

QUANTUMCHEMICAL CALCULATIONS ON THE PHOTOCHEMISTRY OF GERMACRENE
AND GERMACROL. THE EXCLUSIVE ROLE OF THE EXOCYCLIC DOUBLE BOND
ISOMERIZATION

W.J.G.M. Peijnenburg*, G.J.M. Dormans and H.M. Buck

Contribution from the Department of Organic Chemistry, Eindhoven University
of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

(Received in UK 15 February 1988)

Abstract - The different photochemistry of the title compounds (reactions of the endocyclic 1,5-diene moiety versus a photochemical [1,3]-OH shift) can be explained assuming an initial isomerization of the exocyclic double bond. MNDO/CI calculations of the potential energy curves and nonadiabatic couplings for the rotation of this bond showed that the 90° twisted conformation can easily be reached. For germacrol the lowest excited state has a zwitterionic character which is favourable for a planar photochemical [1,3]-OH shift. For germacrene, this polarized state is strongly coupled to two diradicalar states. In these twisted diradicalar states a redistribution of the charges in the endocyclic double bonds is found which is eminently suited for intramolecular bond formation.

Introduction

Our interest in the photochemistry of the germacrene system originates from the unique properties of a 1,5-diene chromophore enclosed in a medium sized ring¹⁻⁴. Upon irradiation of (E,E)-germacra-1(10),4,7,(11)-triene (germacrene 1) under singlet conditions², the main photoproducts arise from a reaction of the 1,5-diene moiety. Products 2 and 6 are formed via a $[\pi_s^2 + \pi_s^2]$ cycloaddition reaction of the two endocyclic double bonds, 5 from a biradicalar reaction, and 3 and 4 from respectively a Cope- and an Ohloff-rearrangement of the 1,5-diene system (see Figure 1).

On the other hand, irradiation of (E,E)-germacra-1(10),4,7(11)-triene-8-ol (germacrol 7a) and its methyl derivative (7b) under the same conditions³ reveals a remarkable [1,3]-OH ([1,3]-OMe) shift in the exocyclic part of the molecule as the primary photoprocess. In a subsequent step, the endocyclic double bonds react to form two cyclobutane derivatives (8a,b, 9a,b) and a Cope rearranged product (10a,b) (see Figure 2).

The exclusive role of the 1,5-diene moiety follows from an experiment where the 4,5-double bond is selectively hydrogenated⁴. Irradiation of (4SR,8SR)- and (4SR,8RS)-4,5-dihydrogermacrol (11 and 15) leads only to E-Z isomerization of the endocyclic double bond (12 and 16) and to a photochemical [1,3]-allyl shift (13, 14 and 17) along the same double bond (see Figure 3).

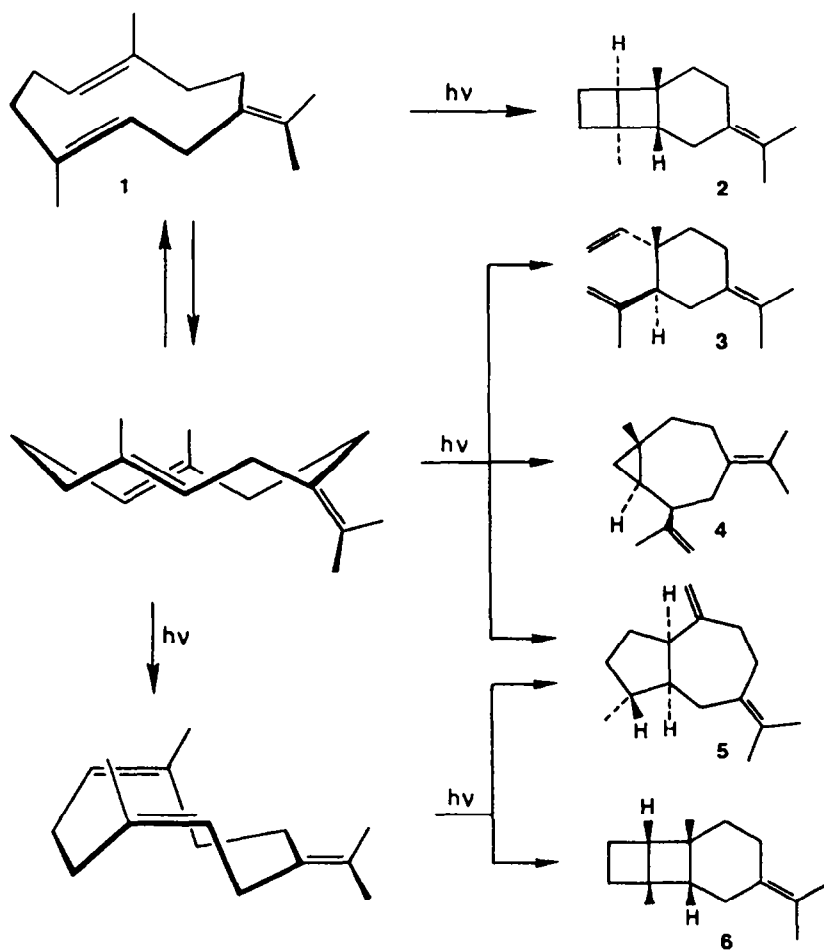


Figure 1. Photochemistry of (E,E)-germacrene (1).

