The Photochemical Formation of Fulvene from Benzene via Prefulvene— A Theoretical Study

Jens Dreyer and Martin Klessinger*

Dedicated to Professor Roy McWeeny on the occasion of his 70th birthday

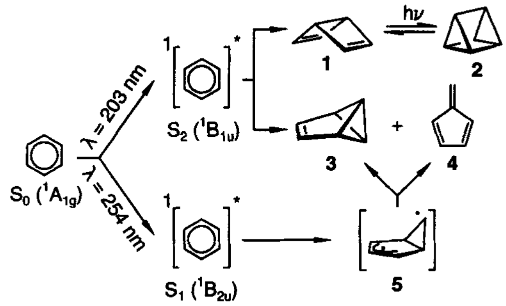
Abstract: Results of semiempirical MNDOC-CI and ab initio CASSCF calculations reveal that fulvene is a primary product of the photolysis of benzene. The photochemical step is assumed to lead to prefulvene, and both a synchronous conversion and a two-step process via bicyclo[3.1.0]hexa-1,3-diene (isofulvene) could be ruled out as possible pathways from prefulvene to benzene. The most probable mechanism for the photochemical isomerization of benzene to fulvene involves the intermediate structures prefulvene and 1,3-cyclopentadienylcarbene and has to compete with the almost barrierless formation of benzvalene and rearomatization to benzene. The short-lived intermediates are rather flexible structures with negligible barriers to inversion at the radical center in the three-membered ring of prefulvene and prebenzvalene and to rotation around the exocyclic single bond in 1,3-cyclopentadienylcarbene.

Keywords
ab initio calculations · benzene · fulvene · isomerization · photochemistry

Introduction

Valence isomers of benzene have attracted much attention in experimental[1-5] as well as theoretical studies.[6-10] While the photochemical formation of dewarbenzene (**1**), prismane (**2**) and benzvalene (**3**) has been studied recently by detailed quantum chemical calculations,[7-10] an investigation of the reaction mechanism for the photochemical formation of fulvene is still lacking. We therefore carried out a combined semiempirical MNDOC-CI (modified neglect of differential overlap plus configuration interaction) and ab initio CASSCF (complete active space self-consistent field) study of different possible reaction pathways as part of our examination of ground and excited states of fulvene and of its photochemical reactivity.[11]

Before going into more detail we briefly mention some experimental and theoretical data on photochemical valence isomerizations of benzene, which are wavelength-dependent singlet reactions as shown in Scheme 1.[12] The first excited singlet state ($^1B_{2u}$) gives benzvalene (**3**) and fulvene (**4**), but no dewarbenzene (**1**).[13-16] In the liquid phase the second excited singlet state ($^1B_{1u}$) leads to the formation of dewarbenzene (**1**) in addition to benzvalene (**3**) and fulvene (**4**),[17] while in the vapor phase only fulvene (and the open chain isomers *cis*- and *trans*-hexa-1,3-diene-5-yne) could be detected.[18-20] It has been suggested that the benzene valence isomers are formed as hot molecules in the liquid as well as in the gas phase.[2] In the liquid phase the excess vibrational energy can be dissipated, whereas in the vapor phase dewarbenzene and benzvalene rearomatize to benzene, and only the thermodynamically more stable fulvene remains. Prismane (**2**) is not produced directly but rather results from an intramolecular [2+2] photocycloaddition of dewarbenzene.[7,21] Although no experimental evidence is available for the existence of transient species in the S_1 photochemistry of benzene, theoretical investigations clearly show that a biradicaloid intermediate called prefulvene (**5**) plays an important role in the formation of benzvalene.[8-10] On the basis of CASSCF/4-31G calculations, Palmer et al. characterized the C_s-symmetric prefulvene structure on the S_0 surface as a transition state connecting two slightly distorted structures named prebenzvalene.[8] The CASSCF/3-21G study of Sobolewski et al.,[9] who considered the benzene–prefulvene interconversion, confirmed these results, although prefulvene was characterized as a minimum structure.



Scheme 1. Photochemical valence isomerizations of benzene.

Conical intersections have been shown in recent years to be common features in nonadiabatic singlet photoreactions.[12,22] This is also true for benzene valence isomerizations: according to recent calculations[8-10] the S_1 (B_{1u}) reaction path from benzene towards prefulvene starts at an excited state minimum with

---

[*] Prof. Dr. M. Klessinger, Dr. Jens Dreyer
Institut für Organische Chemie der Westf. Wilhelms-Universität
Corrensstrasse 40, D-48149 Münster (Germany)
Fax: Int. code +(251)83-9772
e-mail: klessim@uni-muenster.de

D_{6h} symmetry, proceeds over a transition state to an S_1-S_0 conical intersection, and continues on the S_0 surface from the prefulvene geometry mostly back to benzene, but in part on to benzvalene. This mechanism also provides a very plausible explanation for the channel-three phenomenon of benzene.[8, 9] The conversion of benzene into dewarbenzene proceeds from the S_2 state (at vertical geometries this is $^1B_{1u}$ but it soon acquires the character of the E_{2g} state as motion along the reaction path occurs). Calculations suggest that the molecule moves downhill on the S_2 surface to an S_2-S_1 conical intersection and reaches the S_1 surface at the S_1-S_0 conical intersection region that provides further immediate conversion to the S_0 state. The geometry at which the stacked conical intersections are located is calculated to be such that relaxation in S_0 can produce dewarbenzene, benzvalene or benzene.

It has been proposed that fulvene is formed either directly from prefulvene or by secondary isomerization from benzvalene.[2] The benzvalene pathway is supported by the fact that photolysis of benzene initially yields fulvene at a slower rate than benzvalene[14] and that benzvalene is converted into fulvene by quartz catalysis.[15] It has also been suggested that acid-catalyzed rearrangement of benzvalene yields fulvene.[17] On the other hand, rearomatization[14, 23] and, in contrast to an earlier study,[15] photolysis[5] of benzvalene have been shown to yield only benzene and no fulvene. Prefulvene was therefore assumed to be the precursor.[25, 26] More recent matrix photolysis experiments suggest that indeed benzvalene and fulvene are both primary products, although the possibility of secondary isomerization could not be definitely excluded.[24] The actual reaction mechanism leading to fulvene is still unknown. Here we report our investigations of the direct isomerization via prefulvene, which seems to be more likely since prefulvene is a highly reactive transient species and activation barriers towards isomerization are believed to be lower than barriers starting from benzvalene. Nevertheless, the benzvalene pathway is being studied as well; results will be presented elsewhere.[27]

Computational Methods

In order to ensure an economic use of computer time, the semiempirical MNDOC-CI method [28], which is well-suited for investigating open-shell systems, excited states, and photochemical reaction mechanisms [11], was used to calculate potential energy hypersurfaces. Geometry optimizations were performed and the results together with approximate transition state geometries taken from the potential hypersurfaces served as initial guesses for more accurate ab initio calculations. Since semiempirical and ab initio geometries turned out to be in good agreement, only ab initio results are reported for the stationary points.

