excited surfaces at a very low cost.

The excited-state study will be concentrated on the linear polyenes series for several reasons.

(i) The reduction of the Heisenberg effective Hamiltonian to two-body operators is less crucial than for cyclic molecules where four- and six-body operators play an important role in the spacing of the spectrum.[5]

(ii) The famous hidden "^1A_g" state[6] is neutral, and its identification and location have been the subject of hard controversy during the last 10 years. Some theoretical attempts[7] to determine its molecular relaxed geometry were based on semiempirical methods and assumed a planar conformation.

Table I

A. Transition Energies (in eV) of Even Linear Polyenes (C_nH_{n-2})

	vertical absorpn		to the relaxed planar C_{2h} geom		vertical emission	
n	^3B_u	^1A_g	^3B_u	^1A_g	^3B_u	^1A_g
2	4.22		3.44			
4	3.03	7.23	2.45	6.00	1.92	4.96
6	2.44	5.72	1.89	4.75	1.40	3.95
8	2.07	4.88	1.57	3.91	1.14	3.23
10	1.85	4.19	1.36	3.32	0.93	2.72

B. Lowest Transition Energy (in eV) for Odd Linear Polyenes (C_nH_{n-2})

n	vertical absorp	to the relaxed planar geom	vertical emission
3	3.82	3.44	3.06
5	2.89	2.62	2.35
7	2.32	2.10	1.87
9	1.95	1.75	1.56

(iii) The cis–trans isomerization of linear polyenes, which seems the simplest photochemical reaction, occurs in both the triplet and the singlet manifolds; it requires a knowledge of the excited potential surfaces as functions of the twisting angle around a former double bond. The method is especially well suited for such studies. The cis–trans isomerization occurring from the allowed ^1B_u singlet excited state cannot be treated here (since this state is ionic), but it has been argued recently that for large enough polyenes ($n \geq 6$), the twisting cannot occur on this ionic surface[8] and that the ^1A_g neutral singlet excited surface might play a crucial role in explaining the singlet cis–trans isomerization mechanism.

The present work will study successively the vertical excitation energies, the relaxed planar geometries of the lowest triplet and ^1A_g excited singlet, and the rotational properties of these states. Since the 90° twisted conformations may be viewed as the interaction between two π radicals (in ground or excited states) in two orthogonal planes, the planar geometries of the lowest excited doublet state of odd polyenes will be analyzed.

I. Vertical Excitations to the Neutral Excited States of Linear Polyenes

The evolution of the vertical transitions to the lowest ^3B_u and ^1A_g excited states of even polyenes is given in Table I and Figure 1 where it clearly appears that they have an almost linear de-

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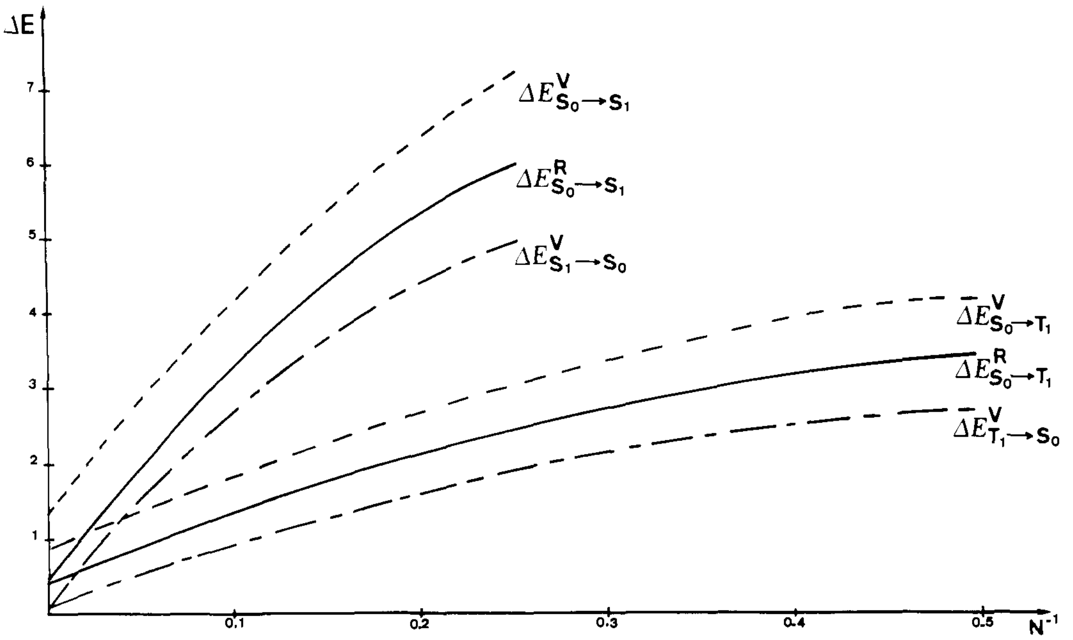

Figure 1. N dependence of the transition energies (in eV) in even linear polyenes H-(CH=CH)$_n$-H ($N = 2n$). V stands for vertical transition and R stands for the well-to-well transitions.

pendence on N^{-1}, where N is the number of conjugated carbon atoms:

$$\Delta E = A + B/N$$

This type of law had been obtained first from experiment for the lowest allowed transition to the ionic ^1B_u excited state.[9] It is amazing that the lowest transitions to neutral triplet and singlet excited states seem to follow a parallel N dependence. A least-squares fitting gives (in eV)

$$\Delta E^{V}{}_{S_0 \to T_1} = 0.87 + 10.68/N - 7.94/N^2 \qquad (1)$$

The asymptotic value for the lowest $S_0 \to T_1$ vertical transition is predicted to be 0.87 eV.

The calculated vertical transition energies should be compared with other ab initio calculations for butadiene and hexatriene, and with experimental evidence. Electron-impact experiments[10] suggest that the vertical ^3B_u should be about 3.2 to 3.45 eV above the ground state, in agreement with optical estimates[11,12] (3.22 eV) and the ab initio CI calculations from Buenker et al.[13] (3.24 eV), Hosteny et al.[14] (3.45 eV), and Nascimento and Goddard[15] (3.35 eV). Our value of 3.03 eV seems to be slightly underestimated. The second triplet state (^3A_g) is located at 5.04 eV according to experiment,[10,16] in good agreement with ab initio CI estimates by Buenker et al.[13] (4.95 eV), Hosteny et al.[14] (5.04 eV), and Nascimento and Goddard[15] (5.08 eV), while we find 5.28 eV.