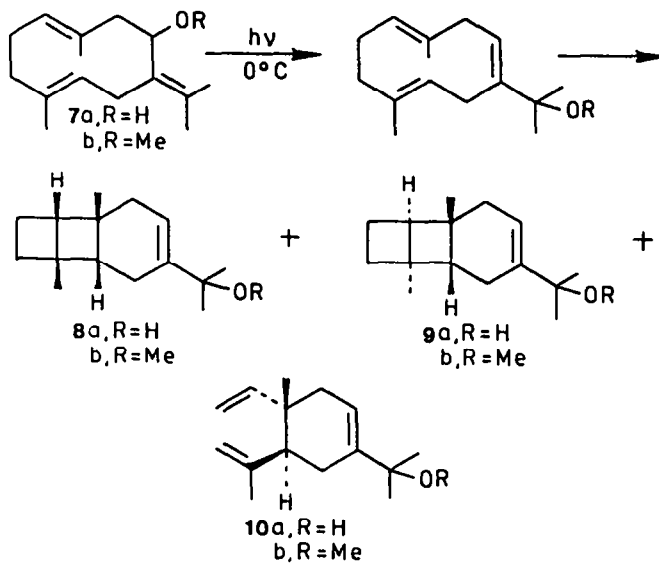


Figure 2. Photochemistry of germacrol (7a) and its methyl derivative 7b.

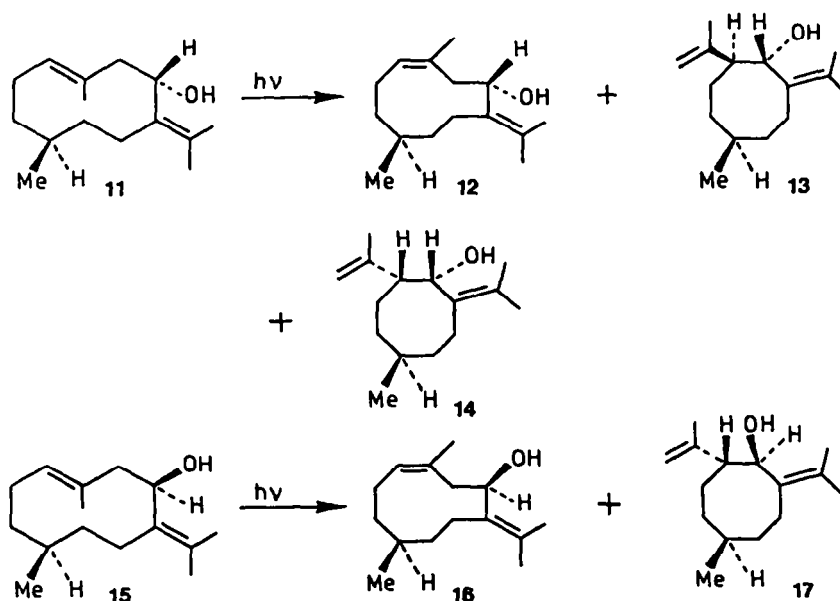


Figure 3. Photochemistry of (4SR,8SR)- and (4SR,8RS)-dihydro-germacrol (11 and 15).

From these experiments two possible explanations arise for the observed behaviour of these germacrene systems.

First, the ground-state conformation of these molecules is known to play an important role in the observed photochemistry^{1,2,4-6}. Due to the presence of three double bonds, the ring skeleton has a certain rigidity and consequently there are eight conformations possible⁷. MNDO-calculations for germacrol⁷ (7a) revealed that the SSS-conformation⁸ is the most stable one. This observation is supported by an X-ray analysis of a germacrene-silver nitrate adduct⁹. The preferential germacrol-conformation is depicted in Figure 4.

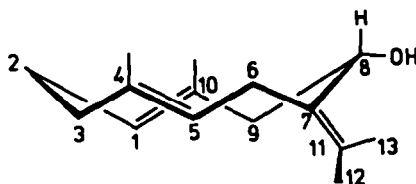


Figure 4. Preferential (SSS-) conformation of germacrol (7a).

It is characterized by a crossed conformation of the two endocyclic double bonds. Another important feature is that the hydroxyl group is oriented almost in the plane spanned by the carbon atoms 7, 8 and 11. Such an orientation is a prerequisite for the occurrence of a planar [1,3]-OH shift, which we propose on the basis of quantumchemical calculations^{10,11}. This mechanism can briefly be illustrated for the photochemical [1,3]-OH shift in propenol¹⁰ (see Figure 5). According to orbital symmetry considerations, this reaction is expected to proceed in a suprafacial fashion. MNDO-calculations reveal an activation enthalpy in the first singlet excited state of 57 kcal/mol. However, upon excitation an electron is promoted from a bonding to an antibonding π orbital, leading to a rotation of the excited double bond. This exothermic process is the essential step in the E-Z isomerization of alkenes. The twist of the double bond is accompanied by a relocalization of the electrons ("Sudden Polarization"¹²). In the 90°-twist region

there are two excited states (Z_1 and Z_2^{13}) close in energy which exhibit an opposite polarization of charge since in these zwitterionic states the electrons may be located at either the central or the terminal carbon atom of the excited double bond.

