Sudden Polarization in Zwitterionic Excited States of Organic Intermediates in Photochemical Reactions. On a Possible Mechanism for Bicyclo[3.1.0]hex-2-ene Formation

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Abstract: It is shown that the "sudden polarization" effect in zwitterionic states is a necessary consequence of the very nature of hetero- and nonsymmetric diradicals when nearly nonbonding orbitals have a leading role. Therefore, the open-shell SCF approach is the appropriate one here. For the centrally twisted *s-cis,s-trans*-diallyl, two energy minima in the first excited singlet surface corresponding to nearly pure ionic structures with opposite polarizations are found. The form with an electron-rich s-trans allylic fragment has the lower energy. The rules for the relative energy of two oppositely polarized diallylic forms when substituted by methyl at different positions are given. These rules are used to predict the stereochemistry of cyclopropane ring closure in the photochemical rearrangement of 1,3,5-hexatriene derivatives to bicyclo[3.1.0]hex-2-enes.

I. Introduction

Dauben and co-workers proposed ionic states as possible intermediates in the photocyclization of dienes and trienes.[1] It is a challenge to attempt a theoretical justification for the appearance of lowest singlet excited states of ionic nature, due to geometrical changes during photochemical processes.

The "sudden polarization" effect[2] offers a possible explanation of the existence of ionic intermediates. The simple theoretical description of diradical states (four states model) gives rise to a pair of close-lying zwitterionic states[3] Z_1 and Z_2 which can be highly polarizable.[4] These two states can become highly polar with opposite polarizations, via the perturbation caused by any very small asymmetry of two radical sites. Calculations yielding the "sudden polarization" effect have been reported for twisted ethylene where the asymmetry of one radical site is introduced by pyramidalization of one CH_2 group;[2] terminally twisted butadiene;[5] *s-cis,s-trans*-diallyl with two orthogonal allylic fragments;[2] and *N*-retinylidene.[6] The "sudden polarization" effect is an important and far-reaching consequence of very specific diradical structural features. Hence, a critical choice of the model and a method is necessary for an investigation of this effect in relatively large intermediates of chemical interest. This method should be capable of a proper qualitative description of important and delicate connections between the structural and electronic properties of diradicals. It would not be surprising if some commonly used quantum chemistry methods may not be able to yield the sudden appearance of excited highly polar states for certain geometries at all. On the other hand, the suspicion that sudden polarization is an artifact of the method can be eliminated by critical analysis. Therefore, in this work the methodical background for appearance of ionic excited states is first discussed before predictions on the mechanism for the photorearrangement of 1,3,5-hexatriene derivatives to bicyclo[3.1.0]hex-2-enes are attempted.

II. The "Sudden Polarization" Effect

Theoretical considerations suggest that the interruption of an olefinic double bond by twisting is favorable for the first excited states of ethylene and other medium-size olefins.[7] A widely accepted model of electronic stated for such geometries, proposed by Salem, is based on the assumption that two almost degenerate molecular orbitals $|a\rangle$ and $|b\rangle$ play a decisive role for their description. The states of such twisted molecular conformations built from the configurations $|a^2\rangle$, $|ab\rangle$, and $|b^2\rangle$, differing mainly in the occupation numbers of the two close-lying MOs, are either of covalent-diradical or of zwitterionic nature.[3]

The form of MOs $|a\rangle$ and $|b\rangle$ is qualitatively different for diradicals belonging to different classes: homo-, hetero-, and nonsymmetric diradicals according to Salem's classification based on symmetry considerations of approximately localized orbitals representing radical sites of the molecule:

If these two localized orbitals (atomic or group orbitals) go into each other under a symmetry operation leaving the molecular framework invariant, which is a property of homosymmetric diradicals (e.g., twisted ethylene, *s-trans,s-trans*-twisted diallyl), the customary SCF procedure yields symmetry-adapted delocalized MOs $|a\rangle$ and $|b\rangle$.

In contrast, if a diradical is heterosymmetric (e.g., twisted ethylene with one pyramidalized CH_2 group, terminally twisted butadiene), two localized orbitals cannot figure in the same MOs because they belong to different irreducible representations of the molecular symmetry group. Therefore, the two nonbonding MOs considered in the model have localized character.

Finally, for nonsymmetric diradicals (e.g., *s-trans,s-cis*-twisted diallyl *N*-retinylidene), free mixing between the two localized orbitals symbolizing the radical sites is allowed.

For an understanding of the main feature of diradical states, it is illustrative to keep the *delocalized* picture for the *homosymmetric* diradicals and to use the *localized* picture for *hetero-* and *nonsymmetric* diradicals.[3] The relevant electronic configurations which we use for the discussion of both pictures can be written in Roothaan notation as

$$|a^2\rangle = (\phi_1\alpha)\cdots(\phi_{N-1}\beta)\cdot(a\alpha)\cdot(a\beta)$$
$$|b^2\rangle = (\phi_1\alpha)\cdots(\phi_{N-1}\beta)\cdot(a\alpha)\cdot(b\beta) \qquad (1)$$
$$|ab\rangle = (\phi_1\alpha)\cdots(\phi_{N-1}\beta)\frac{1}{\sqrt{2}}[(a\alpha)\cdot(b\beta) - (a\beta)\cdot(b\alpha)]$$

The difference between the energy expectation values for the Slater determinants (eq 1) are the well-known expressions

$$E(a^2) - E(ab) = h_a - h_b + \sum_{j\neq a}[2(J_{ja} - J_{jb}) + (K_{ja} - K_{jb})] + J_{aa} - J_{ab} - K_{ab} \qquad (2a)$$

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and

$$E(b^2) - E(a^2) = 2(h_b - h_a) + 2\sum_{j \neq a}[2(J_{ja} - J_{jb}) + (K_{ja} - K_{jb})] + J_{bb} - J_{aa} \quad (2b)$$

where h_a and h_b are matrix elements of the one-electron part of Hamiltonian $\hat{h}_1$, and J_{jk} and K_{jk} are the Coulomb and exchange integrals, respectively. The molecular orbitals $|a\rangle$ and $|b\rangle$ can in general be written as linear combinations of group orbitals $|A\rangle$ and $|B\rangle$ which describe two different regions of the twisted molecular conformation:

$$\begin{aligned} |a\rangle &= \lambda|A\rangle + (1 - \lambda^2)^{1/2}|B\rangle \\ |b\rangle &= \lambda|B\rangle - (1 - \lambda^2)^{1/2}|A\rangle \end{aligned} \quad (3)$$

For the symmetrical situation ($\lambda = 1/\sqrt{2}$) the localized group orbitals have the following form:

$$\begin{aligned} |A\rangle &= \sum_{\nu \in A} c_{A\nu}\phi_\nu \\ |B\rangle &= \sum_{\nu \in A} c_{A\nu}\phi_{T(\nu)} \end{aligned} \quad (4)$$

where ϕ_ν transforms into $\phi_{T(\nu)}$ under the symmetry operation T.

