Hydrogen Activation

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Activation of Molecular Hydrogen by a Singlet Carbene through Quantum Mechanical Tunneling**

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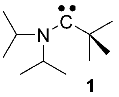
Dedicated to the memory of Michael Winkler

Abstract: *Carbenes are among the few metal-free molecules that are able to activate molecular hydrogen. Whereas triplet carbenes have been shown to insert into H_2 through a two-step mechanism that at low temperature is assisted by quantum mechanical tunneling (QMT), singlet carbenes insert in concerted reactions with considerable activation barriers, and are thus unreactive towards H_2 at cryogenic temperatures. Here we show that 1-azulenylcarbene with a singlet ground state readily inserts into H_2, and that QMT governs the insertion into both H_2 and D_2. This is the first example that shows that QMT can also be important for singlet carbenes inserting into dihydrogen.*

The metal-free activation of molecular hydrogen is an emerging field in chemistry with a large potential for applications, from organic synthesis to energy storage. Only very few organic closed-shell molecules are able to break the strong H–H bond at room temperature, among which are (alkyl)(amino)carbenes[1] and frustrated Lewis acid–base pairs.[2] Whereas singlet (alkyl)(amino)carbenes such as **1** are able to split the H_2 molecule at room temperature, there is still a significant activation barrier of 22–24 kcal mol^{-1} to cross, and for the less reactive di(amino)carbenes even higher activation barriers have been predicted.[1]



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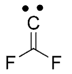

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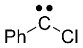

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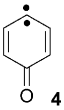

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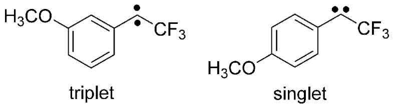
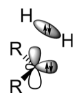
The highly electrophilic difluorovinylidene **2** is the only singlet carbene that has been demonstrated to insert into H_2 even at cryogenic temperatures under the conditions of matrix isolation, and in this case the activation barrier is essentially zero.[3,4] Zuev and Sheridan reported that less electrophilic singlet carbenes such as phenyl(chloro)carbene **3** do not react with H_2 under conditions of matrix isolation,[5] whereas electrophilic triplet carbenes such as 4-oxocyclohexa-2,5-dienylidene **4** rapidly react with hydrogen in H_2-doped argon matrices at temperatures above 20 K.[3,5] A similar observation was reported by Song and Sheridan for two isomeric methoxyphenyl(trifluoromethyl)carbenes.[6] The *m*-methoxy derivative shows a triplet ground state and inserts into H_2 under the conditions of matrix isolation, whereas the *p*-methoxy derivative with a singlet ground state is unreactive under the same conditions.





The mechanisms for reactions of singlet and triplet carbenes with molecular hydrogen are entirely different. Calculations suggest that singlet carbenes undergo a concerted reaction with H_2, and it was proposed to separate the reaction into an electrophilic and a nucleophilic phase.[7] The electrophilic phase is dominated by interactions of the empty p orbital at the carbene center with the σ orbital of H_2, whereas the nucleophilic phase is dominated by interactions between the lone pair at the carbene center and the antibonding σ* orbital of H_2.

The extent of these two phases depends on the philicity of the carbene.[1,8] The least-motion insertion of singlet carbenes into H_2 is an orbital-symmetry-forbidden reaction, and for the least-motion insertion of singlet CH_2 into H_2 a substantial barrier of 27 kcal mol^{-1} was estimated computationally.[9] In contrast, the lower-symmetry non-least-motion pathway of the CH_2 reaction with H_2 proceeds without a significant barrier,[10] whereas for singlet carbene **3** a barrier of 12 kcal mol^{-1} was calculated.[5] This explains why the latter reaction is not observed in low-temperature matrices.