For propenol, the configuration with the two electrons on the central carbon atom is best stabilized. The lowest excited state is thus positively charged at the terminal carbon atom and negatively charged at the central carbon atom. The partially negatively charged hydroxyl group now shifts towards the terminal carbon atom in the plane of the carbon skeleton via a transition state of C_{2v} symmetry. The calculated activation enthalpy for this planar reaction is 17 kcal/mol. The top of this barrier is still below the level of the vertical excited molecule. Comparable calculations for the planar [1,3]-H shift in propene yield an activation enthalpy of 35.5 kcal/mol.

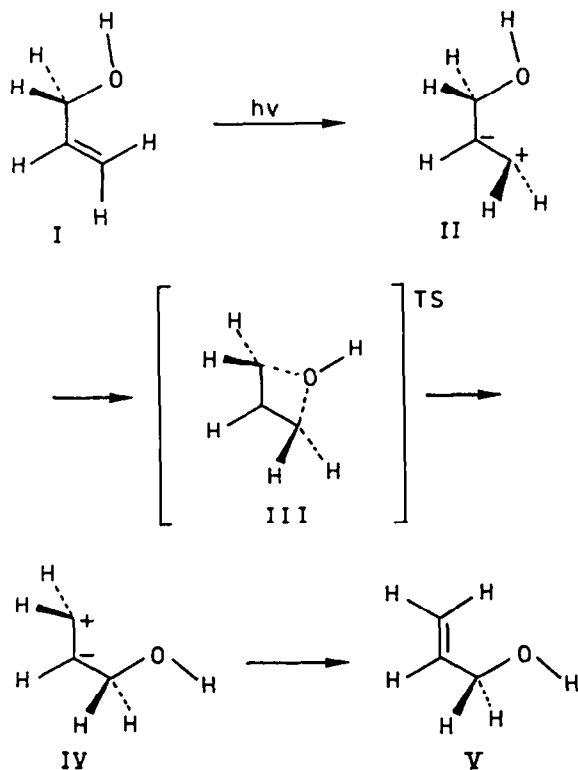


Figure 5. The proposed mechanism for the photochemical [1,3]-OH shift in propenol.

The conclusion of the quantumchemical calculations is that photochemical sigma-tropic shifts in acyclic alkenes proceed via such a planar mechanism which is initiated by a rotation of the excited double bond. Recently we were able to obtain the first experimental evidence in favour of the occurrence of a planar [1,3]-OH shift¹⁴.

Due to the absence of one double bond in 4,5-dihydrogermacrol (11, 15) this system is much more flexible than germacrol (7a) itself and the favourable orientation of the hydroxyl group for a planar shift might be lost. To check this argument, the 4,5-endocyclic double bond was selectively replaced by a cyclopropyl group¹⁵, thus maintaining the rigidity of the molecule while changing the chromophore. Irradiation of this molecule leads essentially to the same reactions as observed for compounds 11 and 15¹⁶. Clearly the rigidity of the molecule is not the only prerequisite for the occurrence of the [1,3]-OH shift.

In order to get a sigmatropic shift it is necessary that the exocyclic double bond is in an excited configuration. Therefore an interaction is needed between the endocyclic 1,5-diene chromophore and the exocyclic double bond. The presence of such an interaction is clear from the UV-absorption spectrum of germacrol and germacrene. Whereas compounds 11 and 15 show maxima near $\lambda = 220$ nm, the latter two compounds have their maxima near $\lambda = 245$ nm.

This bathochromic shift can partly be explained from an increased torsion of the endocyclic double bonds (*vide infra*), but must also be attributed to the above-mentioned interaction between these double bonds. In this way, the excitation energy can be transferred to the exocyclic moiety where it is used for an efficient photochemical reaction.

A question which remains is why germacrol exhibits a [1,3]-OH shift, whereas germacrene does not show a [1,3]-H shift despite their similar UV-absorption characteristics. Part of the answer is that the calculated activation enthalpy for a [1,3]-H shift is about twice the value for a [1,3]-OH shift for the planar mechanism (*vide supra*). This explanation is based on the assumption that the exocyclic double bond can reach a twisted conformation where the lowest excited state has a polarization favourable for a [1,3]-OH shift.

We have now performed semi-empirical calculations for the exocyclic double bond isomerization in both germacrol and germacrene which confirm this assumption and give an additional explanation for their typical difference in photochemistry.

Results and discussion

The calculations have been performed starting from a MNDO-SCF calculation followed by a full CI treatment (170 configurations) for the highest three occupied and first three virtual MOs. These six MOs are mainly built up from the AOs which form the three π -bonds.