A qualitative consideration of the energy sequence of three configurations $E(a^2)$, $E(ab)$, and $E(b^2)$ should help to elucidate specific features of homo-, hetero-, and nonsymmetric diradicals.

Let us recall that for the planar molecular conformations the energy sequence is determined predominantly by the one-electron energy part $h_a - h_b$ (eq 2) and therefore

$$E(a^2) < E(ab) < E(b^2) \quad (I)$$

On the contrary, for twisted conformations, the energy difference (eq 2b) is very small, i.e., $E(a^2) - E(b^2) \approx 0$, mainly because $\langle A|\hat{h}_1|B\rangle = 0$. The second term in eq 2b must be very small in order that $E(a^2) \approx E(b^2)$. Therefore, the energy difference (eq 2a) is approximately

$$E(a^2) - E(ab) \approx J_{aa} - J_{ab} - K_{ab} \quad (5)$$

The energy difference (eq 5) in the localized orbital representation takes the form

$$E(a^2) - E(ab) \approx -\frac{1}{2}(J_{AA} - J_{AB}) + 2[K_{AB} - \langle AA|AB\rangle] \quad (6)$$

with Coulomb and exchange integrals for group orbitals $|A\rangle$ and $|B\rangle$ and $\langle AA|AB\rangle = \langle A(1)A(1)|g(1,2)|A(2)B(2)\rangle$. Since the self-repulsion integral J_{AA} is a large positive quantity, the following energy sequence for delocalized MOs $|a\rangle$ and $|b\rangle$ (eq 3) is expected:

$$E(b^2) \approx E(a^2) < E(ab) \quad (II)$$

The energy sequence II is appropriate for the homosymmetric diradicals.

For $\lambda = 1$ eq 3 describes localized MOs $|a\rangle = |A\rangle$ and $|b\rangle = |B\rangle$. If two fragments of twisted molecular conformations do not considerably differ so that the potentials seen by electrons localized on $|A\rangle$ and $|B\rangle$ are similar, the energy difference (eq 2b) is $E(A^2) - E(B^2) \approx 0$ and eq 2a takes the form

$$E(A^2) - E(AB) \approx J_{AA} - J_{AB} - K_{AB} \quad (7)$$

Evidently, owing to the dominant role of J_{AA}, the energy sequence for heterosymmetric and nonsymmetric diradicals (with two similar molecular fragments) is

$$E(AB) < E(A^2) \approx E(B^2) \quad (III)$$

The customary iterative SCF procedure with the closed-shell Hartree–Fock operator minimizes the energy expectation value for configuration $|a^2\rangle$. The virtual MO $|b\rangle$ is used in two other configurations, $|b^2\rangle$ and $|ab\rangle$ (eq 1). On the other hand, in the procedure with the approximate Nesbet Hartree–Fock operator which is frequently used for a simple description of the open-shell molecular systems,[8] the energy expectation value is minimized for the configuration

$$|a\bar{b}\rangle = (\phi_1\alpha)\cdots(\phi_{N-1}\beta)\cdot(a\alpha)\cdot(b\beta) \quad (8)$$

It is evident that for homosymmetric diradicals, both closed-shell Roothaan and open-shell Nesbet procedures, due to symmetry, yield *delocalized* MOs $|a\rangle$ and $|b\rangle$ of bonding and antibonding character. Therefore, the energy sequence II for three configurations should be obtained. The configuration interaction combines configurations $|a^2\rangle$ and $|b^2\rangle$ giving rise to a covalent singlet ^{1}D and to a higher zwitterionic state Z_2, while the configuration $|ab\rangle$ contributes mostly to the lower zwitterionic state Z_1. The interaction matrix element

$$\langle a^2|\hat{H}|b^2\rangle = K_{ab} = \frac{1}{2}(J_{AA} - J_{AB}) \quad (9)$$

is generally a large quantity.

For heterosymmetric diradicals where $|a\rangle \approx |A\rangle$ and $|b\rangle \approx |B\rangle$ (with MO energies $\epsilon_A \leq \epsilon_B$) the closed-shell approach uses a highly asymmetrical electronic configuration $|A^2\rangle$ for starting the iterative procedure. The coupling between $|A\rangle$ and $|B\rangle$ is forbidden for symmetry reasons. If the MO energies ϵ_A and ϵ_B are close lying, the electron–electron repulsion will tend to push electrons into the electron-poor fragment described by $|B\rangle$ and the procedure starts to oscillate between two polar structures.[9] In this case, convergence can be achieved only if a symmetric electronic distribution is used for starting the iterative procedure (for example, the density matrix of planar configuration is used as the starting electronic distribution in a calculation of the corresponding heterodiradical). Then, an erroneous energy sequence $E(A^2) \approx E(B^2) < E(AB)$ of three configurations is obtained instead of the energy sequence III valid for heterosymmetric diradicals. Obviously the large MO energy difference $|\epsilon_A - \epsilon_B| > 0$, which might be the case of some nonsymmetric diradicals built from two very different fragments, gives rise to the energy sequence I: $E(A^2) < E(AB) < E(B^2)$.