The MNDOC-CI calculations may be characterized as follows. For each state under consideration, one or a few reference configurations were used, and from these reference configurations single and double excitations within a properly chosen active space (AS) were considered in constructing spin-adapted configuration state functions (CSFs). In order to specify the active space and the reference configurations, the occupied ground state orbitals are numbered 1, 2, ... starting at the HOMO, while the virtual orbitals are numbered 1′, 2′, ... starting at the LUMO. Up to 200 CSFs were considered for configuration interaction (CI). If the active space had to be chosen such that not all singly and doubly excited configurations could be included, the CI was further truncated by the use of excitation indices (EI) m,n, which specify the largest single and double excitations to be included; for singly and doubly excited configurations $\Phi_{i\rightarrow k}$ and $\Phi_{i\rightarrow k}^{j\rightarrow l}$ the excitation indices are $(k-i)$ and $[(k-i)+(l-j)]$, respectively. The truncation of the CI leads to inaccuracies in the calculated heats of formation, but yields reliable geometries and, most importantly, comparable accuracies for the ground state and the various excited states [28].

Ab initio CASSCF calculations were accomplished using the GAUSSIAN 92 [29] and MOLPRO [30] program systems. All stationary points were located and characterized as minima or transition states by vibrational analyses using GAUSSIAN 92 and the 3-21 G basis set [31]. Natural orbitals (NO) generated from the total density of a previous UHF calculation were used as initial orbitals. An AS of three occupied and three unoccupied orbitals (six orbitals and six electrons) resulting in 175 CSFs turned out to be suitable for all calculations. In order to estimate basis-set effects, single-point calculations using the 6-31 G + (d,p) basis set [32] were carried out at all 3-21 G-optimized geometries. MOLPRO, which does not provide the possibility of vibrational analysis, was used to calculate the potential energy surfaces for the reaction benzene–prefulvene and excitation energies of the intermediates isofulvene and 1,3-cyclopentadienylcarbene using the DZ basis set [33]. These calculations are dubbed CAS/DZ. Active and closed orbitals were chosen for each irreducible representation of the point group under consideration and are quoted as $n[n(A')n(A'')]$ for C_s, where n refers to the total number of either closed or active orbitals and $n(\Gamma)$ gives the number of orbitals of irreducible representation Γ. The CI wavefunctions are reported in terms of pseudocanonical orbitals.

Results and Discussion

Photoisomerization of benzene to fulvene via prefulvene involves the photochemical step from benzene to prefulvene and the subsequent thermal conversion of prefulvene to fulvene including a [1,2] H shift and the breaking of one CC bond. The photochemical step will be described first, whereas possible reaction pathways from prefulvene to fulvene will be presented in the following sections. The energies of all computed structures are collected in Table 1.

Table 1. Total energies E_{3-21G} and E_{6-31G} in Hartree (1 Hartree = 627.5095 kcal mol^{-1}), relative energies E_{rel} in kcal mol^{-1} with respect to benzene S_0, and dipole moments μ in D for all stationary points (MIN = minimum, TS = transition state, CI = conical intersection; state label, symmetry and point group are also indicated).

Stationary Point				E_{3-21G} [a]	$E_{rel.}$	E_{6-31G} [b]	$E_{rel.}$	μ
benzene	MIN	$S_0\ (A_{1g})$	D_{6h}	– 0.4942	0.0	– 0.7933	0.0	0.0
benzene S_1 (vert.)		$S_1(B_{2u})$	D_{6h}	– 0.3037	119.5	– 0.6099	115.1	0.0
benzene S_1 (adiab.)	MIN	$S_1(B_{2u})$	D_{6h}	– 0.3155	121.1	– 0.6183	109.8	0.0
benzene prefulvene [c]	TS	$S_1(A'')$	C_s	– 0.2407	–	–	–	–
conical intersection [c]	CI	S_1/S_0	C_1	– 0.2368	–	–	–	–
prefulvene (*down*)	TS	$S_0\ (A'')$	C_s	– 0.2980	123.1	– 0.6124	113.5	0.7
	MIN	$T_1\ (A'')$	C_s	– 0.3044	119.1	– 0.6065	117.2	0.6
prefulvene (*up*)	MIN	$S_0\ (A'')$	C_s	– 0.3019	120.7	– [f]	–	0.6
	MIN	$T_1\ (A'')$	C_s	– 0.3051	118.7	– 0.6114	114.1	0.5
prebenzvalene (*down*)	MIN	S_0	C_1	– 0.3031 [d]	119.9	– 0.6121	113.7	0.7
	MIN	T_1	C_1	– 0.3048	118.8	– 0.6117	114.0	0.7
prebenzvalene (*up*)	MIN	S_0	C_1	– 0.3018	120.7	– 0.6076	116.5	0.6
	MIN	T_1	C_1	– 0.3052	118.6	– 0.6145	116.8	0.5
TS 1 (prefulvene–isofulvene)	TS	S_0	C_1	– 0.2285	166.7	– 0.5433	156.9	2.4
isofulvene	MIN	S_0	C_1	– 0.3445	93.9	– 0.6556	86.4	1.1
TS 2 (isofulvene–fulvene)	TS	S_0	C_1	– 0.3432	94.8	– 0.6524	88.4	1.1
TS 3 (prefulvene–carbene)	TS	S_0	C_1	– 0.2903	127.9	– 0.5998	121.4	1.8
1,3-cyclopentadienylcarbene								
inward	MIN	S_0	C_1	– 0.3051	118.7	– [f]	–	2.3
inward (0°)	TS	$S_0\ (A')$	C_s	– 0.3045	119.0	– 0.6140	112.5	1.9
outward	MIN	S_0	C_1	– 0.3018	120.7	– 0.6143	112.3	1.9
outward (180°)	TS	$S_0\ (A')$	C_s	– 0.2989	122.6	– [f]	–	1.6
inward–outward	TS	S_0	C_1	– 0.3009	121.3	– 0.6117	114.0	1.8
TS 4 (carbene–fulvene)	TS	S_0	C_1	– 0.2802	134.3	– 0.6036	119.0	3.3
fulvene	MIN	$S_0\ (A_1)$	C_{2v}	– 0.4301 [e]	40.2	– 0.7365	35.6	0.4

[a] 3-21 G energies relative to –229.0000 Hartree. [b] 6-31 + G(d,p)/3-21 G energies relative to –230.0000 Hartree. [c] Ref. [8]. [d] 3-21 G/STO-3 G. [e] Ref. [11], 3-21 G/DZ. [f] No convergence.

