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Tunneling Rearrangement of 1-Azulenylcarbene

Stefan Henkel, Y-am Huynh, Patrik Neuhaus, Michael Winkler,* and Wolfram Sander*

Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, D-44801 Bochum, Germany

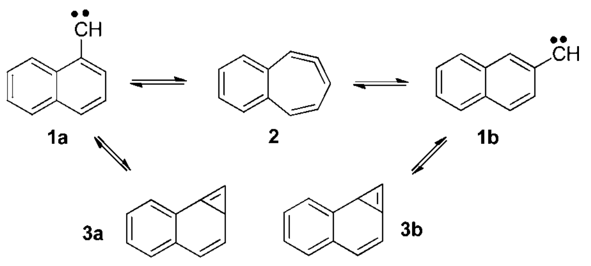
Supporting Information

ABSTRACT: 1-Azulenylcarbene was synthesized by photolysis of 1-azulenyldiazomethane in argon or neon matrices at 3−10 K. The highly polar singlet carbene is only metastable and undergoes a tunneling rearrangement to 8-methylene-bicyclo[5.3.0]deca-1,3,5,6,9-pentaene. After substitution of the 4 and 8 positions with deuterium, the rearrangement is completely inhibited. This indicates a very large kinetic isotope effect, as expected for a tunneling reaction.

Quantum chemical tunneling is an important process that can influence reaction rates of proton and hydrogen atom transfer,[1−5] but also of larger ("heavy") atoms such as carbon.[6−9] In recent years, a number of singlet carbenes have been described that are metastable and, even at cryogenic temperatures, rearrange via tunneling processes.[6,9,10] Since tunneling rates are almost independent of temperature, tunneling becomes rate determining at low temperatures, when classical thermal barriers are prohibitively high.

Arylcarbenes such as phenylcarbene[11,12] or the naphthylcarbenes **1**[13,14] are important reactive intermediates with triplet ground states that have been subject to a large number of experimental and theoretical studies. The chemistry of these carbenes is dominated by rearrangements (Scheme 1) to strained allenes such as **2**, cyclopropenes **3**, or other carbenes. The rich chemistry of arylcarbenes has been explored by matrix isolation spectroscopy,[11,15−17] time-resolved spectroscopy,[18,19] and theoretical methods.[20,21]

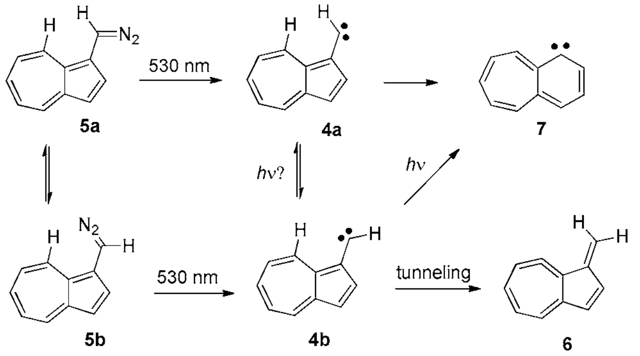
Scheme 1. Rearrangements of Naphthylcarbenes 1



In contrast to the naphthylcarbenes **1**, their isomeric azulenylcarbenes are basically unknown. Only one attempt to trap 1-azulenylcarbene **4** with styrenes is reported in the literature, and the results of those experiments are not conclusive.[22] Azulenylcarbenes are interesting systems, since the spin state and the philicity of these carbenes should depend on the position of the methylene group at the azulenyl moiety. Azulene shows a large dipole moment (μ = 1.08 ± 0.02 D)[23] with a negatively polarized five-membered ring and a positively polarized seven-membered ring. In particular, C1 and C3 are more electron-donating than the other positions, and a carbene unit attached to these centers should result in stabilization of the singlet state. Here, we describe the IR spectroscopic characterization of carbene **4** and its rearranged products using matrix isolation spectroscopy.

1-Azulenyldiazomethane was matrix-isolated in argon as a mixture of the conformers **5a** (major conformer) and **5b** (minor conformer, see Supporting Information (SI) for details). Visible light irradiation (λ > 530 nm) of **5** produces 1-azulenylmethylene **4** (Scheme 2). A comparison of the matrix IR spectrum with spectra calculated (B3LYP/cc-pVTZ, *vide infra*) for the *syn*- and *anti*-conformers **4a** and **4b**, respectively, in both their lowest lying singlet and triplet states, reveals that **4** is formed in its closed-shell ($^1A'$) singlet state. The spectra calculated for the $^3A''$ states of both conformers **4a** and **4b** are clearly distinct and allow one to rule out a triplet ground state for **4** on the basis of its IR spectrum. Attempts to record an EPR spectrum of matrix-isolated **4** failed, which also indicates a singlet ground state of **4**.