The approximate open-shell Nesbet procedure is more suitable for treating the heterosymmetric diradicals because the configuration used for minimization of the energy expectation value

$$|A\bar{B}\rangle = (\phi_1\alpha)\cdots(\phi_{N-1}\beta)\cdot(A\alpha)\cdot(B\beta) \quad (10)$$

gives a nearly symmetrical electronic distribution with one odd electron on each radical site. Therefore, the procedure converges without difficulty giving rise to the correct energy sequence III valid for heterosymmetric diradicals: $E(AB) < E(A^2) \approx E(B^2)$ (which results from the localized MOs $|A\rangle$ and $|B\rangle$). The configuration $|AB\rangle$ again describes the lowest ^{1}D state, while $|A^2\rangle$ and $|B^2\rangle$ describe polar states. If the interaction between configuration $|A^2\rangle$ and $|B^2\rangle$

$$\langle A^2|\hat{H}|B^2\rangle = K_{AB} \quad (11)$$

is sufficiently small[10] (i.e., $K_{AB} \ll |J_{AA} - J_{BB}|$) the configuration interaction, by combining $|A^2\rangle$ and $|B^2\rangle$ in the zwitterionic states, does not balance the excess of charge in the fragment described by the group orbital $|A\rangle$. Therefore, the "sudden polarization" effect occurs, giving rise to the ionic states $Z_1 \approx |A^2\rangle$ and $Z_2 \approx |B^2\rangle$ with opposite polarizations

while the configuration $|AB\rangle$ contributes mostly to the lowest singlet state of covalent character. The highly polar states Z_1 and Z_2 have close lying energies. The same effect should be expected for nonsymmetric diradicals if MO energies ϵ_A and ϵ_B are slightly different.

The above analysis shows that the "sudden polarization" effect in the first excited singlets Z_1 and Z_2 of hetero- and nonsymmetric diradicals with similar fragments is a necessary consequence of the very electronic structure of these diradicals, at least in the model which makes use of three electronic configurations for description of their singlet states.

In principle, more extensive configuration interaction can create mixing between $|A^2\rangle$ and $|B^2\rangle$ in an indirect way through configurations formed by virtual orbitals different from $|B\rangle$. If this interaction is sufficiently large the "sudden polarization" effect in singlet states can be weakened. This will occur only if the virtual energy levels are close to the energies of the frontier orbitals $|A\rangle$ and $|B\rangle$, and if simultaneously each term in the product of interaction matrix elements between configurations forming the link between $|A^2\rangle$ and $|B^2\rangle$ is not too small. Therefore, it is improbable that the highly polarized states of hetero- and nonsymmetric diradicals will change into nonpolar zwitterionic states (resonating between two ionic structures as for homodiradicals) if larger configuration interaction is introduced. Also, in principle, the two polar configurations might finally be dispersed as small contributions within many states with predominantly covalent character. In some cases (mainly if more than two atomic orbitals describe radical sites) the higher ionic state Z_2 might borrow covalent character from the excited covalent states and become the lowest singlet excited state with opposite polarization from that predicted by limited (3 × 3) configuration interaction.[10] The dipole moment resulting from the "sudden polarization" is certainly overestimated within this model and the polarization might be more localized at the ends of the twisted bonds.[11]

We assume that the qualitative features of the "sudden polarization" effect remain independent from the details of the MO open-shell treatment with small configuration interaction. This assumption is supported by an investigation of the "sudden polarization" effect using other theoretical approaches.[11] Therefore, it seems worthwhile to investigate the consequences of the "sudden polarization" effect for photochemical reactions using the Nesbet open-shell SCF method, followed by 3 × 3 CI.

III. Method

It follows from the previous considerations that one of the appropriate methods for a description of the singlet states of hetero- and nonsymmetric diradicals is the ab initio approximate SCF open-shell Nesbet method (with an STO-3G or 4-31G basis set[12]) followed by interaction among the three singlet configurations (cf. eq 1 and 8) which differ in frontier orbitals occupation numbers. This approach is suitable for a description of twisted molecular conformations having two approximately nonbonding molecular orbitals.

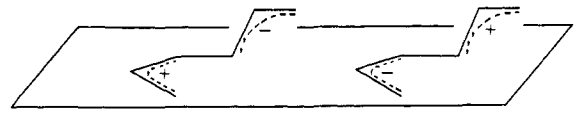
The energies $E(a^2)$, $E(b^2)$, and $E(ab)$ of the three configurations obtained from these calculations yield the sequence II for homosymmetric diradicals and the sequence III for hetero- and nonsymmetric diradicals as expected from the analysis of the frontier orbital method. Calculations using this method are also manageable for fairly large molecules. Therefore, the described method with the minimal basis set[13] is used in this work for a study of diallylic intermediates which should play an important role in the bicyclization of trienes.

IV. On the Mechanism of Bicyclo[3.1.0]hex-2-ene Formation

The assumptions involved in a proposal of the mechanistic pathway through excited ionic states for photorearrangement of 1,3,5-hexatriene derivatives to bicyclo[3.1.0]hex-2-enes as given by Dauben[1b] are (a) existence of s-cis, s-trans orthogonal diallylic conformation; (b) closure of the s-trans fragment to a cyclopropane ring as a one-step process followed by a five-number ring closure.

It seems reasonable to investigate first the influence of geometry on the energy and polarity of the first singlet excited state of unsubstituted *s-cis,s-trans*-diallyl and then to proceed with a study of the effect of substitution at different positions of the diallylic skeleton.

A. Singlet Excited States of *s-cis,s-trans*-Diallyl. Owing to the sudden polarization effect, the singlet excited states Z_1 and Z_2 of the *s-cis,s-trans*-diallylic conformation with a 90° twisted central double bond and an idealized geometry (1.4 Å for all C–C bond lengths except 1.5 Å for the middle bond length) are highly polar states with polarizations shown in **1** and **2**. The energy of Z_1 is lower than the energy of Z_2 by only



1 **2**

1.3 kcal/mol. By twisting the central double bond from 0° to 90°, the energy of Z_1 is lowered by 3 kcal/mol.