Benzene to prefulvene: As the singlet photochemical conversion of benzene to prefulvene has recently been described in detail,[8–10] in Figure 1 we present for this first step of the reaction only the CAS/DZ potential energy hypersurfaces that were obtained for the lowest two singlet states and the lowest two triplet

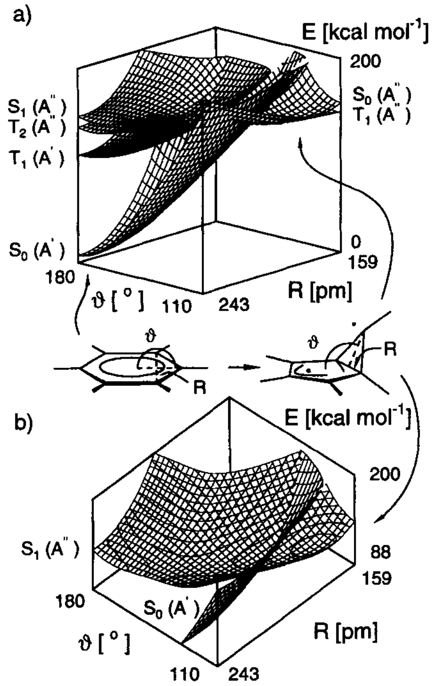


Fig. 1. The photochemical conversion of benzene to prefulvene. CAS/DZ potential energy hypersurfaces with the C1–C5 distance R and the interplanar angle ϑ as coordinates: a) the lowest singlet and triplet A' und A'' surfaces; b) singlet A' and A'' surfaces only. All C–C bond distances and C-C-C bond angles as well as all bond and dihedral angles involving H1, H5 and H6 are linearly interpolated. (Symmetry C_s; closed: 19 [12 7]; active: 4 [2 2]; A': 12 CSFs, A'': 14 CSFs; state-averaged method).

states by plotting the energy as a function of the interplanar angle ϑ and the C1–C5 distance R. Since C_s symmetry is assumed, the states are labeled $^1A'$, $^1A''$ and $^3A'$, $^3A''$, respectively. From Figure 1a it is seen that at benzene geometries the triplet states lie energetically between the two singlet states, while in the prefulvene region the $^3A''$ surface is below the $^1A''$ surface. Full geometry optimization confirmed the ground state of prefulvene to be in fact the $^3A''$ state (Table 1). In Figure 1b only the singlet surfaces involved in the photochemical conversion are shown from a slightly different point of view. From the spectroscopic S_1 minimum of benzene ($^1B_{2u}$ in D_{6h}) near the left-hand corner, the S_0 minimum of prefulvene ($^1A''$ in C_s) at the right-hand corner of the diagram is reached over a small barrier and through a conical intersection. In this diagram the (F-2)-dimensional intersection space[34] appears as a line. Optimization of the stationary points (energies and dipole moments in Table 1, geometries in Fig. 2) confirm this picture.

At the semiempirical level, vibrational analysis confirmed the C_s-symmetric prefulvene geometry as a minimum structure, in agreement with the CAS/3-21G results reported in ref. [9]. For the CAS/3-21G-optimized geometry, however, we obtained one imaginary frequency (380i cm^{-1}) corresponding to an out-of-plane distortion of the five-membered ring, in agreement with results of ref. [8]. Relaxation of the C_s symmetric structure produces a slightly distorted C_1-symmetric structure that has been termed prebenzvalene.[8] We could locate this geometry only using the STO-3G basis set, while optimizations with larger basis sets led to benzvalene after a short stay on a plateau corresponding to prebenzvalene geometries. Although the energy of the optimized prefulvene structure given in Table 1 agrees well with a literature value (– 229.29958 Hartree[9]), we find a shorter C1–C5 bond and correspondingly longer adjacent C–C bonds of the cyclopropane ring. This discrepancy results from the fact that, depending on the choice of the initial orbitals and the CI parameters described in the Methods section, the C1–C5 antibonding σ^* MO is included in the calculations reported in ref. [9], but not in ours, although the size of the active space is the same. A larger active space would be needed for an unambiguous determination of the geometry.

In prefulvene as well as in prebenzvalene the radical center of the three-membered ring is nonplanar, leading to two different conformations with H6 in either a down or an up position (cf. Scheme 2).[35] According to our 3-21G results the *up* conformer in prefulvene (C_s) is more stable than the *down* form by 2.4 kcal mol^{-1}. The barriers between the two conformers are lower than 3 kcal mol^{-1}, in agreement with the RHF value of 3.5 kcal mol^{-1} reported for a C_s geometry.[35] The *up* conformer of prefulvene and both conformers of prebenzvalene are calculated to be true minima, while the *down* form of prefulvene corresponds to a transition state. The conformational flexibility at C6 of these biradicaloid intermediates plays a role in the isofulvene mechanism discussed in the following section. The triplet ground state geometries (cf. Table 1 for energies and dipole moments) are nearly identical with the singlet geometries, as is to be expected from the similarity of the CI wavefunctions. The contribution of the biradical configuration $1^11'^1$ is larger than 85% in all singlet and triplet states considered here.