Scheme 2. Synthesis and Rearrangements of 1-Azulenylcarbene 4



It is more subtle to distinguish between the singlet conformers $^1A'$-**4a** and $^1A'$-**4b**. Whereas the overall computed IR patterns look quite similar for both conformers, there are pronounced differences in the intensities of various bands, which allows one to definitely identify $^1A'$-**4b** as the predominant species present in the matrix.

To further elaborate on the ground state of **4**, extensive *ab initio* computations were carried out (see SI). In qualitative agreement with the DFT results, computations at the

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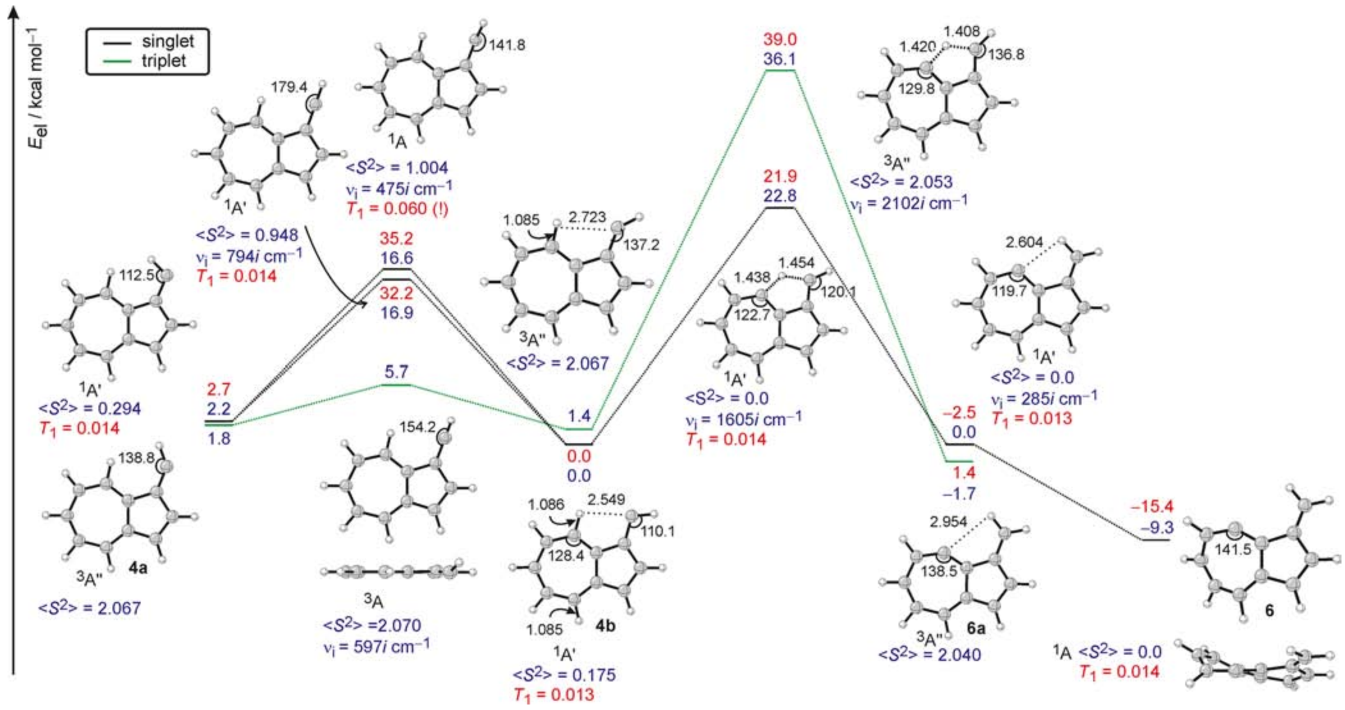


Figure 1. Rearrangements of carbene **4b** on the singlet and triplet PES computed at the RCCSD(T)/cc-pVTZ//(U)B3LYP/cc-pVTZ (red) and UB3LYP/cc-pVTZ levels (blue). Spin expectation values (UB3LYP), *T*1 diagnostics (CCSD), and imaginary frequencies for the transition states (UB3LYP) are given for comparison.