In order to assign a possible physical meaning to the polarized forms, a geometry optimization was performed for the first excited singlet. The geometry optimized for bond lengths of the 90° twisted diallyl, with two orthogonal flat allylic forms, yields the same polarization pattern as obtained for the idealized geometry (**1**). The Z_1 energy is now lowered by 17 kcal/mol relative to the energy of the diallylic idealized geometry, and the energy gap between Z_1 and Z_2 is slightly increased (2.3 kcal/mol).

Furthermore, in analogy to the pyramidalization effect in terminally twisted butadiene observed by Bruckmann and Salem,[5] we investigated whether the nonplanar geometry of one of the two allylic fragments will stabilize one of the polarized forms **1** and **2**. Two energy minimizations were performed allowing pyramidalization of one of the two carbon atoms attached to the twisted central bond in such a way that the three atoms bounded to the pyramidalized carbon atom remain in the same plane as before pyramidalization. The corresponding first singlet excited state potential energy surface yielded two minima I and II as shown in Figure 1. The lower minimum is obtained for pyramidalization at the carbon atom C_4 of the twisted central bond on the s-trans allylic fragment side giving rise to the polarized form TP ("trans-pyramidalized") where the negative charge flows in the s-trans allylic fragment. Pyramidalization at the other carbon atom C_3 of the twisted central bond (which belongs to the s-cis allylic fragment) led to the other minimum yielding the polarized form CP ("cis-pyramidalized") with the charge excess in the s-cis allylic triad. The optimized geometries corresponding to both minima, as well as the optimized geometry for the twisted diallyl with two planar allylic fragments (NP "non-pyramidalized"), are given in Figure 1. The energy difference between the two minima is 3.5 kcal/mol and the intermediate barrier (E(NP) − E(CP)) is 2.6 kcal/mol. It is worth mentioning that the energy difference between two zwitterionic states Z_1 and Z_2 for both pyramidalized forms is very large. The charge distribution at the carbon atoms of the polar forms CP, NP, and TP in Figure 1 is given in Table I.

The pyramidalization can be viewed as a way of passing from sp^2 to sp^3 hybridization. One of the nascent sp^3 orbitals is accessible to the extra charge. Therefore, the negative charge flows into the allylic fragment with the pyramidalized carbon atom.

Such a double-well surface potential indicates the possibility

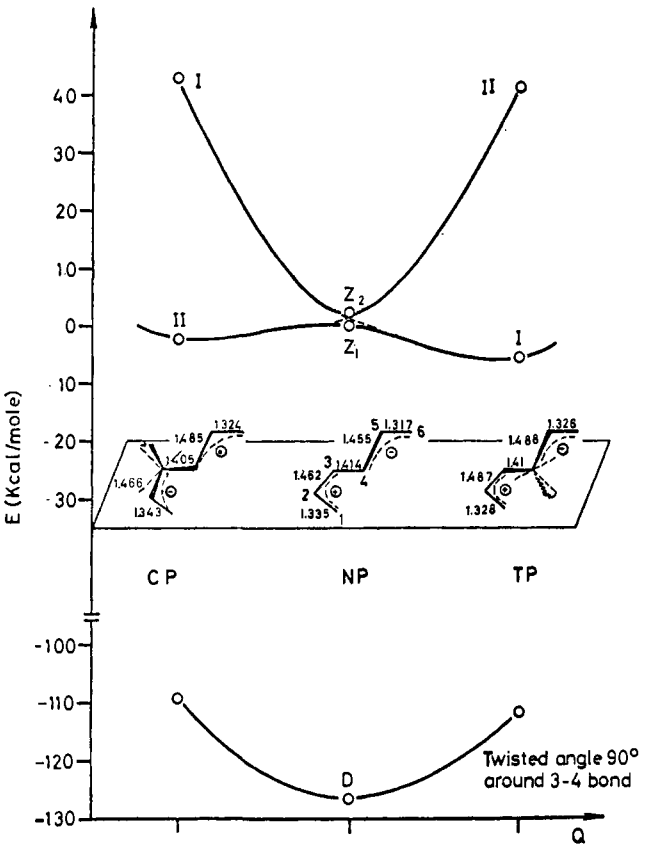


Figure 1. Energy potential surfaces for lowest singlet states of orthogonal s-trans, s-cis diallylic conformation. The coordinate Q connects arbitrarily geometries CP ("cis-pyramidalization" C-3), NP (no pyramidalization"), and TP ("trans-pyramidalization" C-4). Dotted lines show the avoided crossing between the zwitterionic energies I and II.

of two different photochemical pathways as already pointed out by Bruckmann and Salem in the case of terminally twisted butadiene.[5] The two wells which correspond to the two different polarized forms of s-trans, s-cis orthogonal diallylic conformation are relatively close in energy so that photochemical "funneling"[14] through these wells could be competitive. Funneling through I is slightly more favorable. The conclusion about the favored pathway based on the energy difference between the two minima should be handled with care in view of the simple ab initio calculations with small CI and without inclusion of polarized functions.

B. Methyl Substitution Effect on the Bicyclization of Trienes. If we adopt previous assumptions for the mechanistic pathway through excited ionic states for photorearrangement of trienes to bicyclo[3.1.0]hexenes, we can delineate the expected products on the basis of the energy difference between the two energy minima in the Z_1 energy surface corresponding to the two polarized forms. According to the charge in the s-trans triad of the structure with the lower energy it is possible to predict whether the closure to the cyclopropane ring from the s-trans triad should proceed through a conrotatory or disrotatory route. If the energies of both polarized structures are very close, both pathways should be competitive. It seems reasonble to assume that the excitation is essentially localized in the twisted central bond so that the *ground* state orbital symmetry argument can be applied to the allylic triads (in the present case to the s-trans allylic fragment: T+, disrotatory; T−, conrotatory route).