Prefulvene–fulvene pathways: In order to discover possible reaction pathways and intermediate structures for the interconversion of prefulvene and fulvene, a partially optimized MNDOC-CI singlet ground state surface was computed using the [1,2] H shift as one of the coordinates, and the combined CC bond-breaking and planarization as the other. The result is presented in Figure 3 and shows that a concerted isomerization of prefulvene to fulvene is extremely unlikely. Instead, the minimum at

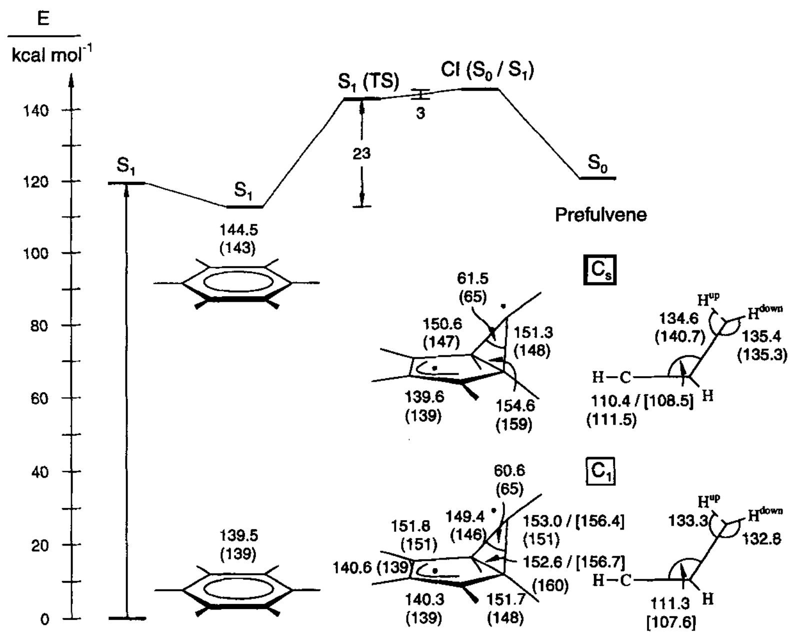


Fig. 2. The photochemical conversion of benzene to prefulvene. 3-21G and 6-31G+(d,p) energy differences in kcal mol^{-1}, the latter in parentheses. 3-21G optimized geometries (in pm and degrees) are shown for the *down* form with literature values [8,9,34] in parentheses and some distinct values for the *up* form in brackets. (TS = transition state, CI = conical intersection).

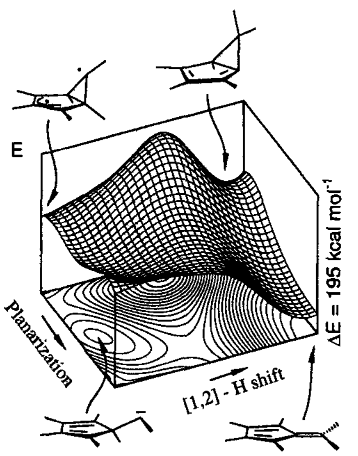
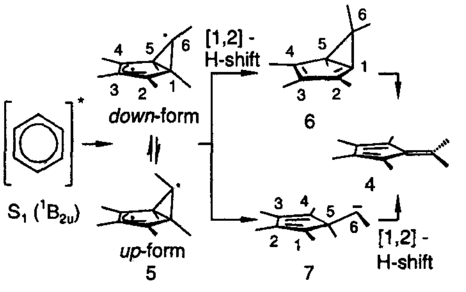


Fig. 3. MNDOC-CI potential energy hypersurface (S_0) for the conversion of prefulvene to fulvene. All geometric parameters are optimized except CH bond distances other than that of the migrating hydrogen and dihedral angles of the planar ring. (AS: 3-3', EI: 5,10; reference configuration 2^21^2; 55 CSFs).

the left-hand front edge of the diagram suggests the occurrence of 1,3-cyclopentadienylcarbene (**7**) as an intermediate in the reaction. The minimum at the rear corner, which represents bicyclo[3.1.0]hexa-1,3-diene (isofulvene, **6**), could correspond to another possible intermediate, if there exists a favorable reaction path behind the maximum that is not included in the surface shown in the diagram. Therefore, two reaction pathways may be formulated, as indicated in Scheme 2. Detailed computational results for the "isofulvene mechanism" corresponding to a pathway from prefulvene to fulvene via **6** and for the "carbene mechanism" via **7** will be discussed in the following sections.



Scheme 2. Possible mechanisms for the photochemical conversion of benzene to fulvene.

Isofulvene mechanism: The isofulvene mechanism involves a [1,2] H shift to yield isofulvene from prefulvene or prebenzvalene and subsequently an opening of the three-membered ring to form fulvene. MNDOC-CI singlet ground state surfaces have been calculated for both steps. In Figure 4 the transformation of prefulvene to isofulvene is shown for the coordinates R_{C1-X} and R_{X-H1} defined in Scheme 3. Owing to the low inversion barrier for the radical center at C6 the [1,2] H shift may start either from the *down* or from the *up* form of prefulvene. The transition state TS1 in the middle of the surface between the prefulvene and isofulvene minima is fairly high in energy, but the barrier is somewhat lower than that for C–H bond dissociation near the front corner of the diagram (large R_{X-H1}).

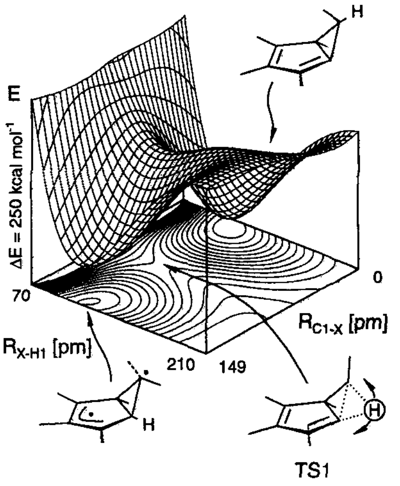
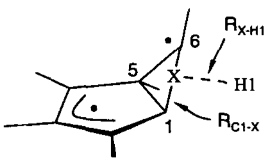


Fig. 4. MNDOC-CI potential energy hypersurface for the [1,2] H shift from prefulvene to isofulvene. The H1-X-C6-C5 dihedral angle and the bond and dihedral angles involving H6 are optimized, C–C bond distances and C-C-C angles are linearly interpolated. (AS: 3-3'; EI: 6,10; reference configuration 2^21^2; 55 CSFs).



Scheme 3. Definition of geometric parameters for the conversion of prefulvene to isofulvene.