For hexatriene the lowest ^3B_u state is about 2.6 eV[17,18] above the ground state and calculated at 2.71 eV by Nascimento et al.,[18] at 2.44 eV by us. The second (^3A_g) triplet state should be at 4.2 eV[17,19] and is calculated at 4.33 eV by Goddard et al.,[18] at 4.25 eV by us. For octatetraene, the lowest triplet is located at 2.20 eV by experiment,[20] at 2.08 eV by us.

The lowest singlet neutral excited state is a major subject of controversy. Most semiempirical[7] and ab initio calculations by Hosteny et al.[14] and by us (unpublished work) place this ^1A_g excited state, the so-called hidden state, below the lowest allowed (ionic) excited state (of ^1B_u symmetry) (ref. 13 gives, however, a reverse order). Experiment failed to prove the existence of this ^1A_g state below the ^1B_u state for butadiene and hexatriene (for some information about this controversy see ref 12, 17, and 21–32), but the experimental demonstration should be very difficult anyway. Our vertical estimate for butadiene (7.23 eV) is slightly larger than the estimates of Nascimento et al.[15] (7.06 eV) and of Hosteny et al.[14] (6.77 eV). McDiarmid[22] suggests 7.07 from UV absorption, and Flicker et al.,[10] 7.05 eV from electron impact. Our result would confirm the $^1B_u < {}^1A_g$ ordering for this molecule.

For hexatriene, Nascimento and Goddard[18] find the vertical ^1A_g at 5.87 eV, which agrees rather well with our estimate of 5.72 eV. A very recent paper[31] suggests its evidence in a highly substituted (isotachysterol) all-trans hexatriene from two-photon excitation. The maximum intensity corresponds to 4.1 × 10^4 cm^{-1} (i.e., 5 eV), but the substituents may decrease significantly the transition energy. The ^1A_g state has been well identified for larger conjugated systems.[33-38] We find it at 4.8 eV for octatetraene

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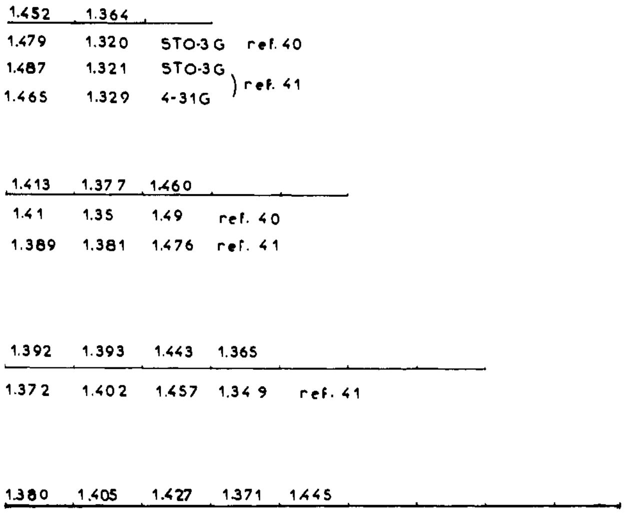


Figure 2. Planar C_{2h} geometries of the lowest ^3B_u excited state (in Å).

(4.54 eV according to the semiempirical work of Lasaga et al.[7]) and 4.19 eV for decapentene. The comparison with experiment will be discussed in the next section.

The N dependence of the vertical $S_0 \rightarrow S_1$ transition energy has been fitted by the polynomial expansion (in eV)

$$\Delta E^{v}_{S_0 \rightarrow S_1} = 1.35 + 31.77/N - 33.02/N^2 \qquad (2)$$

which indicates an asymptotic value of 1.35 eV. This value should be compared to the energy gap for large polyacetylene compounds, corresponding to the vertical transition energy to the allowed $^1B_{1u}$ state; this quantity tends toward 1.8 or 2.04 eV for *trans*-polyacetylene[39] if one considers the absorption peak. Our calculation then shows that the vertical ^1A_g excited state should remain about 0.5 eV below the $^1B_{1u}$ dipole-allowed excited state for large enough polyenes ($n \geq 8$).

II. Relaxed Planar Geometries of Excited States and Corresponding Energies

The relaxed planar geometries of excited states have been calculated assuming a C_{2h} symmetry (which may be broken according to Bonačić-Koutecký[40] and Ohmine[41]). The corresponding transition energies are significantly lower than the vertical one. The ^3B_u state of butadiene is stabilized by 0.6 eV, and the resulting energy (2.45 eV) compares favorably with the experimental (0–0) band (2.58 eV). The relaxation energy is even larger (1.2 eV) for the ^1A_g state of butadiene which remains at 6.0 eV, significantly above the 4.7-eV semiempirical estimate of Lasaga et al.[7] and in the region of the experimental intense ^1B_u transition (5.92–6.05 eV[42,43]). This coincidence would make the experimental identification very difficult.

For hexatriene the relaxation energy is 0.6 eV for ^3B_u, 1 eV for the ^1A_g state. The resulting energy of 4.75 eV for the latter state is in rather good agreement with the experimental (0–0) transition (4.5 eV) recently proposed for the highly substituted hexatriene.[31] The semiempirical prediction of Lasaga et al.[7] (3.97 eV) should be again underestimated. For octatetraene, the relaxation energy of the ^1A_g excited state is 0.9 eV. The resulting (0–0) transition energy is 3.9 eV, somewhat larger than the experimental estimate of 3.54 eV[33] and the semiempirical result (3.44 eV[7]). For decapentene the ^1A_g state is located at 3.3 eV in our calculation while experiment on 2,10-dimethylundecapentene[35] assigned the (0–0) level at 3.08 eV.