Each electronic state is characterized by calculating the bond orders (P_{AB}) and atomic charge densities (P_{AA}) in the basis of natural orbitals from the final multiconfigurational wavefunctions for this state.

$$P_{AB} = \sum_{p \in A} \sum_{q \in B} D_{pq}^{\text{NO}} S_{pq}$$

$$D_{pq}^{\text{NO}} = \sum_{i=1}^N \eta_i C_{pi}^{\text{NO}} C_{qi}^{\text{NO}}$$

S_{pq} is the overlap integral between the AOs p and q (belonging to the atoms A and B respectively) and D_{pq}^{NO} the spinless density matrix in the basis of the natural orbitals (i) with coefficients C_{pi}^{NO} , C_{qi}^{NO} and an occupation number η_i ($\eta_i = 0, 1$ or 2). N runs over all natural orbitals.

All calculations were performed for the optimized structure of SSS-germacrol⁷ (Figure 4) with the only difference that the CC distance of the twisted bond was chosen as 1.40 Å. Germacrene was assumed to have the same geometry as germacrol. In Figures 6 and 7 we present the potential energy curves for the twist of the exocyclic double bond in the interval $0^\circ \leq \theta \leq 90^\circ$ for germacrol and germacrene. In Tables I and II the lowest electronic states are characterized by their π bond orders and atomic charge densities.

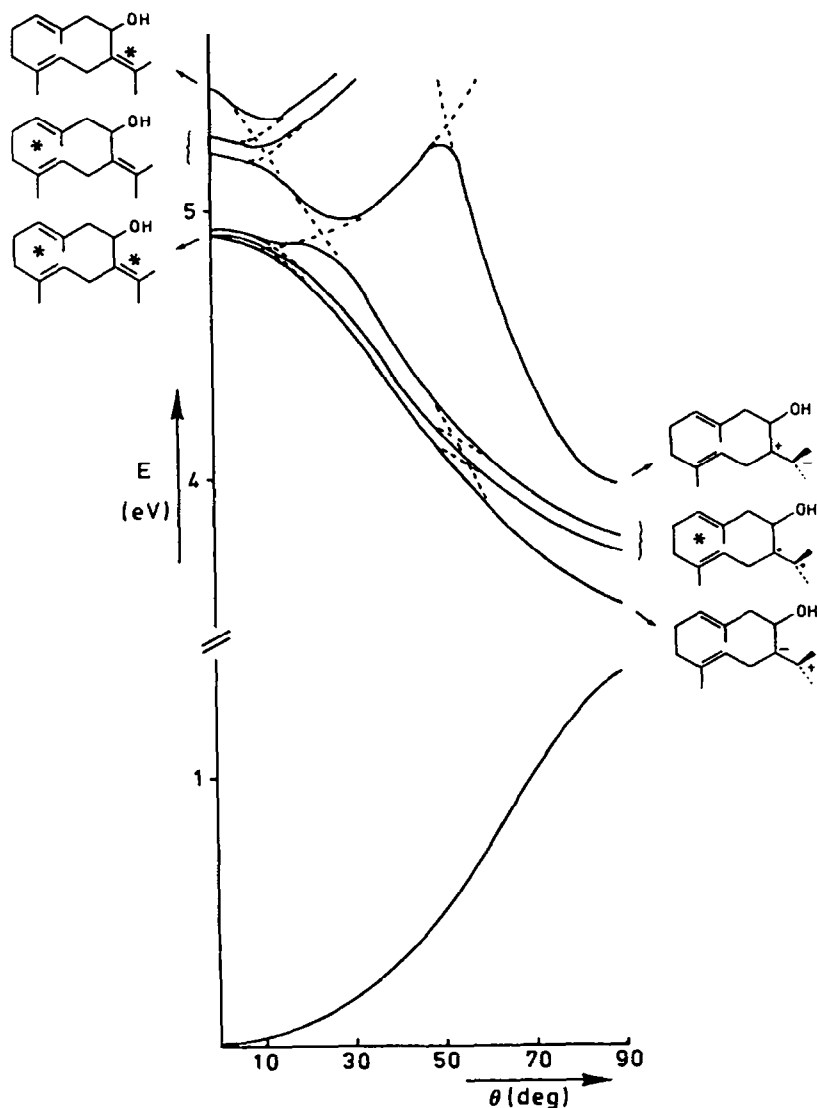


Figure 6. Potential energy curves for the rotation of the exocyclic double bond in germacrol. The localization of the excitation in a certain excited state is indicated by an asteriks.

We start the discussion with the vertical excited molecules. The distribution of the electronic excitation over the molecule can be determined by comparing the bond orders of the excited states with those of the ground state¹⁷. A decrease in bond order going from the ground to the excited state indicates that this particular bond is more antibonding (energy rich) and therefore more reactive. When the bond order remains unchanged, this bond is unaffected by the electronic excitation. Using this concept, we may qualitatively characterize the excited states of germacrol (and germacrene, which are fully comparable).