In order to suggest a possible photochemical pathway for bicyclization of trienes, we systematically investigated the influence of methyl substitution at different positions of the diallylic skeleton. Methyl substitution stabilizes positive charge, and will therefore tend to stabilize those twisted diallyl systems which are polarized with the negative end on the unsubstituted allyl fragment. Since pyramidalization attracts negative charge to the pyramidalized center a combination of methyl substitution and pyramidalization can either reinforce the stability of one polarized form (substitution and pyramidalization on opposite fragment) or leave the two polarized forms with competing energies (substitution and pyramidalization on the same fragment). The structures formed by substitution of methyl groups at different positions of the diallylic skeleton for the three geometries CP, NP, and TP as given in Figure 1 were calculated. The results are illustrated in Figures 2–9 where the Z_1 energies for CP, NP, and TP are arbitrarily connected in order to facilitate the pictorial representation of a possible potential energy surface. The Z_2 energies for corresponding forms are indicated as well. The following discussion refers to the Z_1 energies exclusively. Substitution by methyl at C-1 (1-methyldiallyl) strongly destabilizes the CP diallylic form so that the energy difference $E_{Z_1}(\mathrm{CP}) - E_{Z_1}(\mathrm{TP}) \sim 9$ kcal/mol while the energy difference between TP and CP is only ~1 kcal/mol for methyl substitution at C-6 (6-methyldiallyl) as illustrated in Figures 2a and 2b, respectively. Methyl substitution at C-6 even inverts the polarization in allylic fragment of the nonpyramidalized form NP but at the cost of energy.[15] The energy positions associated with the polar forms of the 1,6-dimethyldiallyl (Figure 3) can be easily interpreted as the result of the approximately additive effects of methyl substitution at C-1 and C-6 which results in stabilization of the TP polarized form.

The substitution effect of one methyl group on one of the ends of the twisted middle bond in *s-trans,s-cis*-diallyl is illustrated in Figure 4. The methyl substitution at the end of the twisted bond belonging to the s-cis fragment (3-methyldiallyl) strongly destabilizes the CP form relative to the NP form because the pyramidalization at the carbon atom C-3 reinforces negative charge flow in the s-cis fragment in opposition to the effect of methyl substitution. As expected, methyl substitution at C-4 is energetically unfavorable for NP and TP forms in comparison with methyl substitution at C-3 of the twisted diallylic skeleton (Figure 4b).

Table I. Charge Distribution on Carbon Atoms for Optimized Geometries of *s-cis,s-trans*-Diallyl in the Z_1 State

Geometries[a]	Singlet excited state	Carbon atoms[a] 1	2	3	4	5	6
CP	^1D	6.13	6.06	6.08	6.04	6.07	6.13
	Z_1	6.37	6.05	6.66	5.49	6.08	5.86
	Z_2	5.86	6.07	5.46	6.63	6.05	6.42
NP	^1D	6.13	6.07	6.05	6.05	6.07	6.13
	Z_1	5.81	6.09	5.48	6.64	6.05	6.44
	Z_2	6.44	6.05	6.61	5.49	6.09	5.83
TP	^1D	6.13	6.07	6.06	6.06	6.06	6.12
	Z_1	5.81	6.09	5.46	6.72	6.05	6.36
	Z_2	6.46	6.05	6.66	5.40	6.07	5.87

[a]Geometries of CP, NP, and TP are given in Figure 1 as well as numeration of carbon atoms.

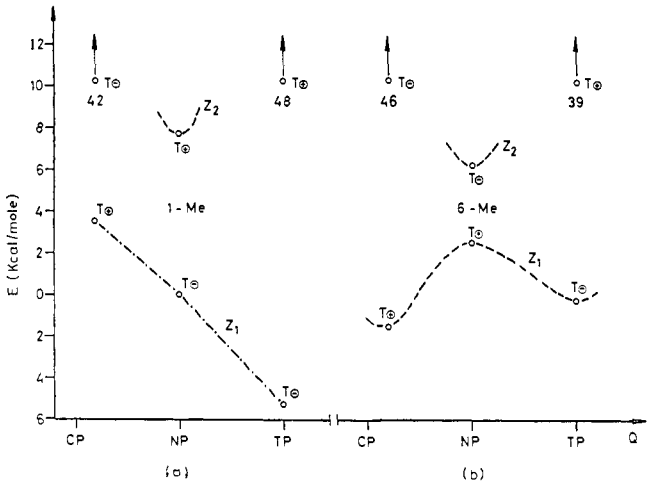


Figure 2. The energies of lowest singlet states Z_1 and Z_2 of polar forms CP, NP, and TP of (a) 1-methyldiallyl; (b) 6-methyldiallyl relative to the energy of NP of 1-Me. The following description is valid for Figures 2–9: Symbols T− and T+ indicate electron-rich and electron-poor s-trans allylic fragment, respectively. Numeration of carbon atoms and geometries of diallylic skeletons (CP, NP, and TP) are given in Figure 1. The interpolation indicated by lines - - - illustrates the probable form of the Z_1 energy surface along the arbitrary coordinate Q which connects geometries CP, NP, and TP. If such an interpolation allows too much freedom, the lines · · · indicate only that the energies lie on the same surface.

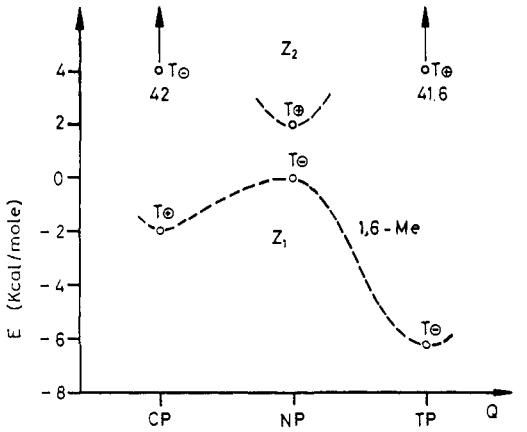


Figure 3. The energies of the lowest singlet states Z_1 and Z_2 of polar forms CP, NP, and TP of 1,6 dimethyldiallyl (cf. description of Figure 2).

The influence of the methyl substitution at the middle carbon atom of an allylic triad (at C-2 or C-5 position) on charge transportation in polarized ionic forms is negligible. The energy difference of TP and CP forms is small as shown in Figure 5.