CAS(6,6)-CISD+Q/cc-pVTZ//CASSCF (12,12)/cc-pVTZ level indicate a ^{1}A′ closed-shell singlet ground state for **4b** that is 1.8 kcal/mol more stable than ^{3}A″-**4b**. In contrast, the *syn* isomer **4a** has a ^{3}A″ ground state that is 1.6 kcal/mol more stable than ^{1}A′-**4a**.

The singlet and triplet states of **4a** are less stable than the corresponding states of **4b** by 3.7 and 0.3 kcal/mol, respectively; hence, the ground-state multiplicity depends on the conformation. The destabilization of **4a** as compared to **4b** is attributed to the repulsion between the hydrogen atom at the carbene center and H8 of the azulene ring system in the *syn* conformer. Because the distance between the hydrogens is smaller in the singlet state (smaller CCH bond angle), the destabilization is more pronounced in ^{1}A′-**4a** than in ^{3}A″-**4a**. In contrast, ^{1}A′-**4b** benefits from a stabilizing electrostatic interaction between the negatively polarized carbene carbon atom (*vide infra*) and H8, although the C···H8 distance is clearly too large to be classified as a hydrogen bond.[24] The open-shell singlet states ^{1}A″-**4a** and ^{1}A″-**4b** are adiabatically less stable than ^{1}A′-**4b** by 10.1 and 9.9 kcal/mol, respectively, with similar CCH bond angles as in the ^{3}A″ states.

At the equilibrium geometries, the closed-shell singlet states of both isomers are rather well-behaved with little multireference character. Accordingly, spin contaminations of the UB3LYP Kohn−Sham solutions for ^{1}A′-**4a** ($\langle S^2 \rangle = 0.294$) and ^{1}A′-**4b** ($\langle S^2 \rangle = 0.175$) are moderate, and structures, energies, and dipole moments computed at the RB3LYP level are very close to those obtained with unrestricted DFT. The same is not true for the vibrational spectra: because triplet contamination of the UDFT solution rapidly increases with increasing CCH bond angle at the carbene center, and because the ^{1}A′ states of **4** are significantly more polar than the ^{3}A″ states (RB3LYP, $\mu(^1\text{A}'\text{-}\mathbf{4b}) = 5.77$ D; UB3LYP, $\mu(^1\text{A}'\text{-}\mathbf{4b}) = 5.35$ D; $\mu(^3\text{A}''\text{-}\mathbf{4b}) = 1.06$ D), those IR absorptions involving significant CCH bending contributions artificially gain intensity. In particular, for the CCH bending mode of ^{1}A′-**4b**, relaxing the orbital constraints in UB3LYP as compared to RB3LYP results in a red-shift of 83 cm^{-1} and in an increase of the IR intensity from 42 to 502 km/mol. Thus, a meaningful comparison of computed and experimental IR data of ^{1}A′-**4** has to be based on restricted B3LYP data, despite the small external instabilities. The extraordinary high polarity of ^{1}A′-**4**, close to those of 1-nitroazulene ($\mu = 6.06 \pm 0.03$ D)[23] and related compounds, highlights the unusual properties of the title carbene.

There are two plausible pathways for the *syn*/*anti* isomerization of **4**: via rotation around the C−CH bond (C_1) or via in-plane flip of the carbene hydrogen (C_s). On the singlet potential energy surface (PES), both transition states (TSs) are similar in structure and energy, and the barriers computed at the CCSD(T)/cc-pVTZ//UB3LYP/cc-pVTZ level amount to 35.2 and 32.2 kcal/mol (relative to **4b**), respectively (Figure 1). The latter is in excellent agreement with the CAS(6,6)-CISD+Q/cc-pVTZ//CASSCF(12,12)/cc-pVTZ value of 33.6 kcal/mol. Although the barrier heights obtained at the UB3LYP level are significantly lower (16.6 and 16.9 kcal/mol, respectively; note the strong spin contamination), they are still prohibitively high for a thermal isomerization in low-temperature matrices. On the triplet PES only one TS can be localized, and the barrier is significantly lower (4.3 kcal/mol). We therefore assume that **4b** is formed during photolysis of the preferred diazomethane **5a** either in a secondary photochemical process (that might involve transition to the triplet PES) or via a hot ground-state reaction.