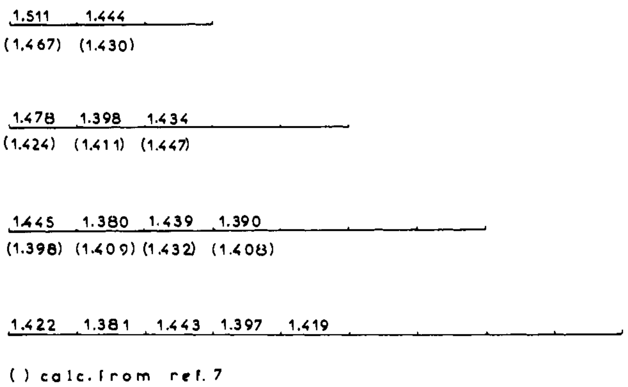
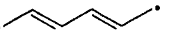
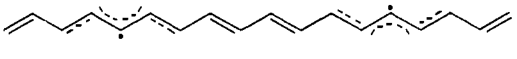


Figure 3. Planar C_{2h} geometries of the lowest ^1A_g excited state (in Å).

As concerns the optimized geometries of the lowest triplet state, one may compare the present prediction with those of recent ab initio[40,41] and semiempirical[41] calculations (cf. Figure 2). The agreement is better than with the ab initio estimates when available. In a qualitative manner one may say that in all cases the center of the molecule tends to restore the bond alternation. For small polyenes the two unpaired electrons tend to be pushed to the extremities of the molecule, according to the qualitative picture



However, a different tendency appears in decapentene, since the most external bonds tend to become shorter; the molecular geometry suggests that the radicalar sites prefer to move back inside the molecular framework. The resulting picture may be schematized accordingly for a large polyene



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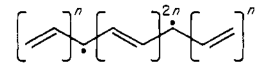

for a $4n+2$ compound. The radicalar sites tend to be localized at one-fourth and three-fourths of the chain length. One may notice that this picture corresponds exactly to the soliton pair description previously obtained in the preceding paper.[1] This "coincidence" will be discussed later.

The planar optimized geometries of the ^1A_g excited state may be compared to the semiempirical estimates of Lasaga et al.[7] (cf. Figure 3). Although the agreement is good for the inner bonds, our external bonds are much larger than theirs. A certain tendency to restore bond alternation in the central part of the molecule is evident for $n = 6$ and 8, but it seems to decrease again for $n = 10$, and we have not been able to propose a qualitative picture of the asymptotic structure. The geometries of ^3B_u and ^1A_g excited states are very different anyway.

From the vibrational structure in their substituted hexatriene, Pierce et al.[31] tried to deduce approximate geometry changes in the ^1A_g excited state, $\Delta r_{C=C} = 0.093 \pm 0.018$ Å, $\Delta r_{C-C} = -0.050 \pm 0.014$ Å, which should be compared with the predictions of Lasaga et al., $\Delta r_{C=C} = 0.077$ Å (external bond) and 0.088 Å (internal bond), $\Delta r_{C-C} = -0.051$ Å, while we find $\Delta r_{C=C} = 0.085$ Å (external bond) and 0.074 Å (internal bond), $\Delta r_{C-C} = -0.044$ Å.

The evolution of the transition energies to the planar relaxed excited states is given in Table I (and in Figure 1) as a function of N^{-1}). Again, despite the geometry relaxation, these transition

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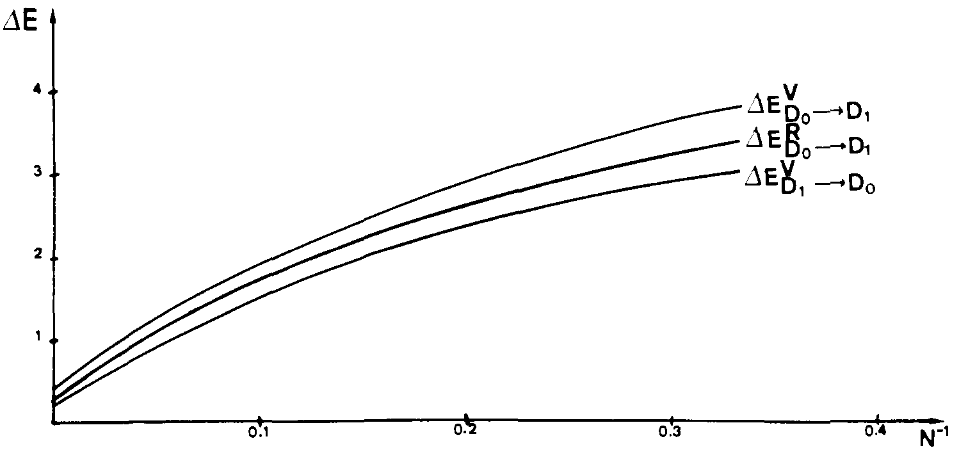


Figure 4. N dependence of the transition $D_0 \to D_1$ between the lowest doublet states of odd linear polyenes (in eV); same comments as in Figure 1.

energies seem to exhibit an almost linear dependence in N^{-1} with a slight negative curvature. Least-squares fittings give, in eV,

$$\Delta E^{\text{rel}}_{S_0 \to T_1} = 0.43 + 10.13/N - 8.23/N^2 \qquad (3)$$

for the lowest ^3B_u triplet state, and

$$\Delta E^{\text{rel}}_{S_0 \to S_1} = 0.47 + 32.84/N - 42.90/N^2 \qquad (4)$$

for the ^1A_g singlet excited state.

III. Vertical Emissions from the Planar Relaxed Geometries of Excited States

From the excited-state optimized planar geometries one may deduce the vertical emission energies relative to $^3B_u \to {}^1A_g$ phosphorescence ($\Delta E^{V}_{T_1 \to S_0}$) or to the (forbidden) $^1A_g \to {}^1A_g$ fluorescence ($\Delta E^{V}_{S_1 \to S_0}$). These values are also reported in Table I. As easily seen from Figure 1, the mirror law is not satisfied for the singlet excited state,

$$\Delta E^{V}_{S_0 \to S_1} - \Delta E^{R}_{S_0 \to S_1} > \Delta E^{R}_{S_0 \to S_1} - \Delta E^{V}_{S_1 \to S_0}$$

The relaxation energy of the excited state singlet state is significantly larger (by about 30%) than the ground-state energy loss to reach the optimal geometry of this excited state.