Figure 5 shows the MNDOC-CI surface for the final step from isofulvene to fulvene, with the interplanar angle α and the rotation angle φ of the exocyclic CH_2 group as coordinates. In this diagram the reaction proceeds from the front corner on the right to the rear corner on the left. The transition state TS2 is located near the isofulvene minimum, and the barrier is low. CAS/3-21G geometry optimizations of all stationary points on these surfaces were carried out. Energies and dipole moments are collected in Table 1, geometries and relative energies are shown in Figure 6. The results fully confirm the semiempirical calculations. At TS1 between prefulvene and isofulvene the migrating hydrogen has moved halfway and forms a three-center bond with C1 and C6 with a long C1–C6 bond. It remains on the *exo* face, while H6 assumes the up position on the *endo* face of the three-membered ring, thus indicating a suprafacial [1,2] H shift. Houk et al. showed that the bond lengths of partially formed C–H bonds range from 129 to 161 pm.[36] The values 135.6 and 136.2 pm for the C–H distances at TS1 fall into the lower region of this range. The double bonds of the five-membered ring are already formed. The normal mode with a rather high imaginary frequency (1728 i cm⁻¹) corresponds to the hydrogen-shift motion. 3-21G and 6-31+G(d,p) calculations yield values of 46.8 kcal mol⁻¹ and 43.4 kcal mol⁻¹, respectively, for the activation barrier between prefulvene and the transition state. This barrier is obviously too high for a realistic reaction path.

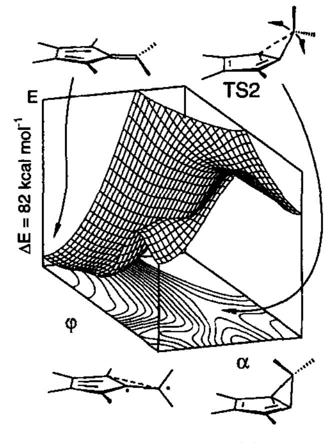


Fig. 5. MNDOC-CI potential energy hypersurface for the conversion of isofulvene (right front corner) to fulvene (left rear corner). All C–C bond lengths, C-C-C and H-C-C angles, and H dihedral angles are optimized. (AS: 4-3'; EI: 6,10; reference configuration: 2^21^2; 176 CSFs).

Isofulvene, which is confirmed by vibrational analysis to be a minimum structure, has two more-or-less localized double bonds and is approximately a closed-shell molecule with the ground configuration contributing 86.5% to the CI wavefunction. The closed-shell character is confirmed by the occupation numbers of the natural orbitals, which are 1.81 for the HOMO and 0.19 for the LUMO. CAS/DZ excited-state wavefunctions, excitation energies, and oscillator strengths *f* for isofulvene are given in Table 2 and might be useful in the interpretation of ultrafast transient absorption spectroscopy experiments. These data show the HOMO–LUMO transition ($S_0 \rightarrow S_2$) to be allowed. Since ab initio CASSCF excitation energies are in general too high, unless a large amount of dynamic correlation is

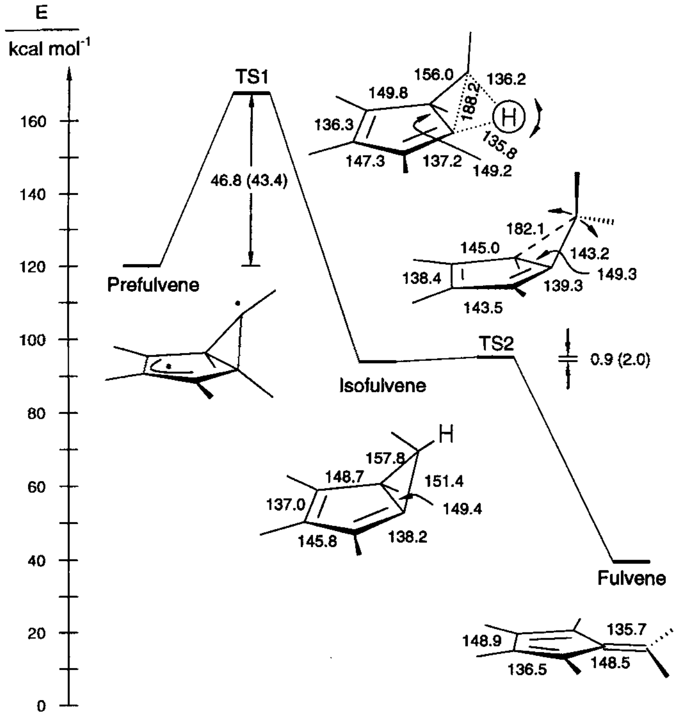


Fig. 6. The isofulvene mechanism of the conversion of prefulvene to fulvene. 3-21 G and 6-31 G+(d,p) energy differences in kcal mol^{-1}, the latter in parentheses, and 3-21 G optimized geometries in pm and degrees. (TS = transition state).

Table 2. Isofulvene: CAS/DZ results for vertical singlet excitation energies (in eV) and oscillator strengths *f*.

	Configuration [a]	CAS/DZ [b]	*f*
S_0	$2^2 1^2$	0.0	–
S_1	$2^1 1^2 1'^1$ $2^2 1^1 2'^1$	4.9	0.004
S_2	$2^2 1^1 1'^1$	6.3	0.190
S_3	$2^1 1^2 1'^1$ $2^2 1^1 2'^1$ $3^1 2^2 1^2 1'^1$	6.7	0.008

[a] Principal configurations contributing to the wavefunction. [b] Closed: 18; active: 6; 175 CSFs; state-averaged method.

taken into account by perturbation theory or multireference CI corrections,[37] the actual excitation energies are assumed to be somewhat lower than the calculated values.

The transition structure TS 2 between isofulvene and fulvene is similar to isofulvene itself, except that the C5–C6 bond is essentially broken and the CH_2 group has moved slightly towards its position in fulvene. The vibration with imaginary frequency (229 i cm^{-1}) corresponds to such a combined planarization and twist motion leading from isofulvene to fulvene. Calculated values for the energy barrier are 0.9 (3-21 G) and 2.0 kcal mol^{-1} (6-31 G+(d,p)), respectively, and confirm the RHF results of Merz and Scott,[38] who describe isofulvene as a shallow minimum that disappears if thermodynamic corrections are taken into account.

Carbene mechanism: The MNDOC-CI results for the two stages of the prefulvene-to-fulvene conversion via 1,3-cyclopentadienylcarbene (**7**) are shown in Figures 7 and 8. As indicated in Scheme 2, the numbering of atoms in **7** is such that it corresponds to breaking the C1–C6 bond, which can conveniently be described with the dihedral angle θ as reaction coordinate. θ = C6-C5-C4-C3 and varies from 62° in prefulvene to 130° in 1,3-cyclopentadienylcarbene. The potential diagram in Figure 7 is therefore two-dimensional, with an early transition state (TS 3) near the prefulvene geometry.