In general, methyl substitution at the allylic fragment with an excess of electrons is energetically unfavorable. Competition between methyl substitution and pyramidalization is energetically very costly. Using these general conclusions, one can understand the substitution effect caused by placing three and four methyl groups on the diallylic skeleton in a straightforward manner.

The energy difference between two polarized forms CP and TP of 1,6,6-trimethyldiallyl is only ~2 kcal/mol as shown in Figure 6b. From a comparison with the energies of polarized forms for 1,6-dimethyldiallyl (Figure 3), it is clear that two methyl groups at the end of the s-trans triad diminish the energy difference between TP and CP. The relative energy destabilization of the TP polar form is even more pronounced for 2,6,6-trimethyldiallyl (Figure 6a) because the methyl group at C-2 in the middle of the s-cis triad has almost no influence

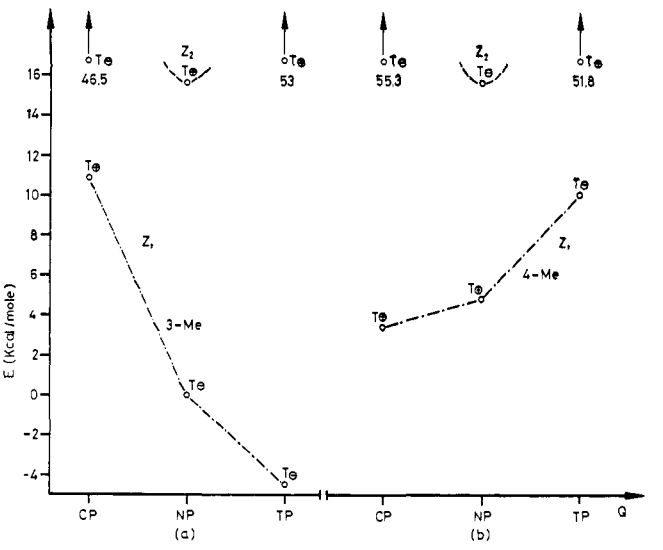


Figure 4. The energies of lowest singlet states Z_1 and Z_2 of polar forms CP, NP, and TP of (a) 3-methyldiallyl; (b) 4-methyldiallyl (cf. description of Figure 2).

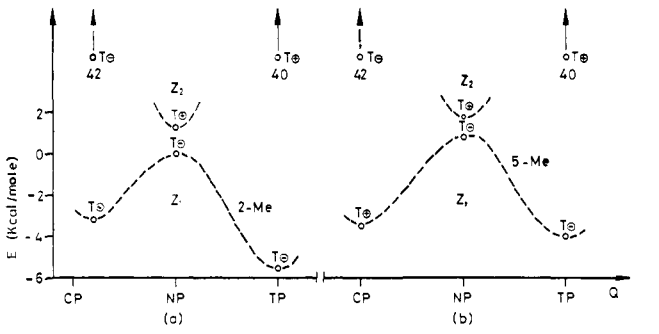


Figure 5. The energies of lowest singlet states Z_1 and Z_2 of polar forms CP, NP, and TP of (a) 2-methyldiallyl; (b) 5-methyldiallyl (cf. description of Figure 2).

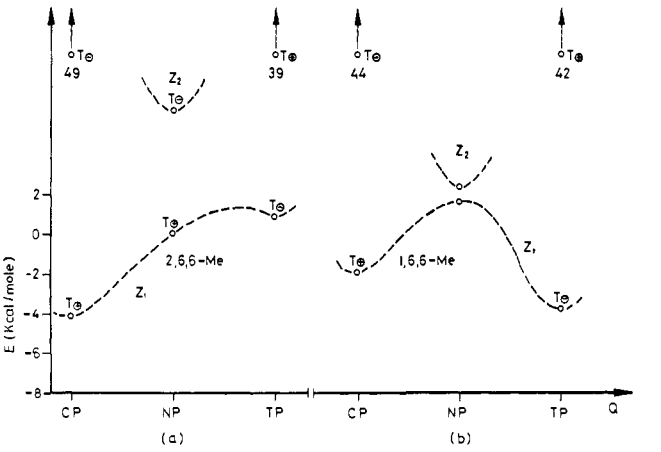


Figure 6. The energies of lowest singlet states Z_1 and Z_2 of polar forms CP, NP, and TP of (a) 2,6,6-trimethyldiallyl; (b) 1,6,6-trimethyldiallyl (cf. description of Figure 2).

on charge of polarized forms. Therefore, the CP polarized form with the electron-poor trans triad is energetically favorable.

The relative energy positions of the polarized diallylic forms TP and CP for tetramethyldiallylic compounds can be viewed qualitatively as the result of an additive influence of substitution effects found for methyldiallylic and trimethyldiallylic compounds. The energies of the polarized forms for 1,2,6,6-

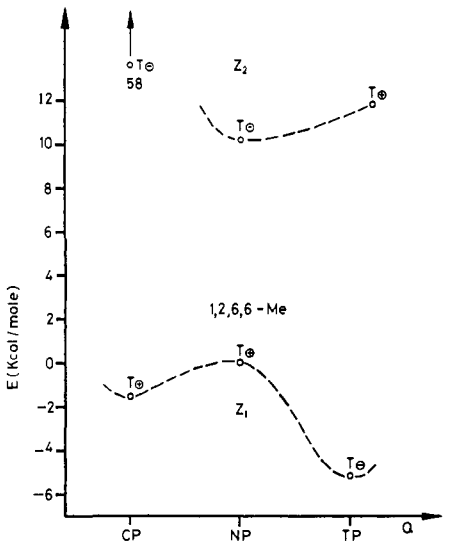


Figure 7. The energies of lowest singlet states Z_1 and Z_2 of polar form CP, NP, and TP of 1,2,6,6-tetramethyldiallyl (cf. description of Figure 2).