The insertion of triplet carbenes into H_2 requires intersystem crossing (ISC) from triplet to singlet, and therefore is a two-step reaction. The first step is the hydrogen abstraction to form a radical pair, for which barriers of 4–6 kcal mol^{-1} were calculated, depending on the substituents.[5] This is followed by a highly exothermic, barrierless radical recombination, which makes it difficult to observe the intermediate radical pairs directly. Zuev and Sheridan found for a series of triplet carbenes that the insertion into H_2 in solid argon is rapid (controlled by the diffusion of H_2) at 30 K. Since the barriers for the first steps are too high for thermally activated

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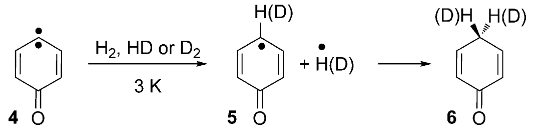
reactions at this low temperature, they concluded that the hydrogen insertion is governed by quantum mechanical tunneling (QMT).

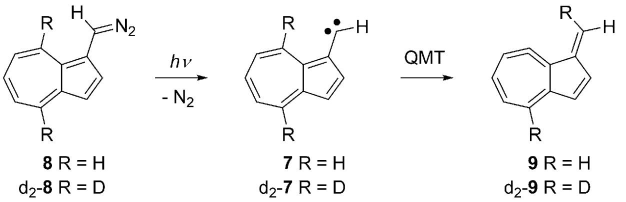
To shed some light on the mechanism of the hydrogen insertion of triplet carbenes, we recently investigated the reaction of carbene **4** in detail using matrix-isolation IR and EPR spectroscopy (Scheme 1).[11] In addition to $\mathrm{H_2}$-doped argon we also used solid $\mathrm{H_2}$, HD, and $\mathrm{D_2}$ at 3 K as matrices to study the mechanism. These experiments allowed us to characterize the intermediate radical pair **5** spectroscopically, and to confirm a tunneling mechanism for both the insertion into $\mathrm{H_2}$ and $\mathrm{D_2}$.



Scheme 1. Reaction of carbene **4** with $\mathrm{H_2}$.

The conclusion of these previous studies is that for most triplet and singlet carbenes the insertion into $\mathrm{H_2}$ shows an activation barrier that depends on the philicity of the carbene. While many triplet carbenes overcome this barrier at low temperature through QMT, this is not observed for singlet carbenes, which tend to be unreactive under similar conditions. Zuev and Sheridan concluded from their experiments that the hydrogenation reaction exhibits a spin state selectivity, and singlet insertion is "less facile either because of the higher classical barriers or because of the lower probability of QMT involving two hydrogens simultaneously".[5]

Recently, we reported that 1-azulenylcarbene **7** has a singlet ground state,[12] in contrast to most other arylcarbenes that show triplet ground states. Carbene **7** can be generated by photolysis of 1-azulenyldiazomethane **8** (Scheme 2), but even at 3 K it is kinetically unstable and rearranges to the strained allene **9** through QMT. The tunneling reaction can be completely blocked by deuteration of position 8 in the seven-membered ring. We here report our investigations on the reaction of singlet carbene **7** with molecular hydrogen. To suppress the rearrangement, and thus loss, of **7** through QMT, only the dideuterated isotopomer $\mathrm{d_2}$-**7** was used in these experiments.



Scheme 2. Tunneling rearrangement of 1-azulenylcarbene.

The hydrogenation of carbene $\mathrm{d_2}$-**7** was investigated in two different types of matrices: 1) solid hydrogen matrices and 2) argon matrices doped with 5% of hydrogen. In both types of matrices $\mathrm{H_2}$, HD, and $\mathrm{D_2}$ were used to investigate isotope effects on the hydrogenation of $\mathrm{d_2}$-**7**. Due to the high vacuum pressure of $\mathrm{H_2}$, temperatures well below 4 K are necessary to keep solid $\mathrm{H_2}$ from evaporation, whereas $\mathrm{D_2}$ matrices are stable up to 5 K. In solid argon, hydrogen is trapped at much higher temperatures and hydrogenation reactions can be studied up to 35 K. Below 20 K diffusion of hydrogen in solid argon is very slow, and thus bimolecular reactions are efficiently suppressed; between 25 and 30 K the diffusion of $\mathrm{H_2}$ is fast, whereas the matrix still does not evaporate, and above 35 K hydrogen evaporates together with the argon.