Fig. 7. MNDOC-CI potential energy diagram for the conversion of prefulvene to 1,3-cyclopentadienylcarbene, together with 3-21 G and 6-31 G+(d,p) energy differences in kcal mol^{-1}, the latter in parentheses. All C–C bond distances, C-C-C angles, and bond and dihedral angles involving H4 and H5 are optimized. (AS: 3-3'; EI: 5,10; reference configurations: $2^2 1^2$, $2^2 1'^2$; 85 CSFs).

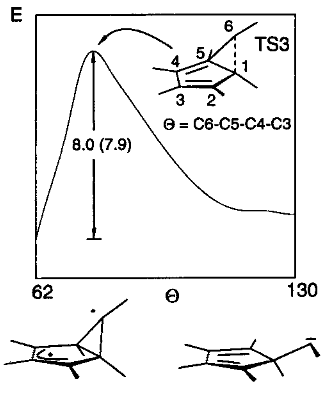
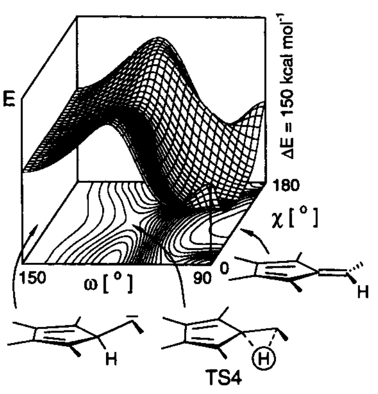
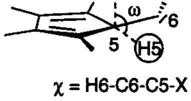


Fig. 8. MNDOC-CI potential energy hypersurfaces for the [1,2] H shift converting 1,3-cyclopentadienylcarbene into fulvene. The H5–C5 and the C5–C6 distances as well as the dihedral angle involving H5 are optimized, the bond and dihedral angles involving C6 are linearly interpolated. (AS: 3-3'; EI: 5,10; reference configurations: $2^2 1^2$, $2^2 1'^2$; 85 CSFs).



Potential energy surfaces for the [1,2] H shift from the carbene to fulvene have been calculated using as coordinates the angles χ and ω defined in Scheme 4. From Figure 8 it is seen that the rotation χ around the C5–C6 bond is almost barrierless for large values of ω at the beginning of the [1,2] H shift, while the transition state TS 4, at which the planarity of the carbon framework is already established, is located in the middle of the rotation coordinate χ. The stationary points of this pathway were again optimized by CAS/3-21 G calculations. Energies and dipole moments are given in Table 1 and geometries are shown in Figure 9. These data fully confirm the MNDOC-CI results. The transition state TS 3 between prefulvene and the carbene has a five-membered ring with bond lengths intermediate between those of the conjugated prefulvene and of the localized 1,3-cyclopentadienylcarbene. The C1–C6 bond is broken and the carbene center is already developed. With calculated energies of 8.0 (3-21 G) and 7.9 kcal mol^{-1} (6-31 G+(d,p)), respectively, the barrier is easily overcome. The imaginary frequency of 817 i cm^{-1} corresponds to the change from prefulvene to carbene.



Scheme 4. Definition of geometric parameters for the conversion of 1,3-cyclopentadienylcarbene to fulvene.

1,3-Cyclopentadienylcarbene is found to be a minimum structure in agreement with previous RHF calculations.[38, 39] The five-membered ring is almost planar with localized double and single bonds similar to ground-state fulvene.[11] The essentially free rotation χ around the C5–C6 bond apparent from Figure 8 has been confirmed by CAS/3-21 G calculations; optimized structures and energies are shown in Figure 10. Two minimum

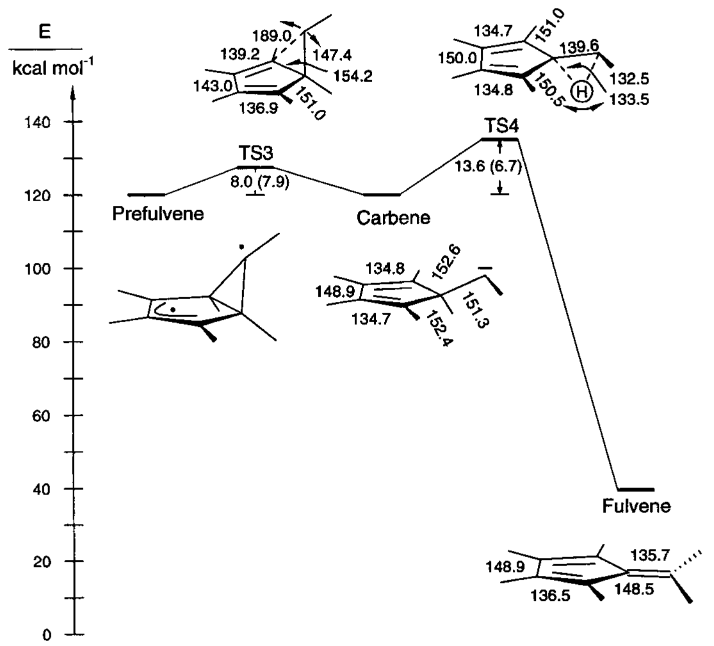


Fig. 9. The carbene mechanism of the conversion of prefulvene to fulvene. 3-21 G and 6-31 G + (d,p) energy differences in kcal mol^{-1}, the latter in parentheses, and 3-21 G optimized geometries in pm and degree. (TS = transition state).

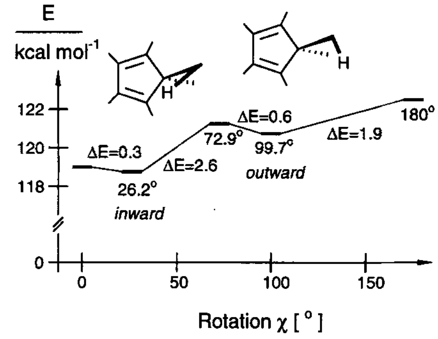


Fig. 10. CAS/3-21 G optimized stationary points for the rotation χ about the exocyclic single bond of 1,3-cyclopentadienylcarbene. Energy differences in kcal mol^{-1}.

structures, named the *inward* and *outward* form by Evanseck et al.,[39] and three transition states connecting the minima have been identified. In agreement with RHF calculations,[36] the *inward* form is calculated to be 2.0 kcal mol^{-1} more stable than the *outward* form, and the largest barrier for *inward–outward* conversion is 2.6 kcal mol^{-1}.