Carbene **4b** is metastable, and even at temperatures as low as 3 K it slowly rearranges to a new compound, which was identified as 8-methylene-bicyclo[5.3.0]deca-1,3,5,6,9-pentaene (**6**, Figure 2). The half-life time of **4b** between 3 and 30 K is

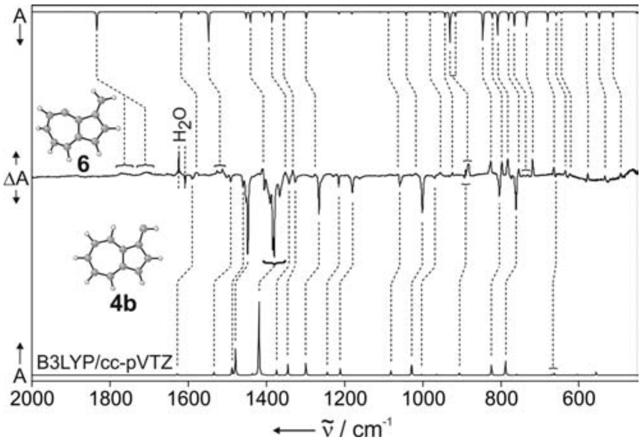
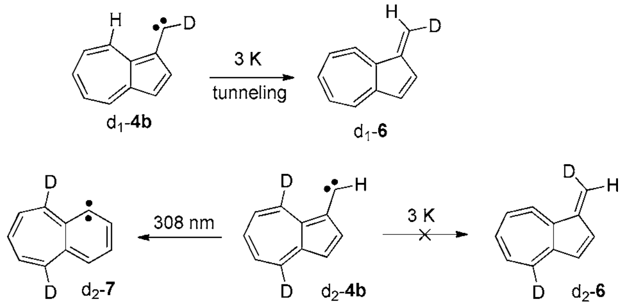


Figure 2. Difference IR spectrum showing the tunneling rearrangement of 1-azulenylcarbene in argon at 3 K. Bands pointing upward increase in intensity; bands pointing downward decrease concomitantly.

approximately 12 h, independent of the temperature in this range and of the matrix material (Ne, Ar, or Xe). A constant rate over a large temperature range (here a factor of 10 in T) points toward a tunneling process. Since a hydrogen atom is migrating from position 8 to the carbene center, a large kinetic isotope effect (KIE) can be expected for this process. This is confirmed by experiment: after deuteration of the 4 and 8 positions, carbene d_2-**4b** is completely stable under the conditions of matrix isolation, and no rearrangement to **6** is observed even after extended periods of time. Deuteration of the carbene hydrogen atom (d_1-**4b**), on the other hand, does not lead to any noticeable KIE (Scheme 3).

Scheme 3. Rearrangements of the Deuterated Isotopomers of 1-Azulenylcarbene 4



The rearrangement of ^{1}A′-**4b** to the chiral allene **6** is a rather complex process. At the (U)B3LYP level, the barrier amounts to 22.8 kcal/mol (CCSD(T)//(U)B3LYP, 21.9 kcal/mol) and leads to the planar carbene **6a** in its ^{1}A′ state. This carbene is the TS for the racemization of the chiral allene **6** with an activation barrier of 9−12 kcal/mol (Figure 1). The formation of chiral **6** from the planar carbene **4b** requires that the symmetry along the reaction coordinate is broken, resulting in a branching point (VRI) on the potential energy surface.

On the triplet PES, the barrier for the **4b**−**6a** rearrangement is much higher (UB3LYP, 36.1 kcal/mol; CCSD(T)//UB3LYP, 39.0 kcal/mol), whereas ^{3}A″-**6a** is by 1.7 kcal/mol more stable than ^{1}A′-**6a**, according to DFT. At the CCSD(T)//UB3LYP level this order is reversed, and the singlet is found to be 3.9 kcal/mol more stable than the triplet. This latter ordering is supported by MRCI computations which show, however, that the ground state of **6a** is a two-determinantal ^{1}A″ open-shell singlet state that is about 1 kcal/mol more stable than ^{1}A′-**6a** and 2−3 kcal/mol more stable than ^{3}A″-**6a**. Thus, all three states of **6a** are very close in energy.