If $\mathrm{d_2}$-**8** is irradiated with visible light ($\lambda > 530$ nm) in 5% $\mathrm{H_2}$-doped argon at 10 K, carbene $\mathrm{d_2}$-**7** is formed as the major product together with small amounts of 4,8-dideutero-1-methylazulene $\mathrm{d_2}$-**10**. The azulene $\mathrm{d_2}$-**10** is identified by comparison of the IR and UV/Vis spectra with that of an authentic matrix-isolated sample (see the Supporting Infomration, SI). Annealing of the $\mathrm{H_2}$-doped matrix at 30 K results in the decrease of $\mathrm{d_2}$-**7** and formation of more $\mathrm{d_2}$-**10**. The rapid reaction of $\mathrm{d_2}$-**7** with $\mathrm{H_2}$ at 30 K indicates that this reaction is controlled by the diffusion of $\mathrm{H_2}$ and proceeds without a noticeable thermal activation barrier. In contrast, when $\mathrm{D_2}$-doped argon is used in the experiments, no reaction is observed, indicating a very large kinetic isotope effect (KIE).

Photolysis of $\mathrm{d_2}$-**8** in solid $\mathrm{H_2}$ at 3 K results in the formation of the hydrogenated product $\mathrm{d_2}$-**10**, whereas carbene $\mathrm{d_2}$-**7** is not formed under these conditions (Figure 1 b). This is in accordance with the assumption of a rapid, barrierless reaction between $\mathrm{d_2}$-**7** and $\mathrm{H_2}$. However, since the carbene is not observed as an intermediate in this experiment, we cannot exclude a photochemical or a hot ground state reaction of either the diazo precursor $\mathrm{d_2}$-**8** or the carbene $\mathrm{d_2}$-**7**. In contrast, the reaction of $\mathrm{d_2}$-**7** in $\mathrm{H_2}$-doped argon at 20–25 K described above is clearly thermal.

To determine if the hydrogenation of $\mathrm{d_2}$-**7** is thermal or photochemical, the photochemistry of $\mathrm{d_2}$-**8** was also investigated in solid $\mathrm{D_2}$. The photolysis ($\lambda > 530$ nm) of $\mathrm{d_2}$-**8** in in solid $\mathrm{D_2}$ at 3 K produces high yields of carbene $\mathrm{d_2}$-**7**, but no deuterated products (Figure 1 e). This clearly demonstrates that $\mathrm{d_2}$-**7** does not react photochemically with $\mathrm{D_2}$. Even more striking, photolysis at shorter wavelength ($\lambda = 450$ nm) produces the previously reported ring expansion product, 2,6-dideuteriobicyclo[5.4.0]undeca-2,4,6,9,11-pentaen-8-ylidene $\mathrm{d_2}$-**11**,[12] demonstrating that $\mathrm{d_2}$-**7** in solid $\mathrm{D_2}$ exhibits the same photochemistry as in argon.

A slow reaction of $\mathrm{d_2}$-**7** with $\mathrm{D_2}$ to give $\mathrm{d_4}$-**10** (Scheme 3) was only observed after extended periods of time at 3 K (see SI). The rate constant for the insertion into $\mathrm{D_2}$ is in the order of $10^{-8}\,\mathrm{s^{-1}}$. Considering that in solid $\mathrm{H_2}$ the carbene reacts too fast to be observable in our experiments, the H/D KIE is estimated to be larger than 10^6. The large KIE could be further demonstrated by photolysis of $\mathrm{d_2}$-**7** in a 5% $\mathrm{H_2}$-doped $\mathrm{D_2}$ matrix at 3 K. This results in a mixture of carbene $\mathrm{d_2}$-**7** and $\mathrm{d_2}$-**10**, but only trace amounts of the deuterium insertion product $\mathrm{d_4}$-**10** (see SI). Thus, $\mathrm{H_2}$ is reacting with a large preference in a mixture with $\mathrm{D_2}$.