In the CAS-optimized transition structure TS 4 connecting the carbene and fulvene, the migrating hydrogen has moved halfway from C 5 to C 6. Its distances from these atoms are 132.5 and 133.5 pm, which are actually slightly less than the partially formed CH bonds in TS 1 connecting prefulvene and isofulvene. The dihedral angle χ is 92.7°, and the C 5–C 6 bond, the length of which is between those of a single and a double bond, is still 10° out of the molecular plane. The calculated values for the activation barrier show a considerable basis-set effect. Using as a reference point the energy of the *outward* carbene, which is the conformation closest to that of the transition state, barrier heights of 13.6 and 6.7 kcal mol^{-1} are obtained using the 3-21 G and the 6-31 + G(d,p) basis set, respectively. The reported RHF value for this barrier is 5.9 kcal mol^{-1}.[38] After passing the transition state a steep descent to the fulvene structure occurs. The activation barrier appears to be low enough to be passed, but large enough to expect a sufficient lifetime for 1,3-cyclopentadienylcarbene to be detected by transient absorption experiments. Therefore, excited-state wavefunctions, CAS/DZ excitation energies, and oscillator strengths *f* are collected in Table 3. Although the lowest excitations are calculated to occur in the visible region (608 and 400 nm), these absorptions might be difficult to detect because of the small values of the calculated oscillator strengths.

Table 3. 1,3-Cyclopentadienylcarbene: CAS/DZ results for vertical singlet excitation energies (in eV) and oscillator strengths *f*.

	Configuration	CAS/DZ [a]	*f*
S_0	$2^2 1^2$	0.0	–
S_1	$2^2 1^1 1'^1$	2.0	0.006
S_2	$2^1 1^1 1'^1 2'^1$ $2^2 1^0 1'^1 2'^1$	3.1	0.0003
S_3	$3^1 2^2 1^1 1'^1 2'^1$ $2^1 1^1 1'^1 3'^1$	4.8	0.0002

[a] Closed: 18, active: 6; 175 CSFs; state-averaged method.

Conclusion

The results of our calculations have shown that the carbene mechanism offers an explanation for the direct photochemical formation of fulvenes from prefulvene. Alternatively it has been proposed that a secondary isomerization of benzvalene may yield fulvene. Preliminary results for different thermal pathways from benzvalene to fulvene indicate, however, that the lowest activation barrier is to be expected for the back reaction of benzvalene to prefulvene. For this barrier an experimental value of 25.9 kcal mol^{-1} has been found.[40] As it is extremely unlikely that sufficient excess energy will be available to cross an even higher barrier in the ground state it may be concluded that rearomatization to benzene is the only possible thermal isomerization reaction of benzvalene. The formation of fulvene from benzvalene can therefore be ruled out.

The situation is quite different for the photochemical formation of fulvene via prefulvene. The photochemically generated prefulvene will have sufficient excess energy to overcome the much smaller barrier on the pathway to 1,3-cyclopentadienylcarbene. The barrier for the [1,2] H shift from 1,3-cyclopentadienylcarbene to fulvene is also low, in agreement with the finding that hydrogen migrations in singlet carbenes can be very fast.[39,41,42] Basis-set effects may be estimated from the 6-31 G + (d,p) single point calculations at 3-21 G optimized geometries.[43] The larger basis leads to stabilizations by 5–10 kcal mol^{-1} with respect to benzene S_0. Activation energies are hardly affected; only the barrier between 1,3-cyclopentadienylcarbene and fulvene is reduced considerably. In order to get more accurate results for the various stationary points, and in particular for the excitation energies, dynamic correlation should be taken into account.[37]

The conversion of prefulvene to fulvene has to compete with the formation of benzvalene and the rearomatization to benzene. Since these isomerizations are almost without barriers,[8] the yield of fulvene should be low because of barriers of 7.9 and 6.7 kcal mol^{-1}. To explain the actual experimental yield of fulvene, arguments like dynamic reaction control and a superior dissipation of vibrational excess energy in the case of fulvene have to be taken into account. The calculated dipole moments (Table 1) indicate that in polar solvents activation barriers will be reduced, since the transition states TS 3 and TS 4 occurring in the carbene mechanism have considerably higher dipole moments than the intermediates prefulvene and 1,3-cyclopentadienylcarbene.

In conclusion, our results indicate that fulvene is a primary product of the photolysis of benzene and is formed in a three-step process via prefulvene and 1,3-cyclopentadienylcarbene. This mechanism is in perfect agreement with the analogous mechanism for the photochemical conversion of benzocyclobutene to 1,2- and 1,5-dihydropentalene that has been derived by Turro et al. on the basis of deuterium-labeling experiments.[44]

Acknowledgements: Financial support from the Deutsche Forschungsgemeinschaft (Bonn), the Graduiertenkolleg "Hochreaktive Mehrfachbindungssysteme" (Münster), and the Fonds der Chemischen Industrie (Frankfurt) is gratefully acknowledged.

Received: July 6, 1995 [F162]

---

[1] L. T. Scott, M. Jones, Jr., *Chem. Rev.* **1972**, *72*, 181–202.

[2] D. Bryce-Smith, A. Gilbert, *Tetrahedron* **1976**, *32*, 1309–1326.

[3] A. H. Schmidt, *Chem. Unserer Zeit* **1977**, *11*, 118–129.

[4] J. E. Kent, P. J. Harman, M. F. O'Dwyer, *J. Phys. Chem.* **1981**, *85*, 2726–2730.

[5] P. J. Harman, J. E. Kent, M . F. O'Dwyer, D. W. T. Griffith, *J. Phys. Chem.* **1981**, 85, 2731–2733.

[6] J. M. Schulmann, R. L. Disch, *J. Am. Chem. Soc.* **1985**, *107*, 5059–5061.

[7] I. J. Palmer, M. Olivucci, F. Bernardi, M. A. Robb, *J. Org. Chem.* **1992**, *57*, 5081–5087.

[8] I. J. Palmer, I. Ragazos, F. Bernardi, M. Olivucci, M. A. Robb, *J. Am. Chem. Soc.* **1993**, *115*, 673–682.

[9] A. L. Sobolewski, C. Woywod, W. Domcke, *J. Chem. Phys.* **1993**, *98*, 5627–5641.

[10] W. Domcke, A. L. Sobolewski, C. Woywod, *Chem. Phys. Lett.* **1993**, *203*, 220–225.