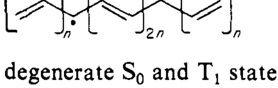
On the contrary, the mirror law is nicely satisfied by the lowest triplet state, as may be seen from Figure 1 and Table I

$$\Delta E^{V}_{S_0 \to T_1} - \Delta E^{R}_{S_0 \to T_1} = \Delta E^{R}_{S_0 \to T_1} - \Delta E^{V}_{T_1 \to S_0} \qquad (5)$$

If this law is satisfied the vertical emission from the relaxed excited triplet to the surface ground state should tend toward

$$\Delta E^{V}_{T_1 \to S_0}(\infty) = \Delta E^{V}_{S_0 \to T_1}(\infty) - 2\Delta E^{R}_{S_0 \to T_1}(\infty) \simeq 0 \qquad (6)$$

which, according to eq 1 and 38 gives a numerical value equal to zero, since $\Delta E_{S_0 \to T_1}(\infty) = 0.86$ eV, $\Delta E^{R}_{S_0 \to T_1}(\infty) = 0.43$ eV. The vertical phosphorescence emission should then tend toward zero when N tends to infinity. This statement might be considered with some skepticism if it only rested on numerical extrapolations; it can be rationnalized more convincingly as follows. The relaxed geometrical structure of the excited triplet corresponds to a diradicalar structure with two unpaired electrons located at respectively one-fourth and three-fourth of the chain length; this is the proposed structure of the soliton pair given in paper I, and one may notice the coincidence between extrapolated value $\Delta E^{R}_{S_0 \to T_1}(\infty)$ (10.8 kcal/mol) and the asymptotic value of the energy to form a soliton pair from the ground-state equilibrium geometry, predicted in paper I from a completely independent approach to be 10.2 kcal/mol. This coincidence is not fortuitous since the diradicalar soliton pair



should give nearly degenerate S_0 and T_1 states, the interaction between the two remote solitons becoming negligible. This remark makes easy the understanding of both the nullity of $\Delta E^{V}_{T_1 \to S_0}(\infty) = 0$ and of the equality

$$\Delta E^{R}_{S_0 \to T_1} = \text{energy to create a soliton pair}$$

It also confirms the qualitative structural scheme proposed for the lowest triplet equilibrium.

As will be shown in the next section, the planar optimized geometries are likely to be real minima for the ^1A_g excited state, although we did not study the possible pyramidalization angles. This is not the case for triplet states, which undergo a torsion around double bonds, as well known from the triplet photosensitized cis–trans isomerizations of linear polyenes. The behavior of the torsion of a double bond will be discussed in a further section, but a full discussion requires the preliminary study of the odd polyenes planar excited states.

IV. Odd Polyenes Vertical Excitation Energies and Planar Equilibrium Excited-State Conformations

The excitation energies of free radicals are not well known. Figure 4 and Table I report the lowest vertical transition energies and the transition energies toward the planar equilibrium excited state. This state of $^2A_1$ symmetry should be dipole allowed, but its essentially neutral nature should maintain the transition moment to low values. For allyl, our calculated vertical transition (3.82 eV) should be compared with the ab initio results of Buenker and Peyerimhoff[44] (3.79 eV) and Levin and Goddard[45] (3.20 eV) in a double-ζ basis set. The vertical transition energy decreases linearly with N^{-1} (cf. Figure 4). We find 1.95 eV for $n = 9$, while Yamabe et al.[46] find 1.39 eV in PPP calculation. Our results suggest a low asymptotic value (0.42 eV), the best fitting being given by

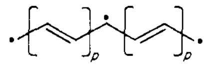
$$\Delta E^{V}_{D_0 \to D_1} = 0.42 + 15.63/N - 16.25/N^2 \qquad (7)$$

This value is much lower than the 1.0-eV asymptote of ref 46 in which the CI was limited to single excitations.

The relaxation energy is smaller than in even polyenes; it is only 0.2 eV for $n = 7$ and $n = 9$ (instead of 0.5 eV for ^3B_u and 0.9 eV for ^1A_g of $n = 8$ even polyenes), and the asymptotic value is given by the best fit (in eV)

$$\Delta E^{R}_{D_0 \to D_1} = 0.31 + 14.79/N - 16.23/N^2 \qquad (8)$$

to be 0.31 eV. The corresponding relaxed geometries exhibit large bond lengths, and the bond-length alternation is not very clear (cf. Figure 5). The $n = 9$ compound suggests a qualitative structure with three radicalar sites for a $2p + 3$ compound.



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[45] G. Levin and W. A. Goddard, *Theor. Chim. Acta*, **37**, 253 (1975).

[46] T. Yamabe, K. Akagi, T. Matsui, K. Fukui, and M. Shirikawa, *J. Phys. Chem.*, **86**, 2365 (1982).

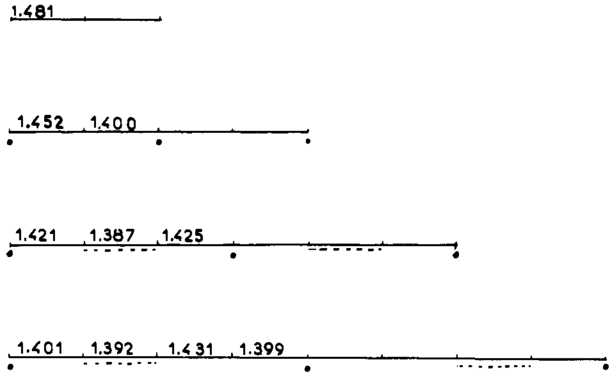


Figure 5. Planar geometries of the lowest doublet and excited states of odd polyenes.