Finally, the hydrogenation of carbene $\mathrm{d_2}$-**7** with HD was investigated. Annealing of an argon matrix containing carbene $\mathrm{d_2}$-**7** and 5% of HD at 30 K produced the triply deuterated methylazulene α,4,8-$\mathrm{d_3}$-**10**, identified by compar-

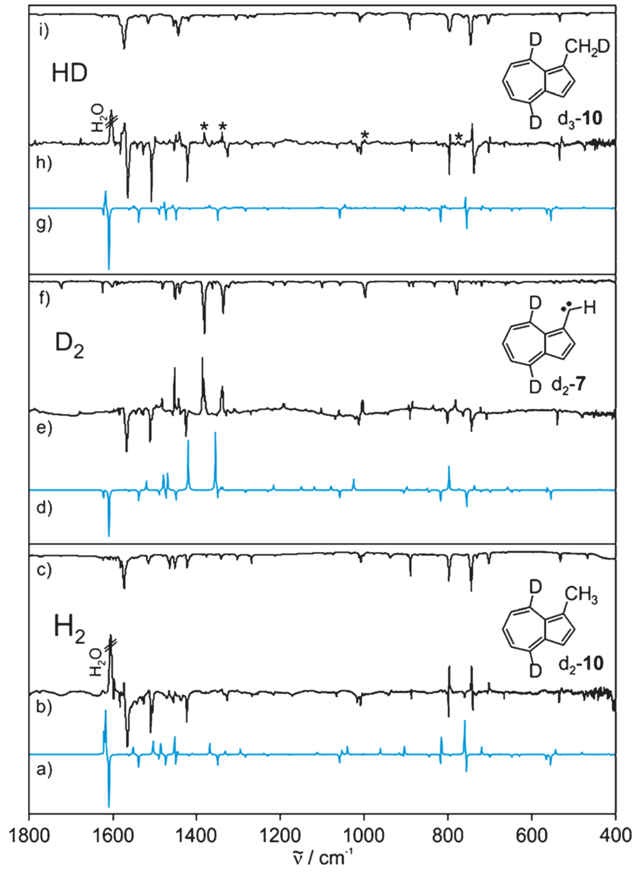
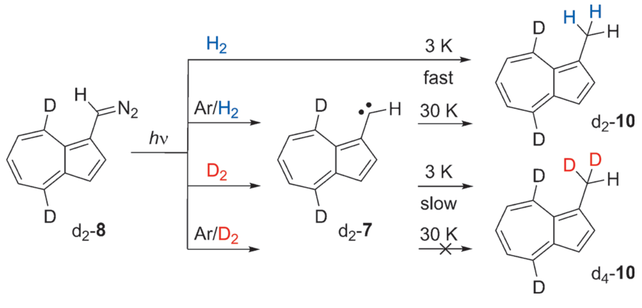


Figure 1. IR difference spectra showing the 530 nm photochemistry of d$_2$-**8** in H_2, HD, and D_2 at 3 K. Bands pointing upward increase in intensity; bands pointing downward decrease concomitantly. a) d$_2$-**8**→d$_2$-**10** calculated at B3LYP/6-311+G(d,p) level of theory. b) Photolysis of d$_2$-**8** in H_2. c) d$_2$-**7** in argon at 10 K. d) d$_2$-**8**→d$_2$-**7** calculated at B3LYP/6-311+G(d,p) level of theory. e) Photolysis of d$_2$-**8** in D_2. f) d$_2$-**7** in argon at 10 K. g) d$_2$-**8**→d$_3$-**10** calculated at B3LYP/6-311+G(d,p) level of theory. h) Photolysis of d$_2$-**8** in HD. Asterisks denote signals due to d$_2$-**7**. e) d$_3$-**10** in argon at 10 K.



