The Rearrangement of the Cubane Radical Cation in Solution

Peter R. Schreiner,*[a] Alexander Wittkopp,[a] Pavel A. Gunchenko,[b] Alexander I. Yaroshinsky,[b] Sergey A. Peleshanko,[b] and Andrey A. Fokin*[b]

Abstract: The rearrangement of the cubane radical cation (**1**$^{\cdot+}$) was examined both experimentally (anodic as well as (photo)chemical oxidation of cubane **1** in acetonitrile) and computationally at coupled cluster, DFT, and MP2 [BCCD(T)/cc-pVDZ//B3LYP/6-31G* + ZPVE as well as BCCD(T)/cc-pVDZ//MP2/6-31G* + ZPVE] levels of theory. The interconversion of the twelve C_{2v} degenerate structures of **1**$^{\cdot+}$ is associated with a sizable activation energy of 1.6 kcal mol^{-1}. The barriers for the isomerization of **1**$^{\cdot+}$ to the cuneane radical cation (**2**$^{\cdot+}$) and for the C–C bond fragmentation to the secocubane-4,7-diyl radical cation (**10**$^{\cdot+}$) are virtually identical ($\Delta H_0^{\ddagger} = 7.8$ and 7.9 kcal mol^{-1}, respectively). The low-barrier rearrangement of **10**$^{\cdot+}$ to the more stable *syn*-tricyclooctadiene radical cation **3**$^{\cdot+}$ favors the fragmentation pathway that terminates with the cyclooctatetraene radical cation **6**$^{\cdot+}$. Experimental single-electron transfer (SET) oxidation of cubane in acetonitrile with photoexcited 1,2,4,5-tetracyanobenzene, in combination with back electron transfer to the transient radical cation, also shows that **1**$^{\cdot+}$ preferentially follows a multistep rearrangement to **6**$^{\cdot+}$ through **10**$^{\cdot+}$ and **3**$^{\cdot+}$ rather than through **2**$^{\cdot+}$. This was confirmed by the oxidation of *syn*-tricyclooctadiene (**3**), which, like **1**, also forms **6** in the SET oxidation/rearrangement/electron-recapture process. In contrast, cuneane (**2**) is oxidized exclusively to semibullvalene (**9**) under analogous conditions. The rearrangement of **1**$^{\cdot+}$ to **6**$^{\cdot+}$ via **3**$^{\cdot+}$, which was recently observed spectroscopically upon ionization in a hydrocarbon glass matrix, is also favored in solution.

Keywords: computer chemistry · cubanes · oxidation · radical ions

Introduction

While alkane radical cations play an increasingly important role in understanding some fundamental reaction mechanisms,[1, 2] our knowledge about the structures and energies of these highly reactive intermediates is still rather limited. This is due to the fast rearrangement or fragmentation of these so-called σ$^{\cdot+}$ species (C–C or C–H bonds are partially broken), which makes purely experimental investigations difficult. A case in point is the radical cation derived from cubane (**1**),[3, 4] which is probably one of the most rigid and strained hydrocarbons prepared to date. The exceptional kinetic stability of **1** is presumably due to the fact that breaking just one C–C bond homolytically[5] or heterolytically[6, 7] causes only minor changes in the cage structure and may simply not be enough for opening the entire cage.[8] Hence, the cubane radical cation (**1**$^{\cdot+}$) is expected to maintain some of the basic features of the cubane structure, at least at very low temperatures. It is not clear whether **1**$^{\cdot+}$ actually *was* observed by ESR spectroscopy; neither its structure nor the rearrangements of this fascinating molecule have been resolved. The present paper reports on a combined experimental/computational study on the structures and rearrangements on the $C_8H_8^{\cdot+}$ hypersurface starting from cubane.

Paquette et al. first claimed to have observed sharp ESR signals for **1**$^{\cdot+}$ in neon matrices at 4–9 K[9] but this finding was refuted later.[10] Eaton's subsequently recorded ESR spectrum[11] was first interpreted in terms of dynamically interconverting, Jahn–Teller distorted C_{2v} structures of **1**$^{\cdot+}$ but it was noted later "*…that the cubane radical cation was not observed previously…*".[10] Strong evidence for **1**$^{\cdot+}$ comes from a fluorescence-detected magnetic-resonance (FDMR) study at 190 K by Eaton et al.; fast equilibration of twelve equivalent C_{2v} structures (where one bond is suggested to be significantly lengthened in **1**$^{\cdot+}$) was indicated based on

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[a] Prof. Dr. P. R. Schreiner, Dipl. Chem. A. Wittkopp
Institut für Organische Chemie, Georg-August-Universität Göttingen
Tammannstr. 2, 37077 Göttingen (Germany) and
Department of Chemistry, The University of Georgia
Athens, GA 30602-2556 (USA)
Fax: (+1) 706-542-9454
E-mail: prs@sunchem.chem.uga.edu

[b] Prof. Dr. A. A. Fokin, Dr. P. A. Gunchenko, Dr. A. I. Yaroshinsky,
Dipl. Chem. S. A. Peleshanko
Department of Organic Chemistry, Kiev Polytechnic Institute
pr. Pobedy, 37, 252056 Kiev (Ukraine)
Fax: (+38) 044-274-20-04
E-mail: aaf@xtf.ntu-kpi.kiev.ua

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/or from the author. Table with relative and absolute energies and *xyz*-coordinates of all computed structures.