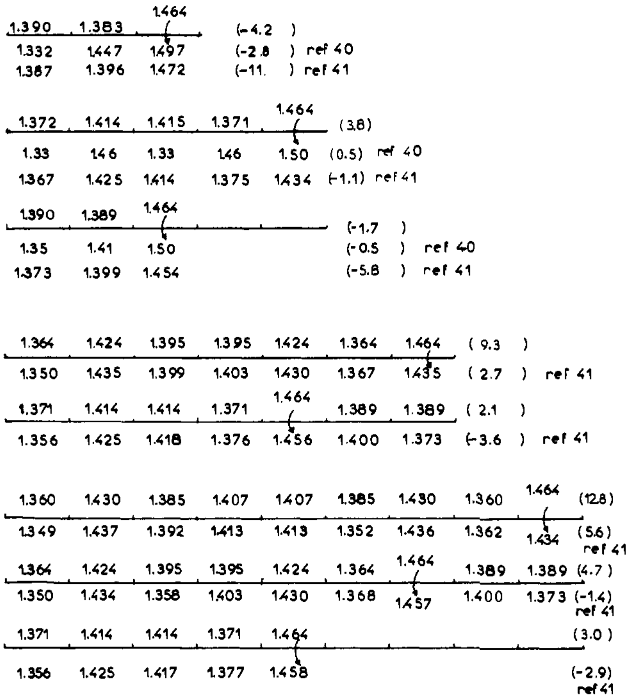


Figure 6. Relaxed twisted conformations (in Å) and their energies (in kcal/mol) relative to the planar C_{2h} triplet minimum.

V. Triplet Cis–Trans Isomerization

The triplet-state equilibrium geometry of ethylene is twisted, and so are the triplet minima of several linear polyenes. The torsion occurs around double bonds of the ground state, either external or internal double bonds. These minima have been studied at the ab initio (STO 3G without CI) level by Bonačić-Koutecký and Ishimaru[40] for butadiene and hexatriene, and by Ohmine and Morokuma[41] (STO 3G and 4-31G UHF for butadiene, MINDO/3 for larger polyenes) including a full relaxation of geometric parameters. The latter paper indicates that the carbon atom of a twisted bond may pyramidalize during the course of the twisting; the pyramidalization angle is zero for planar and perpendicular conformations (except in MINDO/3 calculations[41]), and we did not include this degree of freedom, which would require a special extraction and which is essentially important for the twisted minima of the *ionic* singlet states.

For butadiene the qualitative picture of the twisted conformation is, of course, an allyl + methyl orthogonal interaction (Figure 6), and our bond lengths agree with that description and the calculated bond lengths of Ohmine and Morokuma.[41] The 90° twisted conformation is a real minimum (cf. Figure 7); the energy lowering under the twisting is less significant in our calculation than in ref 41.

When twisted around the terminal bond, hexatriene becomes a pentadienyl + methyl system (cf. Figure 6), and our geometries may be compared with those given for pentadienyl in ref 1. We find this twisted conformation to be a low saddle point (cf. Figure 8) while Ohmine and Morokuma[41] find a slight minimum. The torsion around the central double bond is preferred and leads to a real minimum, representing an allyl + allyl system in both our work and ref 41. The geometry optimization of ref 40 was centainly incomplete since it does not delocalize the two unpaired electrons (this may be due to the use of the Nesbet approximate HF operator which handles spurious coulomb and exchange terms). For higher polyenes the geometries and energies of the twisted minima are immediately obtained from our previous calculations on odd polyenes ground states[1] (cf. also ref 47) and our geometries agree with those calculated by Ohmine[41] within 0.02 Å. The relative energies of the twisted conformations are in perfect agreement with a definite preference for the twisting around the *central* bond (cf. decapentene in Figure 6). The relative position of the twisted conformations with respect to the relaxed planar geometry are in slight disagreement; our method gives a smaller stabilization under the twisting than theirs, but the twisted conformations are lower than the vertical transition energy (cf. Table I) and the cis–trans isomerization remains possible around *all* double bonds.

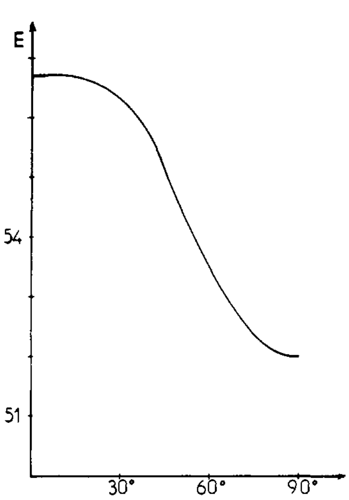
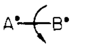


Figure 7. Energy variation of the lowest triplet state of butadiene under the torsion of one doublet bond (all bond lengths are optimized for each value of θ) with respect to the ground-state energy, in kcal/mol.

The geometries for partial torsions (θ = 30, 45, and 60°) have been optimized in order to study the possibler existence of barriers between the planar relaxed and the twisted conformations. Such barriers ($\simeq$2 kcal/mol) had been found by Bonačić-Koutecký[40] for hexatriene, since they did not optimize the bond lengths, assuming a regular progression of the bond-length changes. These barriers are not present in the ab initio calculation on butadiene[41] once the geometry is properly relaxed for every value of θ as confirmed by our calculations (Figure 7). For hexatriene twisted around the central bond, we did not find any barrier (cf. Figure 8a), in agreement with the MINDO/3 calculation of ref 41, while we find a slight barrier for the torsion around the external bond (cf. Figure 8b), as does ref 41.

The energies of the lowest triplet and ground-state singlet are nearly degenerate for 90° twisted conformations, since the torsion defines two delocalized radicals in their doublet ground state coupled by a very weak antiferromagnetic interaction (which decreases a N^{-2} with the dimension of the system, as will be shown elsewhere)



S < T by ~0.5 kcal/mol

The relative positions of the various twisted triplet conformations is immediately given by the consideration of the ground-state rotational barriers. The preference for cis–trans isomerization around the inner double bonds can be viewed as a ground-state

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(47) T. Yamabe, K. Akagi, Y. Tanabe, K. Fukui, and M. Shirikawa, *J. Phys. Chem.*, **86**, 2359 (1982).