Scheme 3. Reactivity of 1-azulenylcarbene with hydrogen and deuterium in doped argon and in pure H_2 and D_2.

ison with the IR spectrum of an authentic sample (see SI). The reactivity of HD in this experiment is comparable to that of H_2, whereas D_2 does not react under similar conditions. In solid HD at 3 K, the insertion product d$_3$-**10** is the main product. However, unlike to the experiments in solid H_2, small amounts of carbene d$_2$-**7** are also observed in HD (Figure 1 h). Upon standing at 3 K, the carbene slowly reacts with HD to d$_3$-**10**.

To shed some light on these experimental findings, the reaction of **7** with H_2 was studied computationally. At the B3LYP-D3/6-311+G(d,p) level of theory a very weakly bound *Cs* symmetrical complex between **7** and H_2 is predicted. This complex could well be an artefact of the calculation, since the binding energy is zero if zero point vibration energy (ZPVE) is considered. In the transition state $\mathbf{TS_{7,10}}$ the hydrogen is oriented side on with respect to the carbene, to allow for an efficient overlap between the π orbital of the carbene and the σ orbital of H_2 on one hand, and between the σ orbital of the carbene and the σ* orbital of H_2 on the other hand. This transition state structure is similar to that calculated for the hydrogenation of nucleophilic amino carbenes.[1]

The barrier for the concerted hydrogenation reaction of singlet carbene **7** is calculated to 5.6 kcal mol^{-1} (including ZPVE; 3.8 kcal mol^{-1} without ZPVE), which is prohibitively high for a reaction to occur thermally at 3 K. This finding strongly supports the assumption that tunneling is involved in the hydrogen insertion reaction of carbene **7**. Interestingly, the thermal activation barrier for the insertion into D_2 is with 5.3 kcal mol^{-1} predicted to be slightly lower than that for the H_2 insertion. The very large KIE observed for the D_2 insertion can therefore not be explained by a conventional thermal reaction.

For the HD insertion the barrier depends on the orientation of HD with respect to the carbene in the initial step of the reaction: if D is closer to the carbene center the barrier is predicted to 5.3 kcal mol^{-1}, whereas if H is closer it is predicted to 5.4 kcal mol^{-1}. Our experiments clearly reveal that d$_2$-**7** is stable enough in HD to be spectroscopically characterized, although the yield is much lower than in D_2. Although the subsequent reaction with HD could be monitored by IR spectroscopy, the low yield of d$_2$-**7** did not allow us to measure the kinetic data with the accuracy necessary to determine the HD/D_2 KIE. The behavior of singlet carbene **7** in HD is clearly distinct from that of triplet carbene **4**, which under similar conditions reacts too fast to be observed in HD.[11] The rates for the reaction of **7** with D_2 are also considerably lower than that of **4**. Zuev and Sheridan proposed that triplet carbenes react faster with hydrogen than singlet carbenes because the rate-determining hydrogen atom abstraction in the triplet reaction requires only one hydrogen atom to move.[5] In contrast, the concerted hydrogenation of singlet carbenes requires that both hydrogen atoms move, resulting in lower tunneling rates. Whether the lower reactivity of **7** compared to **4** toward hydrogen reflects this change in mechanism cannot be answered from our experiments.