[11] J. Dreyer, M. Klessinger, *J. Chem. Phys.* **1994**, *101*, 10655–10665.

[12] M. Klessinger, J. Michl, *Excited States and Photochemistry of Organic Molecules*, VCH, New York, **1995**.

[13] H. J. F Angus, J. M. Blair, D. Bryce-Smith, *J. Chem. Soc.* **1960**, 2003–2007.

[14] K. E. Wilzbach, J. S. Ritscher, L. Kaplan, *J. Am. Chem. Soc.* **1967**, *89*, 1031–1032.

[15] L. Kaplan, K. E. Wilzbach, *J. Am. Chem. Soc.* **1968**, *90*, 3291–3292.

[16] L. Kaplan, D. J. Rausch, K. E. Wilzbach, *J. Am. Chem. Soc.* **1972**, *94*, 8638–8640.

[17] H. R. Ward, J. S. Wishnok, *J. Am. Chem. Soc.* **1968**, *90*, 1085–1086.

[18] L. Kaplan, K. E. Wilzbach, *J. Am. Chem. Soc.* **1967**, *89*, 1030–1031.

[19] L. Kaplan, S. P. Walsh, K. E. Wilzbach, *J. Am. Chem. Soc.* **1968**, *90*, 5646–5647.

[20] H. R. Ward, J. S. Wishnok, *J. Am. Chem. Soc.* **1968**, *90*, 5353–5357.

[21] N. J. Turro, V. Ramamurthy, T. J. Katz, *Nouv. J. Chim.* **1977**, *1*, 363–365.

[22] M. Klessinger, *Angew. Chem.* **1995**, *107*, 597–599; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 549–551.

[23] H. R. Ward, J. S. Wishnok, P. D. Sherman, Jr., *J. Am. Chem. Soc.* **1967**, *89*, 162–163.

[24] D. E. Johnstone, J. R. Sodeau, *J. Phys. Chem.* **1991**, *95*, 165–169.

[25] D. Bryce-Smith, H. C. Longuet-Higgins, *J. Chem. Soc. Chem. Commun.* **1966**, *17*, 593–594.

[26] I. Yano, Y. Mori, *Chem. Phys. Lett.* **1968**, *2*, 185–188.

[27] J. Dreyer, thesis, WWU Münster, **1995**.

[28] a) W. Thiel, *J. Am. Chem. Soc.* **1981**, *103*, 1413–1420; b) *ibid.* **1981**, *103*, 1420–1425; c) A. Schweig, W. Thiel, *ibid.* **1981**, *103*, 1425–1431; d) M. Reinsch, U. Höweler, M. Klessinger, *Angew. Chem.* **1987**, *99*, 250–252; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 238–240; e) M. Reinsch, U. Höweler, M. Klessinger, *J. Mol. Struct. (Theochem)* **1988**, *167*, 301–306; f) M. Reinsch, thesis, WWU Münster, **1988**; g) T. Pötter, thesis, WWU Münster, **1991**; h) M. Klessinger, T. Pötter, C. Van Wüllen, *Theor. Chim. Acta* **1991**, *80*, 1–7.

[29] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, J. A. Pople, GAUSSIAN 92, Revision B, Gaussian, Pittsburgh PA, **1992**.

[30] *MOLPRO* is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions by J. Almlöf, R. Amos, S. Elbert, K. Hampel, W. Meyer, K. Peterson, R. Pitzer, and A. Stone; a) H.-J. Werner, P. J. Knowles, *J. Chem. Phys.* **1985**, *82*, 5053–5063; b) H.-J. Werner, P. J. Knowles, *Chem. Phys. Lett.* **1985**, *115*, 259–267; see also c) H.-J. Werner, P. J. Knowles, *J. Chem. Phys.* **1980**, *73*, 2342–2356; d) H.-J. Werner, P. J. Knowles, *ibid.* **1981**, *74*, 5794–5801; e) H.-J. Werner, *Adv. Chem. Phys.* **1987**, LXIX, 1–62.

[31] a) J. S. Binkley, J. A. Pople, W. J. Hehre, *J. Am. Chem. Soc.* **1980**, *102*, 939–947; b) M. S. Gordon, J. A. Pople, W. J. Hehre, *ibid.* **1982**, *104*, 2797–2803.

[32] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724–725.

[33] a) T. H. Dunning, Jr., *J. Chem. Phys.* **1970**, *53*, 2823–2833; b) T. H. Dunning, Jr., P. J. Hay in *Methods of Electronic Structure Theory* (Ed.: H. F. Schäfer III), Plenum, New York, **1977**.

[34] G. J. Atchity, S. S. Xantheas, K. Ruedenberg, *J. Chem. Phys.* **1991**, 95, 1862–1876.

[35] S. Oikawa, M. Tsuda, Y. Okamura, T. Urabe, *J. Am. Chem. Soc.* **1984**, *106*, 6751–6755.

[36] K. N. Houk, L. Yi, J. D. Evanseck, *Angew. Chem.* **1992**, *104*, 711–739; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 682–708.

[37] R. D. Roos, K. Andersson, M. P. Fülscher, *Chem. Phys. Lett.* **1992**, *192*, 5–13.

[38] K. M. Merz, Jr., L. T. Scott, *J. Chem. Soc. Chem. Commun.* **1993**, 412–414.

[39] J. D. Evanseck, J. Mareda, K. H. Houk, *J. Am. Chem. Soc.* **1990**, *112*, 73–80.

[40] N. J. Turro, C. A. Renner, T. J. Katz, K. B. Wiberg und H. A. Connon, *Tetrahedron Lett.* **1976**, *46*, 4133–4136.

[41] a) R. H. Nobes, L. Radom, W. R. Rodwell, *Chem. Phys. Lett.* **1980**, *74*, 269–272; b) K. Raghavachari, M. J. Frisch, J. A. Pople, P. von R. Schleyer, *ibid.* **1982**, *85*, 145–149; c) J. D. Evanseck, J. Mareda, K. N. Houk, *J. Am. Chem. Soc.* **1990**, *112*, 73–80.

[42] W. Sander, G. Bucher, S. Wierlacker, *Chem. Rev.* **1993**, *93*, 1583.

[43] Supplementary material: internal coordinates for all reported geometries are available from the authors.

[44] N. J. Turro, Z. Zhang, W. S. Trahanovsky, C.-H. Chou, *Tetrahedron Lett.* **1988**, *29*, 2543–2546.