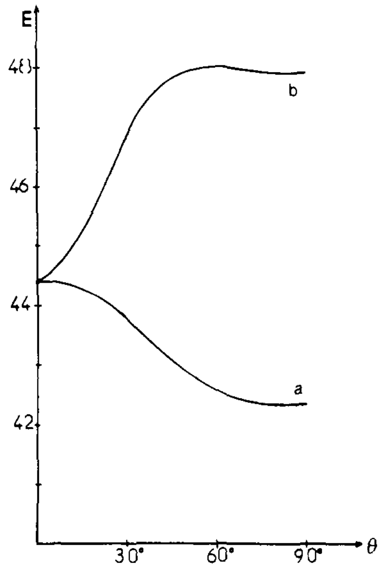


Figure 8. Energy variation of the lowest triplet state of hexatriene under the torsion of (a) the internal double bond, (b) an external double bond (same comments as in Figure 7).

characteristic (i.e., the preferences to define two delocalized A· and B· free radicals of equal dimension rather than a large one and a small (methyl) one. The possibility of a cis–trans isomerization from the vertical triplet is therefore given by the comparison between the vertical transition energy (given in Figure 1) and the ground-state rotational barrier (cf. Table II of ref 1), provided that no significant barrier occurs between the two corresponding conformations. The evolution of these quantities as functions of N^{-1} are plotted in Figure 11 and it immediately appears that:

(1) The cis–trans isomerization from vertical $S_0 \rightarrow T_1$ absorption is always possible around the *internal* double bond; it becomes impossible from $N = 10$ around the *external* double bonds. For intermediate double bonds, e.g., the *p*th double bond, there exists a critical value N_p with which the vertical $S_0 \rightarrow T_1$ absorption becomes insufficient to induce the cis–trans isomerization around the *p*th double bond. This value may be obtained from the expression of the rotational barriers (see paper I)

$$\Delta R^{(2n)}{}_{2p-1,2p} = 2B - B' + C\left[\frac{1}{2p-1} + \frac{1}{2n-2p+1}\right] - \frac{C'}{2n} \tag{9}$$

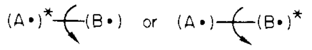
with $2B - B' = 0.79$ eV, $C = 1.78$ eV, $C' = -0.12$ eV (which is valid only for min $(2p - 1, 2n - 2p + 1) \leq 5$), by comparing with the $\Delta E^{V(2n)}_{S_0 \rightarrow T_1}$ vertical absorption energy given by eq 1

$$0.79 + 1.78[(2p-1)^{-1} + (2n-2p+1)^{-1}] + 0.12(2n)^{-1} > 0.87 + 10.7(2n)^{-1} - 7.9(2n)^{-2}$$

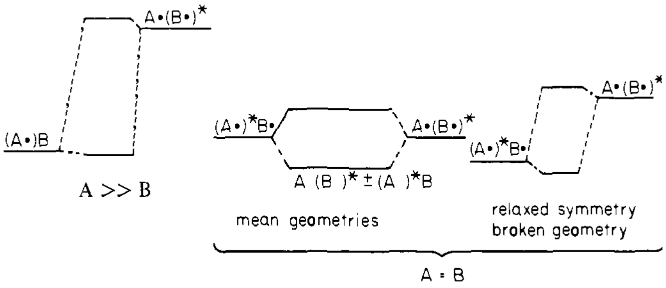
(2) The cis–trans isomerization around the internal double bond (and all other double bonds) may become impossible for large N ($2n > 6$) if the polyene is populated in the lowest triplet state minimum energy.

VI. Behavior of the Neutral (^1A_g) Singlet Excited State under the Torsion of Double Bonds and Its Possible Role in Singlet Cis–Trans Isomerization

The twisted singlet excited state connecting with the ^1A_g neutral excited state may be viewed as a weak interaction between two π radicals A· and B·, in two orthogonal planes, one of them being in its ground state and the other one being in its lowest doublet excited state (which is also neutral in the sense of VB theory, as previously discussed)



The two forms are in competition; if A is much larger than B (torsion around a terminal bond), the excitation will tend to localize on A, while if A and B have equal dimensions a resonance might possibly occur between the two forms. But it is easy to demonstrate that the resonance interaction is very weak, and it can only occur to a significant amount when A and B have the same geometry, intermediate between the ground and the excited geometries. The resonance is much weaker than the stabilization under a specific geometry optimization of, say, (A·)*, which breaks the symmetry, localizes the excitation on side A, and cancels almost completely the interaction with A·(B·)*. This general phenomenon of localization of the excitation which occurs in many problems (for a general discussion see footnote 48 and references herein) as soon as the localizing relaxation is larger than the resonance.



The final geometries of the twisted excited singlet are immediately obtained from those of the ground and excited geometries of odd polyenes as given in Figure 6 of ref 1 and Figure 5 of the present work.

For butadiene, this problem does not occur since one deals with a (allyl)* methyl interaction. The optimized bond lengths (C_1C_2 = 1.482, C_2C_3 = 1.480, C_3C_4 = 1.464 Å for a torsion around the C_3C_4 bond) confirm this interpretation (cf., the geometries of allyl excited state in Figure 5). The twisted excited singlet state is much lower than in its planar relaxed geometry (by 7 kcal/mol). As can be seen in Figure 9, the 90° twisted conformation is not a real minimum; the minimum is obtained for an angle $\theta \simeq 70°$, which lies 1 kcal/mol below the 90° saddle point.

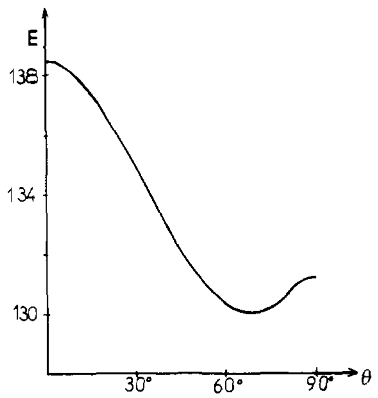


Figure 9. Energy variation of the lowest neutral singlet excited state of butadiene under the torsion of a double bond (same comments as in Figure 7).

Our predictions should be compared to the recent ab initio attemps to locate it; in ref 8 the twisted bond was lengthened to 1.45 Å and the other bonds had been kept constant; this guess does not appear to be very well adapted to the optimal twisted geometry of the neutral singlet state. The energy obtained was in rather good agreement with the present calculation. Bonačić-Koutecký[49] proposed a potential curve for the neutral excited state under the twist of a double bond. In this work the geometries are not optimized and rather arbitrary (the twisted bond is lengthened to 1.416 Å; the others are kept constant); the vertical excited ^1A_g state is located at 6.7–6.9 eV (as ours), below

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(48) J. P. Malrieu, *Theor. Chim. Acta*, **59**, 281 (1981).

(49) V. Bonačić-Koutecký, M. Persico, D. Döhnert, and A. Sevin, *J. Am. Chem. Soc.*, **104**, 6900 (1982).