The S–T gap of carbene **7** (1.8 kcal mol^{-1} at the CAS(6,6)-CISD+Q/cc-pVTZ//CASSCF(12,12)/cc-pVTZ level of theory)[12] is calculated to be smaller than the barrier for the hydrogen insertion. We therefore additionally calculated the mechanism for the reaction of the triplet carbene T-**7** with H_2 (Figure 2). At the UB3LYP-D3/6-311+G(d,p) level of theory the triplet barrier for hydrogen abstraction is predicted to be 6.8 kcal mol^{-1} (5.9 kcal mol^{-1} with ZPVE). The first step of the triplet reaction is the formation of a radical pair **12**, in a slightly exothermic reaction. After ISC in the radical pair to

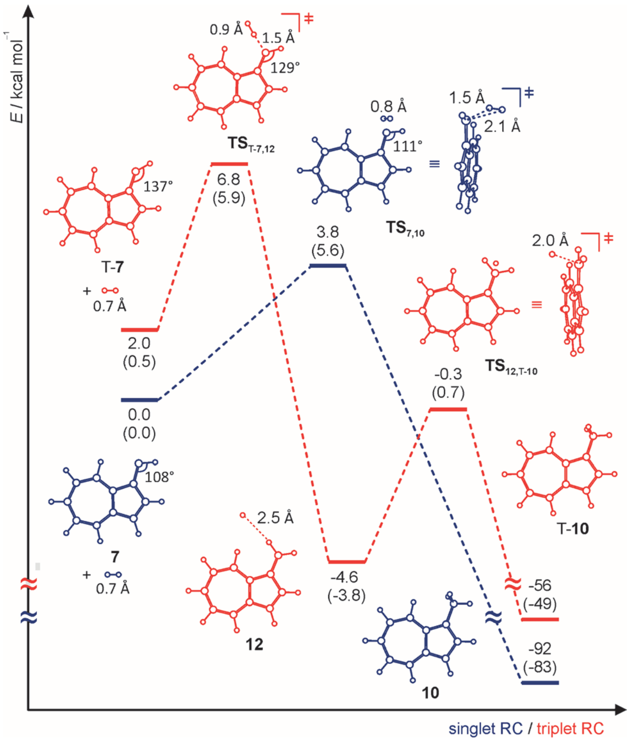


Figure 2. Optimized geometries of the hydrogenation reaction of 1-azulenylcarbene **7** in the singlet (blue) and triplet (red) state calculated at (U)B3LYP-D3/6-311+G(d,p) level of theory. Energies are given in kcal mol^{-1} relative to noninteracting singlet carbene and hydrogen **7**+H_2 (values in parentheses include ZPVE).

the singlet surface, **12** will combine to **10**, in a highly exothermic reaction. Alternatively, the triplet radical pair could combine to triplet **10** with an activation barrier of 4.4 kcal mol^{-1}. These calculations suggest that the thermal hydrogenation of carbene **7** is more favorable on the singlet than on the triplet surface. This is in accordance with our EPR investigations: The hydrogenation of d_2-**7** under various conditions inside an EPR cavity did not give any hint for the formation of paramagnetic species (triplets or radicals).

We therefore conclude that the hydrogenation reaction of carbene **7** proceeds on the singlet surface, and therefore **7** is the only known singlet carbene besides difluorovinylidene **2** that inserts into molecular hydrogen at cryogenic temperatures. Compared to **2** the activation barrier for the insertion is much higher, and at the very low temperatures in our experiments the insertion proceeds only through QMT. Obviously, tunneling is not only important for the hydrogenation of triplet carbenes, but also for the singlet carbenes.

It is interesting to compare the three singlet carbenes **2**, **7**, and **1** with respect to their hydrogenation reactions. Qualitatively, the transition state structures are similar for all three carbenes, but the barriers increase from almost zero in **2** to 7 kcal mol^{-1} in **7** to more than 20 kcal mol^{-1} in **1**. The first phase in the hydrogenation is the electrophilic interaction between the π orbital at the carbene center with the σ orbital of hydrogen. This phase is rate-determining, and therefore the barriers increase with decreasing electrophilicity from **2** with an early TS via **7** to **1** with a late TS.