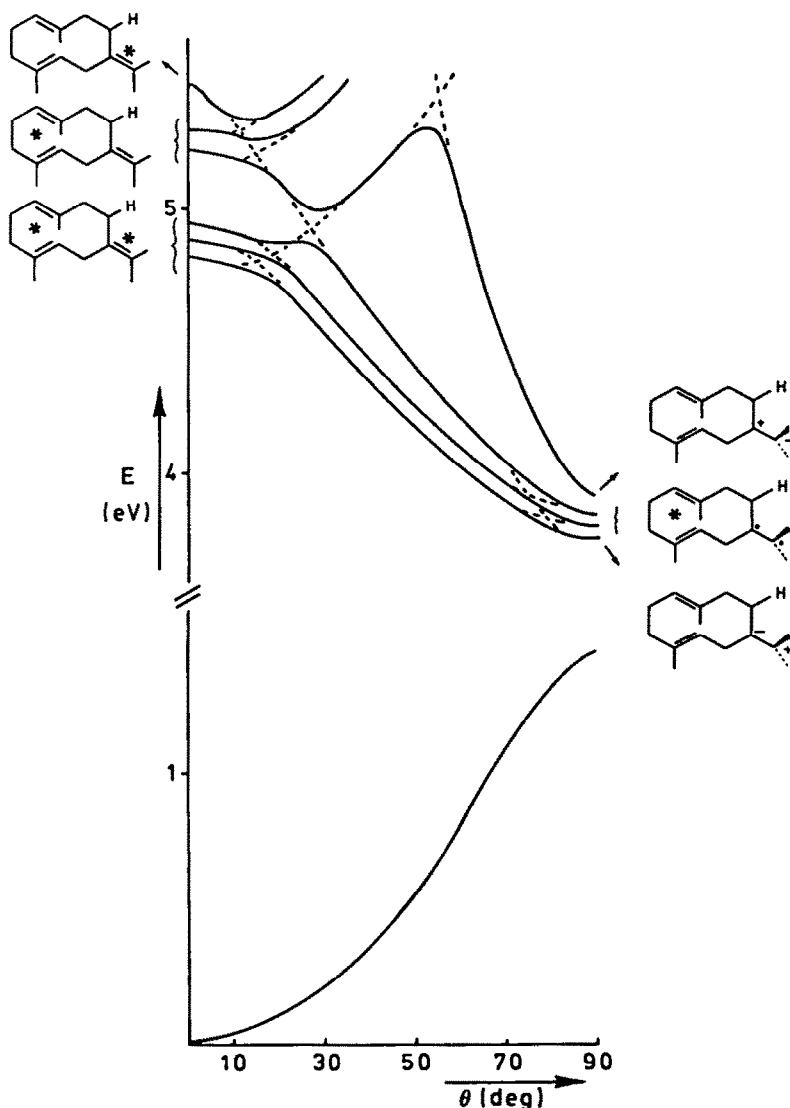


Figure 7. Potential energy curves for the rotation of the exocyclic double bond in germacrene. The localization of the excitation in a certain excited state is indicated by an asteriks.

As can be seen from Tables I and II the lowest three excited states are each excited mainly in two double bonds. The ordering of these biexcited states can be explained from the reactivity of the three double bonds due to their torsional strain. So it was found⁷ that the 4,5 double bond is more reactive than the 1,10 double bond, whereas the torsional strain for the exocyclic double bond is negligible. The energy difference between the π and π^* orbital of the 4,5 double bond is thus smallest, followed by the 1,10 and 7,11 double bonds respectively. Therefore the electronic state which involves an excitation to the endocyclic double bonds has the lowest excitation energy.

Table I. Calculated π bond orders and atomic charge densities of the lowest electronic states of germacrol.

			P _{AA} ^a						P _{AB} ^b		
θ	$ \psi_K\rangle$	$\Delta E^c(f_{osc}^d)$	C ₁	C ₁₀	C ₄	C ₅	C ₇	C ₁₁	1,10	4,5	7,11
0°	S ₀	0	-0.09	-0.15	-0.14	-0.08	-0.14	-0.12	0.91	0.91	0.91
	S ₁	4.89(0.004)	-0.06	-0.11	-0.18	-0.10	-0.19	-0.18	0.81	0.76	0.85
	S ₂	4.89(0.000)	-0.17	-0.14	-0.09	-0.02	-0.12	-0.17	0.77	0.87	0.76
	S ₃	4.93(0.001)	-0.04	-0.12	-0.21	-0.15	-0.14	-0.17	0.85	0.79	0.77
	S ₄	5.17(0.519)	-0.06	-0.16	-0.17	-0.09	-0.15	-0.13	0.91	0.80	0.85
	S ₅	5.21(0.365)	-0.05	-0.21	-0.15	-0.08	-0.15	-0.12	0.78	0.91	0.88
	S ₆	5.47(0.167)	-0.06	-0.16	-0.17	-0.07	-0.17	-0.12	0.88	0.87	0.79
90°	S ₀	1.38	-0.07	-0.15	-0.15	-0.08	-0.14	-0.16	0.91	0.91	0.81
	Z ₁	3.53	-0.09	-0.13	-0.14	-0.08	-0.71	+0.39	0.91	0.91	0.81
	D ₁	3.77	-0.24	-0.31	+0.00	+0.09	-0.14	-0.17	0.87	0.80	0.81
	D ₂	3.78	+0.09	+0.00	-0.32	-0.27	-0.14	-0.16	0.80	0.87	0.81
	Z ₂	3.98	-0.06	-0.16	-0.13	-0.09	+0.46	-0.74	0.91	0.91	0.81

^a Atomic charge density. ^b Bond order. ^c Energy difference in eV.