Table 1. Adiabatic (CASSCF(12,12)/cc-pVTZ geometries) Electronic Energies (in kcal/mol) of the Lowest States of Several Isomers of 4 Relative to ^{1}A′-4b[a]

	state	RS2c[b]	RS2[c]	RS3[c]	CISD+Q[c]	AQCC[c]
4b	^{1}A′	0.0	0.0	0.0	0.0	0.0
	^{3}A″	−2.9	−2.0	2.6	1.8	0.4
	^{1}A″	5.9	5.4	10.7	9.9	8.1
4a	^{3}A″	−2.6	−1.8	2.9	2.1	0.5
	^{1}A′	3.3	4.9	4.3	3.7	3.3
	^{1}A″	5.8	5.5	10.8	10.1	8.1
6a	^{1}A″	−6.6	−2.9	−1.2	−0.9	−2.1
	^{1}A′	−0.4	3.9	−0.3	0.1	−1.1
	^{3}A″	−4.8	−4.0	2.6	1.8	0.5
7	^{3}A″	−22.7	−24.3	−17.9	−16.7	−18.3
	^{1}A″	−21.2	−23.4	−16.3	−15.7	−17.4
	^{1}A′	−2.9	0.0	−4.7	−4.8	−5.2
TS[d]	^{1}A′	28.3	29.6	32.2	33.6	33.0

[a] See SI for details. The most reliable energies are given in the last two columns. [b] CAS(12,12). [c] CAS(6,6). [d] Transition state **4a** → **4b**.

All attempts to locate an additional stationary point on the singlet PES at the UB3LYP level failed and inevitably converged to the (externally stable) ^{1}A′ structure. Because the barrier height for the **4b** → **6a** rearrangement is central to the present work, we investigated the energies of various states at the geometries of the ^{1}A′- and ^{3}A″-TSs using different multireference methods and different active spaces. At all levels and geometries, the ^{1}A′ state remains significantly below the ^{1}A″ state, so that the ^{1}A′-TS(**4b**/**6a**) computed at the B3LYP level can safely be considered the lowest electronic singlet state at the TS geometries, even though the ^{1}A″ state is not directly amenable to a description by DFT. Overall, the large calculated barrier of >22 kcal/mol for the **4b** → **6** rearrangement, combined with the observation of a thermal reaction at 3 K, is another clear evidence for a tunneling process.

Because the tunneling rearrangement of **4b** is essentially blocked in carbene d_2-**4b**, this isotopomer can be generated in much higher yields (free of d_2-**6**) than the non-deuterated **4b**. This allows one to study its bimolecular reactions and its photochemistry. The very slow bimolecular reaction with O_2 in oxygen-doped argon matrices is in accordance with reactions of typical singlet carbenes[25,26] and will be reported elsewhere.

UV irradiation (308 nm) of d_2-**4b** results in the formation of several photoproducts. The main product could be identified as triplet carbene d_2-**7** by IR and EPR spectroscopy (see SI for details). It is worth noting that the EPR spectrum of triplet d_2-**7** is clearly observable after UV irradiation of its EPR silent precursor, the singlet carbene d_2-**4b**. According to MRCI computations, the ^{3}A″ ground state of **7** is approximately 1 kcal/mol more stable than ^{1}A″-**7**. The rearrangement **4b** → **7** is classified as a 1,2 carbon migration that is exothermic by roughly 16 kcal/mol. The same photochemistry is also observed for the non-deuterated carbene **4**, although here the yield is lower due to the competing tunneling rearrangement to **6**.

In summary, 1-azulenylcarbene **4** is a metastable carbene with a singlet ground state that even at lowest temperatures rearranges to cycloheptatetraene **6** via quantum chemical tunneling. This assumption is confirmed by the following observations: (i) the rates are independent of temperature within a range of a factor of 10 in *T*, (ii) a very large kinetic isotope effect is found, and (iii) a large activation barrier is calculated that, without tunneling, should result in slow rates even at room temperature. This tunneling rearrangement is of particular interest since it is one of the rare cases where during the rearrangement the molecular symmetry is broken, and a pair of enantiomers is formed from the achiral precursor.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials and methods, spectroscopic data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

wolfram.sander@rub.de; michael.winkler@rub.de

Notes

The authors declare no competing financial interest.

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(24) This point was brought to our attention by Prof. Wes Borden. Note that the C8−H bond is of almost identical length in 1A′-**4b** and in the less polar 3A″-**4b**. Still, a stabilizing electrostatic C···H interaction is likely to contribute to the stabilization of 1A′-**4b**, as can be conjectured from atomic NPA charges, indicating a polarization of the C8−H bond. See SI for details.

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