The second phase is nucleophilic with the carbene σ orbital donating electron density into the σ* orbital of H_2, thus weakening the H−H bond. Although the philicity of carbenes can be predicted with some confidence, it is difficult to estimate whether tunneling influences the reaction rates significantly. To gain insight into hydrogenation reactions of singlet carbenes it is necessary to study substituent effects on tunneling[13,14] in a more systematic way. However, it is safe to predict that QMT plays a dominant role in hydrogenation reactions of both singlet and triplet carbenes at low temperatures.

Experimental Section

4,8-Dideuterio-azulenyldiazomethane (d_2-**8**) was prepared by thermal decomposition of the sodium salt of 4,8-dideutero-azulen-1-carbaldehyde tosylhydrazone and was directly used for the matrix isolation experiments as reported earlier.[12] H_2 (Air Liquide, 99.999%) and D_2 (Merck, 99.5%) were used as commercially available. HD was initially prepared by reacting $LiAlD_4$ with H_2O according to literature.[15] MS analysis showed a ratio of 100:4:0.4 for m/z 3:2:4. Additionally, experiments were carried out using commercially available HD (Sigma Aldrich, 96%).

The isomeric methylazulenes d_2-**10** and d_3-**10** were prepared by Wolff–Kishner–Huang–Minlon reduction of the corresponding aldehydes as described in literature.[16]

4,8-Dideuterio-1-methylazulene (d_2-**10**) from 4,8-dideutero-1-azulenylcarbaldehyde:[12] ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.70$ ppm (s, 3H, CH_3), 7.01–7.13 (m, 2H, H^5,H^7), 7.33 (d, $J = 3.7$ Hz, 1H, H^2), 7.54 (t, $J = 9.9$ Hz, 1H, H^6), 7.76 ppm (d, $J = 3.5$ Hz, 1H, H^3). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 12.89$, 116.53, 121.16, 121.95, 126.25, 136.39, 137.44, 138.12, 140.57 ppm. MS (EI): $m/z = 144$ (53%, M^+), 143 (100%, $M^+{-}H$), 117 (20%, $M^+{-}C_2H_3$). HRMS m/z calcd. for $C_{11}H_8D_2$: 144.09080; found: 144.08090.

α,4,8-Trideuterio-1-methylazulene (d_3-**10**) from α,4,8-trideuterio-1-azulenylcarbaldehyde:[12] ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.69$ (t, $J = 2.2$ Hz, 2H, CH_2D), 7.07 (d, $J = 10$ Hz, 1H, H^5 or H^7), 7.10 (d, $J = 9.9$ Hz, 1H, H^5 or H^7), 7.35 (d, $J = 3.7$ Hz, 1H, H^2), 7.55 (t, $J = 9.9$ Hz, 1H, H^6), 7.78 ppm (d, $J = 3.7$ Hz, 1H, H^3). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 12.64$ (t, $J = 19.3$ Hz, CH_2D), 116.50, 121.15, 121.94, 126.22, 137.45, 138.10, 140.50 ppm. MS (EI): $m/z = 145$ (60%, M^+), 144 (100%, $M^+{-}H$), 117 (25%, $M^+{-}C_2H_2D$). HRMS m/z calcd. for $C_{11}H_7D_3$: 145.09708; found: 145.07952.

All calculations were performed using Becke's three-parameter hybrid functional[17] and the correlation functional of Lee, Yang and Parr[18] (B3LYP) as implemented in Gaussian 09.[19] The 6-311+G-(d,p) basis set[20] was used for geometry optimization and vibrational frequency calculations. Minima and transitions structures were identified by their number of imaginary frequencies. For comparison of the relative energies, the geometries were re-optimized using the D3 empirical dispersion correction at the same level of theory.[21]

Keywords: carbenes · hydrogen activation · matrix isolation · spectroscopy · tunneling

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