^d Oscillator strength.

Table II. Calculated π bond orders and atomic charge densities of the lowest electronic states of germacrene.

			P _{AA} ^a						P _{AB} ^b		
θ	$ \psi_K\rangle$	$\Delta E^c(f_{osc}^d)$	C ₁	C ₁₀	C ₄	C ₅	C ₇	C ₁₁	1,10	4,5	7,11
0°	S ₀	0	-0.07	-0.14	-0.15	-0.08	-0.10	-0.15	0.91	0.91	0.90
	S ₁	4.82(0.002)	-0.12	-0.16	-0.09	-0.11	-0.09	-0.13	0.77	0.76	0.88
	S ₂	4.88(0.000)	-0.12	-0.18	-0.13	-0.06	-0.13	-0.16	0.76	0.89	0.76
	S ₃	4.92(0.001)	-0.06	-0.12	-0.20	-0.13	-0.13	-0.16	0.88	0.77	0.76
	S ₄	5.18(0.598)	-0.05	-0.16	-0.17	-0.08	-0.10	-0.17	0.91	0.81	0.84
	S ₅	5.22(0.262)	-0.06	-0.19	-0.15	-0.08	-0.10	-0.15	0.79	0.90	0.88
	S ₆	5.47(0.189)	-0.06	-0.17	-0.17	-0.08	-0.11	-0.16	0.88	0.86	0.80
90°	S ₀	1.45	-0.07	-0.14	-0.15	-0.08	-0.13	-0.16	0.91	0.91	0.81
	Z ₁	3.79	-0.12	-0.23	+0.01	-0.10	+0.23	-0.52	0.91	0.88	0.81
	D ₁	3.81	-0.31	+0.00	+0.09	-0.04	-0.25	-0.17	0.90	0.83	0.81
	D ₂	3.82	+0.18	+0.16	-0.46	-0.40	-0.13	-0.17	0.76	0.90	0.81
	Z ₂	3.90	-0.14	-0.21	-0.16	-0.05	-0.58	+0.28	0.91	0.87	0.81

^a Atomic charge density. ^b Bond order. ^c Energy difference in eV.

^d Oscillator strength.

Of course the situation is more complicated as the various π orbitals are strongly mixed up at the MO level. This is why the wavefunctions are built up from several configurations with large coefficients. The fact that these states are biexcited species explains why the oscillator strengths for these transitions are negligible (see Tables I and II).

On the other hand, the next three excited states are predominantly described by a single excitation into one particular double bond and are therefore photoactive. The energy ordering can again be explained from the reactivity of the three double bonds. The calculated absorption spectrum starts at about $\lambda = 238$ nm (5.2 eV, see Tables I and II) for both molecules, in reasonable agreement with the observed absorption maximum at $\lambda = 245$ nm.

The behaviour of an excited state upon twisting the exocyclic double bond is directly related to its bond order. For those states in which this value is near to the ground state value of 0.90 (S_1 , S_4 and S_5) this double bond has no anti-bonding character and a rotation is highly unfavourable. These electronic states therefore show a strong increase in energy (indicated by the dashed lines in Figures 6 and 7) comparable with that of the ground state.

For S_2 and S_3 the electronic excitation is distributed partly in one endocyclic double bond and partly in the exocyclic double bond. In this case the twisting results in a decrease of the potential energy. For S_6 the excitation is located merely in the exocyclic double bond and for this configuration twisting leads to a strong decrease in energy, thereby crossing the energy curves of the lower excited states (see Figures 6 and 7).

However, due to avoided crossings the excited molecule does not follow these diabatic curves (dashed lines) but the adiabatic curves (full lines, these are in fact the calculated potential curves). From these curves it is seen that the molecule would never reach the 90° twisted structure without passing a potential barrier when it is excited to one of the states bearing oscillator strength.

The situation however is more complicated as the Born Oppenheimer approximation becomes less valid in regions where the adiabatic curves come close in energy. In this particular case, the nonadiabatic coupling (g_{KL}) between two electronic wavefunctions ($|\psi_K\rangle$ and $|\psi_L\rangle$) is induced by the operator $\partial/\partial\theta$, where θ is the twisting motion around the excited double bond of the molecule:

$$g_{KL} = \langle \psi_K | \frac{\partial}{\partial \theta} | \psi_L \rangle$$

The value of g_{KL} is a measure for the transfer of population from one electronic state to another¹⁸. In regions where g_{KL} is large and ΔE_{KL} is small, the lower electronic state becomes rapidly populated (within fractions of picoseconds¹⁹). In this case the molecule merely follows the diabatic curve rather than the adiabatic curve.

We have calculated these nonadiabatic couplings for the twist of the exocyclic double bond using the method of finite differences, which is described in detail elsewhere²⁰. The stepsize for the numerical procedure was $\Delta\theta = 0.02^\circ$. A selection of the coupling curves for both germacrol and germacrene is presented in Figure 8. As can be seen from this figure, the nonadiabatic couplings are indeed very large (several au^{-1}) in regions where the adiabatic curves show an avoided crossing.