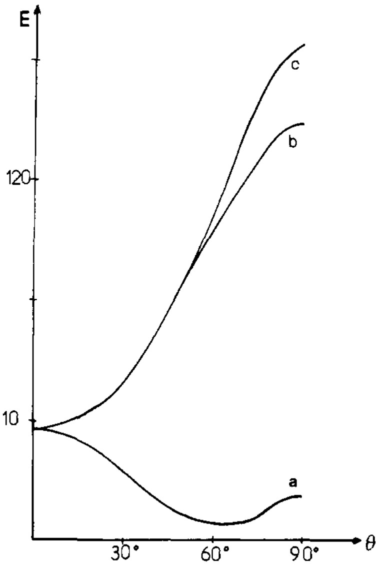

Figure 10. Energy variation of the lowest neutral singlet excited state of hexatriene under the torsion of (a) an external double bond, (b) the internal double bond with symmetry breaking, (c) the internal double bond, maintaining the central symmetry.

the vertical ^1B_u ionic state (at 7.8 eV). The two states are suggested to cross when the double bond is twisted (for $\theta \simeq 45°$), but large uncertainties remain on the CI extrapolations.

For hexatriene (cf. Figure 10), the torsion around the terminal bond leads to a weaker energy stabilization with respect to the planar relaxed geometry ($\simeq$ 1 kcal/mol at 90°), with an intermediate minimum for $\theta \simeq 70°$ (2 kcal/mol below the planar relaxed geometry). The torsion around the inner double bond increases the energy by 12 kcal/mol; the advantage of localizing the excitation is apparent from Figure 10. The geometries are reported in Figure 6 and confirm that the systems are respectively (pentadienyl)* methyl and (allyl)* allyl. A striking result is that while triplet states should preferably undergo cis–trans isomerizations around inner bonds (except for kinetic reasons), the neutral singlet excited states of small polyenes should prefer to undergo cis–trans isomerizations around external bonds, as seen in respectively Tables IIand III.

The preference for external bond torsion in singlet cis–trans isomerization may be less pronounced for larger polyenes, as seen for decapentene (cf. Table III), and it should disappear for large enough compounds.

Table II. Lowest Triplet Energies with Respect to the Equilibrium Ground State (in kcal/mol)

	vertical	planar C_{2h} relaxed	90° twisted around C_1C_2	C_3C_4	C_5C_6
ethylene	96.7	62.4	62.5		
butadiene	69.8	56.6	52.2		
hexatriene	56.2	44.4	48.0	42.5	
octatetraene	47.7	36.6	45.7	38.5	
decapentene	42.6	31.4	44.3	36.2	34.5

Table III. Lowest Singlet Neutral Excited-State Energies with Respect to the Equilibrium Ground State (in kcal/mol)

	vertical	planar C_{2h} relaxed	twisted around C_1C_2	C_3C_4	C_5C_6
butadiene	166.6	138.7	130.4		
hexatriene	131.8	109.4	110	122	
octatetraene	111.0	90.1	94	100	
decapentene	96.5	76.6	85	85	96

The position of the twisted singlet excited state is easy to predict from the nknowledge of the ground-state barriers and energy excitations of the odd polyenes (eq 10). The ground-state ro-

$$\Delta E^{\perp}_{S_0\rightarrow S_1}(2n,2p-1) =$$

$$\underset{\text{ground-state equilibrium}}{E^{*(2n)}_{(2p-1,2p)\text{twisted}} - {}^1E^{0\,(2n)}} = \underset{\text{ground-state rotational barrier}}{\Delta R^{2n}_{2p-1,2p}} + \underset{\text{excitation energy of the longest odd fragment}}{\underset{D_0 \rightarrow D_1}{\Delta E^{R}_{\max(2p-1,2n-2p+1)}}} \qquad (10)$$

tational barrier $\Delta R_{2p-1,2p}$ is minimum for inner bond rotations, but $\Delta E^*_{\max(2p-1,2n-2p+1)}$ is minimum when $2p - 1$ is maximum, i.e., for external bond rotations. There is therefore a competition between two factors; the second factor (minimization of the free radical excitation) is more important for small polyenes, but an

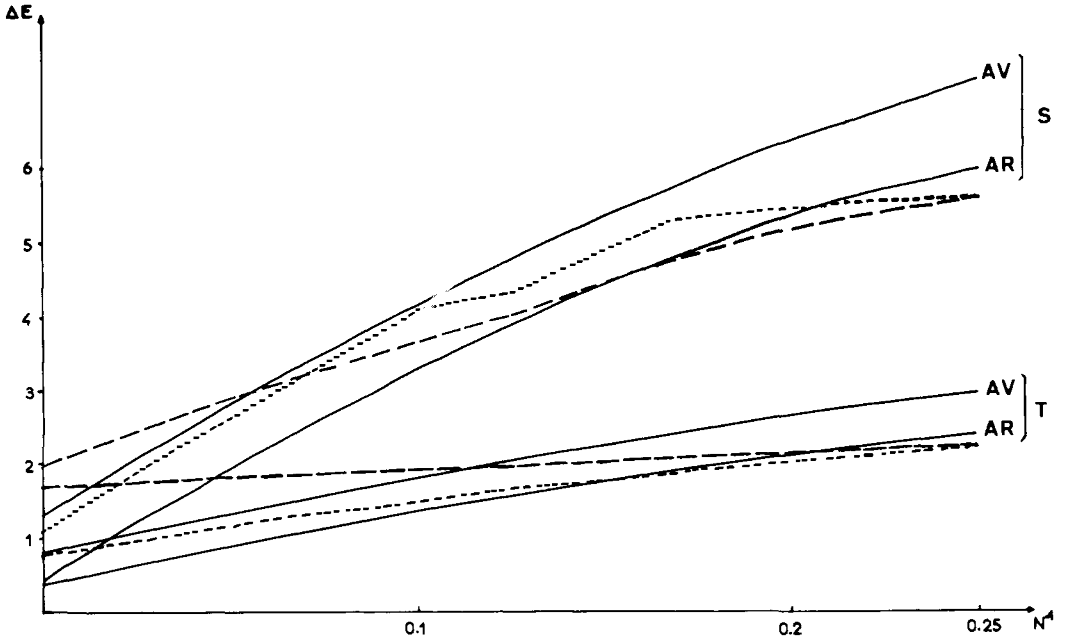

Figure 11. N dependence of the transition energies (in eV) in even linear twisted polyenes; AV, AR stand for ΔE^V and ΔE^R of Figure 1. Rotational barriers around double bond: (- - -) twisting around an external bond, (———) twisting around the most internal bond.