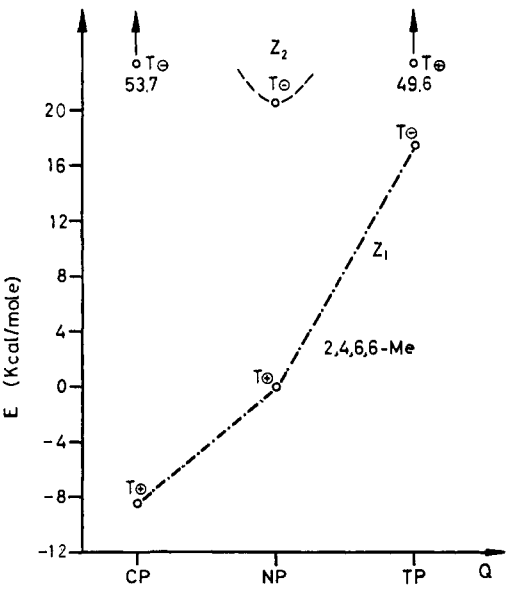
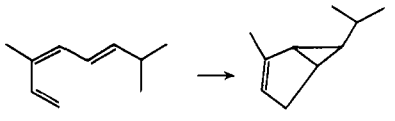


Figure 8. The energies of lowest singlet states Z_1 and Z_2 of polar forms CP, NP, and TP of 2,4,6,6-tetramethyldiallyl (cf. description of Figure 2).

and 2,4,6,6-tetramethyldiallyl are given in Figures 7 and 8, respectively. In the case of 1,2,6,6-tetramethyldiallyl (Figure 7) the TP polarized form is energetically favorable. The same qualitative result can be obtained by a comparison of energy differences between the two polarized forms, TP and CP, for 1,6,6-trimethyldiallyl and 2-methyldiallyl (compare Figures 6b and 5a) or for 2,6,6-trimethyldiallyl and 1-methyldiallyl (compare Figures 6a and 2a).

On the other hand, in the case of 2,4,6,6-tetramethyldiallyl the TP form is very strongly destabilized (Figure 8) as expected because the polarized form with electron excess in the s-trans triad lies energetically very high for 4-methyldiallyl (Figure 4b) as well as in the case of 2,6,6-trimethyldiallyl (Figure 6a).

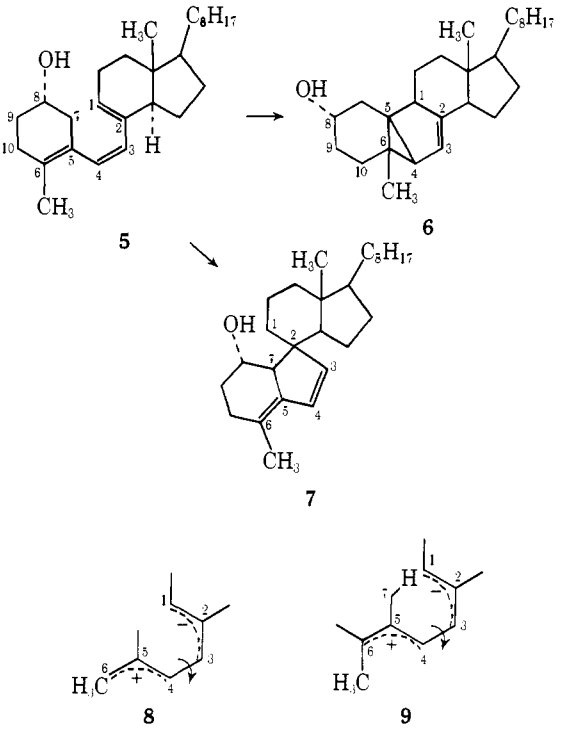
The calculations of the first excited singlet for the three different forms CP, NP, and TP of the acyclic triene **3** yield destabilization of the CP polar form (Figure 9) similar to that in 3-methyldiallyl. (Compare Figures 4a and 2b for qualitative addition of 3-Me and 6-Me substitution.) The last column of Table II indicates the charge distribution in the s-trans part of "nonpyramidalized" diallyl and its methyl derivatives. If the CP form has the lowest energy, then, in the NP form, the



3 **4**

electron excess in the s-cis fragment is already present. The experimentally found conrotatory route[2b] for cyclization leading from **3** to **4** is in agreement with the theoretical prediction (cf. Table II).

The photocyclization of the compound **5** leading to products **6** and **7** was recently reported.[16] The reaction leading to the product **6** can be interpreted as conrotatory closure at 4-6 via **8**, analogous to the TP form of 6-methyldiallyl (Table II). The product **7** occurs via a H shift from position 7 to 1 via **9**, analogous to the CP form of 6-methyldiallyl, followed by bond formation between 7 and 2. The negative charge on the s-cis allylic fragment in **9** should make carbon 1 a good proton abstractor, while the positive charge on 5 should help the departure of proton. If the rate of proton transfer in **9** is faster than the rate of closure of the s-trans moiety to a cyclopropane ring the spiro compound **7** will be observed instead of the expected bicyclo[3.1.0]hexene with stereochemical labeling specific for disrotatory closure.



5 **6** **7** **8** **9**

V. Conclusions

Assuming that the bicyclization of a twisted diallyl proceeds first by closure of the s-trans triad to a cyclopropane ring and that this cyclization at 4-6 occurs through the polar form with the lower Z_1 energy (T− or T+), we can formulate the following predictions:

Methyl substitution at the s-cis triad reinforces the intrinsic tendency for electron excess in the s-trans triad of the unsubstituted s-cis, s-trans "nonpyramidalized" and "transpyramidalized" diallylic forms.

Methyl substitution at the s-trans triad tries to push electrons away from the fragment. This effect requires more energy

Table II. Results of Calculations for First Singly Excited States Z_1

Compd	Disrotatory closure (T+)	Conrotatory closure (T−)	Charge in the s-trans triad of NP form
s-cis,s-trans-Diallyl		TP[b]	T−
1-Methyldiallyl		**TP**[c]	T−
6-Methyldiallyl	*CP*[a]	TP[a]	T+
1,6-Dimethyldiallyl		**TP**[c]	T−
3-Methyldiallyl		**TP**[c]	T−
4-Methyldiallyl	**CP**[c]		T+
2-Methyldiallyl	CP[a]	*TP*[a]	T−
5-Methyldiallyl	CP[a]	*TP*[a]	T−
1,6,6-Trimethyldiallyl	CP[a]	*TP*[a]	Neutral
2,6,6-Trimethyldiallyl	**CP**[c]		T+
1,2,6,6-Tetramethyldiallyl		TP[b]	T+
2,4,6,6-Tetramethyldiallyl	**CP**[c]		T+
Twisted triene **3**		**TP**[c]	T−

[a] Both polar structures are indicated if the energy difference between them is ≤2 kcal/mol (italicized form has lower energy). [b] One form with lower energy is indicated if the energy difference of two forms is between 2 and 4 kcal/mol. [c] The polar form in bold face indicates that the energy difference is >4 kcal/mol.