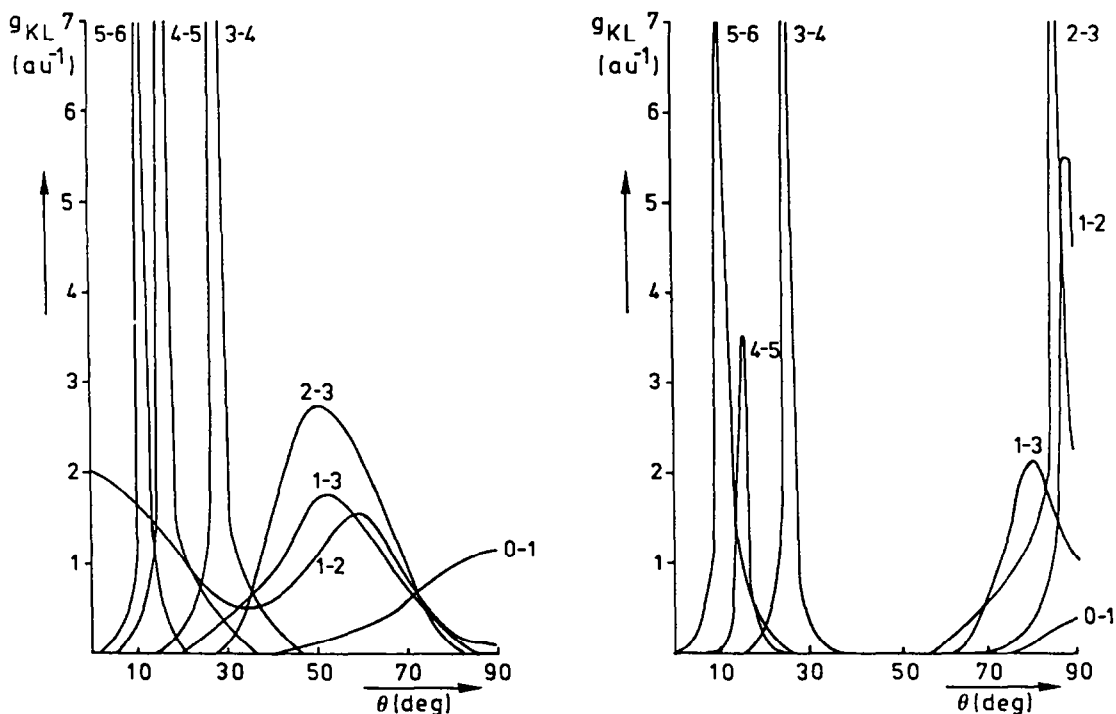


Figure 8. Selection of the nonadiabatic coupling curves for rotation of the exocyclic double bond of germacrol (left hand side) and germacrene (right hand side).

The dynamics of the excited molecule can now be described as follows. The molecule is excited to one of the states S_4 , S_5 or S_6 , of which the former two induce an increased reactivity in the endocyclic part of the molecule. These states might lead to E-Z isomerization or other photochemical reactions of these double bonds. Due to the constraints of the ring it is expected that these reactions demand a certain activation energy. On the other hand, an E-Z isomerization of the exocyclic double bond is very feasible as the diabatic curve for this motion monotonically decreases till $\theta = 90^\circ$. Even in the case of a rapid internal conversion to the lower singlet excited states, their energy curves show that the 90° twisted structure can be reached.

So far, the situation is comparable for germacrol and germacrene. The main differences arise in the 90° region. They are a direct result of the presence of the hydroxyl group in germacrol. The perturbing effect of this substituent on the stability of the two zwitterionic states (Z_1 and Z_2) is larger than for the hydrogen atom in germacrene. Consequently, the energy splitting between these two states is larger (0.46 eV in germacrol, 0.11 eV in germacrene). The lowest excited state at $\theta = 90^\circ$ for germacrol is the one with a positively charged exocyclic carbon atom. The situation is reversed in germacrene (see Tables I and II).

For both molecules there are two diradicalar states (D_1 and D_2) which lie in between the two zwitterionic states. For germacrene these four states not only lie in an interval of only 0.11 eV but their mutual nonadiabatic couplings are very large as well (see Figure 8). The properties (e.g. polarization) of these states are therefore strongly mixed. For germacrol the energy splitting between Z_1 and D_1 is 0.24 eV and the coupling is small (see Figure 8). Therefore at least the

lowest vibrational level of Z_1 will show the properties of this electronic configuration: a polarization which is favourable for a planar [1,3]-OH shift i.e. a negative charge at the central carbon atom C_7 and a positive charge at the terminal carbon atom C_{11} .

The nonadiabatic coupling between Z_1 and the ground state is in the order of 1 au^{-1} . From this value it may be concluded that the molecule will not convert directly to the ground state potential curve once the twisted conformation is reached^{11,18b,19}. It will start to oscillate in this minimum thereby having a certain probability for a radiationless transition to the ground state in competition with the photochemical [1,3]-OH shift. We estimated the activation energy for this shift in the order of 17 kcal/mol which is less than the increase of kinetic energy obtained from the twisting of the double bond (approximately 35 kcal/mol). The estimated activation energy for a planar [1,3]-H shift was calculated to be twice as large (35.5 kcal/mol). The top of the energy barrier for this shift in germacrene will lie above the level of the vertical excited molecule. This makes this reaction rather unlikely to occur.