J. Am. Chem. Soc. **1984**, *106*, 587-590

inversion occurs for large polyenes. The previously defined *n* dependence of ΔR and $\Delta E^{*}_{\text{odd}}$ makes the study of the two extreme cases, namely the rotation around external and most internal double bonds, easy. For the twisting around one external double bond the energy of the singlet excited state is given by eq 10 and 8 and ref 1, if one neglects again the weak effective exchange on the twisted double bond

$$\Delta S^{\perp}{}_{S_0\rightarrow S_1}(2n,2n-1) = \Delta E^{2n}{}_{2n-1,2n} + \Delta E^{R}{}_{D_0\rightarrow D_1}(2n-1) = 2.02 + 16.50(2n-1) \text{ (in eV)}$$

For twisting around the most internal double bond, in a $4n + 2$ molecule, one obtains

$$\Delta E^{\perp}{}_{S_0\rightarrow S_1}(4n+2,2n+1) = \Delta R^{4n+2}{}_{2n+1,2n+2} + \Delta E^{R}{}_{D_0\rightarrow D_1}(2n-1) = 1.1 + 18.4/2n + 1 - 16.2/(2n+1)^2 \text{ (in eV)}$$

The corresponding curves have been plotted in Figure 11. From these considerations it appears that (i) the cis–trans photoisomerization around double bonds should be impossible from the relaxed planar minima of the covalent S_1 singlet excited states, except for butadiene and hexatriene (for its external double bond only); (ii) the photoisomerization should always remain possible from the *vertically* excited neutral singlet if it occurs around *internal* double bonds; (iii) the singlet photoisomerization around external *double* bonds is *prefered up to 20 carbon* atoms, but for larger compounds it should *become impossible*.

In Figure 11 we have not reported the experimental energy dependence of the allowed vertical singlet excitation toward the ^1B_u (ionic) excited state, for two reasons: (i) our neutral ^1A_g excited states apparently are somewhat too high by 0.5 (octatetraene) to 0.25 eV (decapentene) with respect to experiment; (ii) the relevant experimental X $^1A_g \rightarrow {}^1B_u$ transition energies should concern the gaseous phase, while most experimental data for heavy polyenes concern the liquid phase.[50] The difference is not negligible (0.25 for hexatriene and octatetraene) and the solvent effect may be larger for the ionic excited states (in which important instantaneous dipoles appear, creating larger dispersion forces with the solvant) than for the covalent states. The experimental vertical transition energies (in solvent) to the ^1B_u state would follow in Figure 11 the straight line representing the energy of the singlet excited state twisted around a *terminal* double bond. This proves at least that the vertical absorption energy is always larger than the energy of the twisted covalent excited state, especially for *inner* bonds rotations. A previous paper[8] has shown that the photoisomerization could not occur on the ionic singlet excited surface, and that the molecule had to undergo a conversion into either the neutral ^1A_g covalent excited singlet, the ^3B_u excited state (which would require an intersystem crossing), or the ground ^1A_g state in a high vibrational level. The present results show that the three hypotheses remain valid for large polyenes.

Registry No. Ethylene, 74-85-1; butadiene, 106-99-0; hexatriene, 2235-12-3; octatetraene, 1482-91-3; decapentaene, 2423-91-8; propene, 115-07-1; pentadiene, 504-60-9; heptatriene, 2196-23-8; nonatetraene, 31699-36-2.

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(50) F. Sondheimer, D. A. Ben Ephraim, and R. Wolovsky, *J. Am. Chem. Soc.*, **83**, 1675 (1961).

A UV Photoelectron Spectroscopic and Hartree–Fock–Slater MO–LCAO Study of Tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene and Related Strained Compounds

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Abstract: The UV photoelectron (PE) spectra of tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene, tetracyclo[3.3.0.0^{2,4}.0^{3,6}]octane, and deltacyclene have been measured. Spectra have been analyzed and assigned by using nonempirical Hartree–Fock–Slater (HFS) calculations. From this analysis and from a comparison with related molecules a remarkable destabilization of the high-lying antisymmetric Walsh orbital (e_A) upon contraction of the molecular cage becomes apparent.

Compounds with the general formula $(CH)_{2n}$ ($n = 1, 2, ...$) have generated much interest in organic chemistry for both synthetic and theoretical reasons. Within such families of valence isomers the CH building blocks can be connected in many different ways, often leading to highly strained hydrocarbons. The synthetic challenge posed by such compounds is obvious. One of the most strained molecules of the $(CH)_8$ family is tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene (**1**; see Figure 1). Since its first successful synthesis in 1977,[1a] the reactivity of this compound has been under active investigation.[1b]

In view of the large amount of strain present in **1**, a study of its molecular orbital structure is of interest. A suitable method for obtaining reliable information about the occupied molecular orbitals in the valence region is UV photoelectron (PE) spectroscopy. Since unambiguous assignment of PE spectra usually requires PE information on a series of related compounds, the saturated analogue of **1**, tetracyclooctane (**2**), and a homologue of **1**, deltacyclene (**3**), have been studied as well. In the literature a large body of PE data is available on related systems containing a cyclopropane ring but lacking the C_4C_5 bridge.[2] Bischof et al.[3]

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(1) (a) Klumpp, G. W.; Stapersma, J. *Tetrahedron Lett.* **1977**, 747. (b) The thermal and the photochemical rearrangements of **1** have been reported: Stapersma, J.; Rood, I. D. C.; Klumpp, G. W. *Tetrahedron* **1982**, *38*, 2201. Stapersma, J.; Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 274.

(2) Gleiter, R. "Topics in Current Chemistry"; Springer-Verlag: Berlin, 1979; Vol. 86, p 197.

(3) Bischof, P.; Heilbronner, E.; Prinzbach, H.; Martin, H. D. *Helv. Chim. Acta* **1971**, *54*, 1072.

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