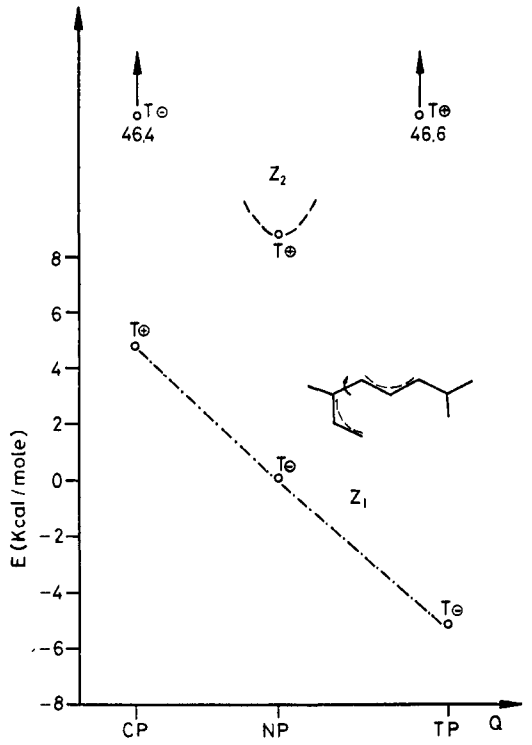


Figure 9. The energies of lowest singlet states Z_1 and Z_2 of polar forms CP, NP, and TP of the acyclic triene **3** (cf. description of Figure 2).

in order to come into play, since it goes counter to the intrinsic tendency for anionic character of the s-trans fragment. For example, in the NP form of 1,6,6-trimethyldiallyl, two methyl groups on the s-trans fragment are required to compensate the effect of one methyl group on the s-cis fragment (cf. Table II and Figure 5b).

In both cases, substitution at the internal allylic terminus (at the twisted double bond, where charge tends to concentrate[11]) is more effective than substitution at the external allylic terminus. The described trends are very weak for the substitution at the central carbon atom of an allylic fragment.[17] The substitution effects are qualitatively additive. If the influence of substitution in the s-cis and in the s-trans triad prevails then the closure of the cyclopropane ring follows the conrotatory and disrotatory route, respectively. This is reflected in the lower Z_1 energy of the TP form (T−) in the former case and in the lower Z_1 energy for the CP form (T+) in the later case. For example, the closure is conrotatory for 1,2,6,6-tetramethyldiallyl and twisted triene **3** and disrotatory for 2,6,6-trimethyldiallyl and 2,4,6,6-tetramethyldiallyl.

Similar considerations should be valid for the influence of any electron donor substituents on the polar state of an intermediate. The opposite effect may be expected for electron acceptor substitution.

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References and Notes

(1) W. G. Dauben and J. S. Ritscher, *J. Am. Chem. Soc.*, **92**, 2925 (1970); (b) W. G. Dauben, M. S. Kellog, J. I. Seemann, N. D. Vietmeyer, and P. H. Wendschuh, *Pure Appl. Chem.*, **33**, 197 (1973).
(2) V. Bonačić-Koutecký, P. Bruckmann, P. Hiberty, J. Koutecký, C. Leforestier, and L. Salem, *Angew. Chem.* **87**, 599 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 575 (1975).
(3) L. Salem and C. Rowland, *Angew. Chem.*, **84**, 86 (1972); *Angew. Chem. Int. Ed. Engl.*, **11**, 92 (1972); L. Salem, *Pure Appl. Chem.*, **33**, 317 (1973).
(4) C. E. Wulfman and S. Kumei, *Science*, **172**, 1061 (1971).
(5) P. Bruckmann and L. Salem, *J. Am. Chem. Soc.*, **98**, 5037 (1976).
(6) L. Salem and P. Bruckmann, *Nature (London)*, **258**, 526 (1975).
(7) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969); S. Shih, R. J. Buenker, and S. D. Peyerimhoff, *Chem. Phys. Lett.*, **16**, 244 (1972); J. Langlet and J. P. Malrieu, *Theor. Chim. Acta*, **33**, 307 (1974); V. Bonačić-Koutecký and S-Ishimaru, *J. Am. Chem. Soc.*, **99**, 8134 (1977).
(8) Compare L. Salem, L. Leforestier, G. Segal, and R. Wetmore, *J. Am. Chem. Soc.*, **97**, 479 (1975), and references cited therein.
(9) V. Bonačić-Koutecký and J. Koutecký, *J. Chem. Phys.*, **55**, 2408 (1971).
(10) L. Salem, *Science*, **191**, 822 (1976).
(11) M. C. Bruni, J. P. Dandey, J. Langlet, J. P. Malrieu, and F. Momicchioli, *J. Am. Chem. Soc.*, **99**, 3587 (1977).
(12) Program Gaussian 70 (W. J. Hehre, W. A. Lathan, R. D. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, QCPE, University of Indiana, Bloomington, Ind.).
(13) The calculations with extended basis yield qualitatively the same results.
(14) J. Michl, *J. Mol. Photochem.*, **4**, 243, 257 (1972).
(15) Notice that the energy difference between the states Z_1 and Z_2 is increased for the most stable polar form as well as for "nonpyramidalized" form by methyl substitution.
(16) E. Havinga, *Chimica*, **30**, 27 (1976).
(17) A node on the central carbon atom in the nonbonding MO of allyl does not allow an electronic substituent effect as pointed out by W. G. Dauben in a private communication.