Looking at the charge densities of the twisted diradical states (Tables I and II), a redistribution of the charges in the two endocyclic double bonds is found. The charges at the carbon atoms of the anti-bonding double bond become more positive whereas a more negative character of the carbon atoms of the other endocyclic double bond is perceptible. This is a situation which is eminently suited for an intramolecular bond formation in this part of the molecule. These twisted diradical states can thus be seen as precursors for the observed photoproducts of germacrene.

Acknowledgements

This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

References and notes

- 1 P.J.M. Reijnders, H.M. Buck, *Recl. Trav. Chim. Pays-Bas*, **97**, 263 (1978).
- 2 P.J.M. Reijnders, R.G. van Putten, J.W. de Haan, H.N. Koning, H.M. Buck, *Recl. Trav. Chim. Pays-Bas*, **99**, 67 (1980).
- 3 H.R. Franssen, H.M. Buck, *J. Chem. Soc. Chem. Commun.*, 786 (1982).
- 4 H.R. Franssen, G.J.M. Dormans, G.J. Bezemer, H.M. Buck, *Recl. Trav. Chim. Pays-Bas*, **103**, 115 (1984).
- 5 U. Jacobsson, T. Norin, M. Weber, *Tetrahedron*, **41**, 2033 (1985).
- 6 P.M. Ivanov, N.V. Bozhkova, A.S. Orahovats, *J. Mol. Struct. (Theochem)*, **86**, 393 (1982).
G.D. Neykov, N.V. Bozhkova, A.S. Orahovats, *J. Mol. Struct. (Theochem)*, **90**, 279 (1982).
- 7 H.R. Franssen, G.J.M. Dormans, H.M. Buck, *Tetrahedron*, **39**, 2981 (1981).
H.R. Franssen, Thesis, Eindhoven University of Technology (1983).
- 8 The prefix SSS denotes the planar chirality of the 4,5; 1,10 and 7,11 double bonds respectively, according to Prelog's rules of planar chirality: R.S. Cahn, C. Ingold, V. Prelog, *Angew. Chem.*, **78**, 413 (1966).
- 9 F.H. Allen, D. Rogers, *J. Chem. Soc. (B)*, 257 (1971).
- 10 G.J.M. Dormans, H.R. Franssen, H.M. Buck, *J. Am. Chem. Soc.*, **106**, 1213 (1983).

- 11 G.J.M. Dormans, W.J.G.M. Peijnenburg, H.M. Buck, *J. Mol. Struct. (Theochem)*, **119**, 367 (1985).
G.J.M. Dormans, H.M. Buck, *J. Mol. Struct. (Theochem)*, **136**, 121 (1986).
- 12 V. Bonačić-Koutecký, P. Bruckmann, P. Hiberty, J. Koutecký, C. Leforestier, L. Salem, *Angew. Chem. Int Ed. Eng.*, **14**, 575 (1975).
L. Salem, *Acc. Chem. Res.*, **12**, 87 (1979).
- 13 Z stands for Zwitterionic, whereas the Diradicalar states are denoted by a D.
- 14 W.J.G.M. Peijnenburg, H.M. Buck, to be published.
- 15 W.J.G.M. Peijnenburg, G.J.M. Dormans, G.J. Bezemer, H.M. Buck, *Tetrahedron*, **40**, 4959 (1984).
- 16 W.J.G.M. Peijnenburg, unpublished results.
- 17 This approach is known as the ΔP matrix concept which was first introduced by Zimmerman and co-workers. See e.g.:
H.E. Zimmerman, W.T. Gruenbaum, R.T. Klun, M.G. Steinmetz, T.R. Welter, *J. Chem. Soc. Chem. Commun.*, 228 (1978).
H.E. Zimmerman, M.G. Steinmetz, *J. Chem. Soc. Chem. Commun.*, 230 (1978).
H.E. Zimmerman, *Acc. Chem. Res.*, **15**, 312 (1982).
- 18a J.C. Tully in "Dynamics of Molecular Collisions", ed. W.H. Miller (Plenum Press, New York, 1976), part B, p. 217.
R.M. Weiss, A. Warshall, *J. Am. Chem. Soc.*, **101**, 6131 (1979).
- 18b M. Persico, *J. Am. Chem. Soc.*, **102**, 7839 (1980).
M. Persico, V. Bonačić-Koutecký, *J. Chem. Phys.*, **73**, 6018 (1982).
- 19 G.J.M. Dormans, G.C. Groenenboom, H.M. Buck, *J. Chem. Phys.*, **86**, 4895 (1987).
- 20 C. Galloy, J.C. Lorquet, *J. Chem. Phys.*, **67**, 4672 (1977).
C. Hirsh, P.J. Bruna, R.J. Buenker, S.D. Peyerimhoff, *Chem. Phys.*, **45**, 335 (1980).
R. Cimraglia, M. Persico, J. Tomasi, *Chem. Phys.*, **53**, 357 (1980).