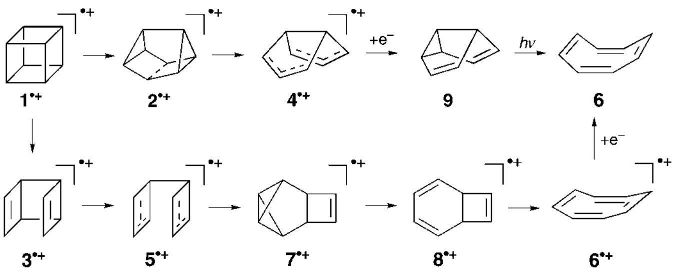
MINDO/3 calculations; however, no transition structures were computed, and it was noted that much higher level computations were needed to address this question properly.[11]

Two reaction pathways for $\mathbf{1}^{\cdot+}$ were previously proposed; that is, isomerization to the cuneane radical cation, $\mathbf{2}^{\cdot+}$, and C–C bond breaking to give the *syn*-tricyclooctadiene radical cation, $\mathbf{3}^{\cdot+}$ (Scheme 1).[11, 12] It was suggested that the isomerization of $\mathbf{1}^{\cdot+}$ via $\mathbf{2}^{\cdot+}$ to the bicyclooctadienediyl radical cation, $\mathbf{4}^{\cdot+}$, (Scheme 1) occurs under γ irradiation of **1** at 77 K in $CF_2ClCFCl_2$.[11, 12] In contrast, C–C bond cleavage of $\mathbf{1}^{\cdot+}$ to $\mathbf{3}^{\cdot+}$ and further to the bis(cyclobutenylium) radical cation, $\mathbf{5}^{\cdot+}$, was recently found under pulse radiolysis in hydrocarbon glasses at 30 K.[12] It was suggested that the latter reaction involves a [2π+2π]cycloreversion, because the ring opening of $\mathbf{1}^{\cdot+}$ is activated, in contrast to the reaction from $\mathbf{3}^{\cdot+}$ to $\mathbf{5}^{\cdot+}$ which occurs spontaneously.[12] The rearrangement of the strained radical cation $\mathbf{3}^{\cdot+}$, generated independently from the corresponding neutral molecule, to the cyclo-octatetraene radical cation ($\mathbf{6}^{\cdot+}$) via $\mathbf{7}^{\cdot+}$ and $\mathbf{8}^{\cdot+}$ was recently studied experimentally and computationally by Bally.[13]

Abstract in German: *Die Umlagerung des Cuban-Radikalkations (**1**$^{\cdot+}$) wurde sowohl experimentell (durch anodische bzw. photochemische Oxidation von Cuban (**1**) in Acetonitril) als auch mittels theoretischer Berechnungen auf dem Coupled Cluster-, Dichtefunktionaltheorie- und MP2-Niveau [BCCD(T)/cc-pVDZ//B3LYP/6-31G* + ZPVE und BCCD(T)/cc-pVDZ//MP2/6-31G* + ZPVE] untersucht. Die Umwandlung der zwölf entarteten* C_{2v}*-Strukturen von **1**$^{\cdot+}$ hat eine Aktivierungsbarriere von 1.6 kcal mol*$^{-1}$*. Die Barrieren für die Isomerisierung von **1**$^{\cdot+}$ in das Cunean- (**2**$^{\cdot+}$) bzw. in das Secocuban-4,7-diyl Radikalkation (**10**$^{\cdot+}$) sind praktisch identisch (*$\Delta H_0^{\ddagger} = 7.8$ *bzw. 7.9 kcal mol*$^{-1}$*). Die ebenfalls von niedrigen Barrieren begleitete Umlagerung von **10**$^{\cdot+}$ in das stabilere syn-Tricyclooctadien-Radikalkation **3**$^{\cdot+}$ ist etwas bevorzugt und ergibt schließlich das Cyclooctatetraen-Radikalkation **6**$^{\cdot+}$. Die Einelektronenoxidation (SET) von Cuban in Acetonitril (mittels photoangeregtem 1,2,4,5-Tetracyanbenzol, TCB) und Elektronen-Rücktransfer zum intermediären Radikalkation zeigt ebenfalls, daß **1**$^{\cdot+}$ vorzugsweise über **10**$^{\cdot+}$ und **3**$^{\cdot+}$ aber nicht über **2**$^{\cdot+}$ zu **6**$^{\cdot+}$ umlagert. Dies wurde durch die Oxidation von syn-Tricyclooctadien (**3**) gezeigt, welches, in Analogie zu **1**, ebenfalls **6** in einem SET-/Umlagerungs-/Elektroneneinfangschritt bildet. Im Gegensatz dazu lagert Cunean (**2**) nach der SET-Oxidation ausschließlich zu Semibullvalen (**9**) um. Die Umlagerung von **1**$^{\cdot+}$ zu **6**$^{\cdot+}$ über **3**$^{\cdot+}$, die kürzlich auch spektroskopisch in einer Kohlenwasserstoff-Matrix nachgewiesen wurde, ist damit auch in Lösung bevorzugt.*

Abstract in Ukrainian:

Досліджено перегрупування катіон-радикалу кубана $\mathbf{1}^{\bullet+}$ як експериментально (анодне та (фото)хімічне окиснення кубана **1** в ацетонітрилі), так і розрахунково на CC, DFT, та MP2 {BCCD(T)/cc-pVDZ//B3LYP/6-31G* + ZPVE та BCCD(T)/cc-pVDZ//MP2/6-31G* + ZPVE} рівнях теорії. Взаємоперетворення дванадцяти вироджених C_{2v}-структур $\mathbf{1}^{+}$ пов’язані з енергіями активації у 1.6 ккал моль$^{-1}$. Бар’єри ізомеризації $\mathbf{1}^{+}$ в катіон-радикал кунеана ($\mathbf{2}^{+}$) та розриву C–C зв’язку з утворенням секокубан-4,7-диільного катіон-радикалу ($\mathbf{10}^{+}$) майже ідентичні ($\Delta H_0^{\ddagger} = 7.8$ та 7.9 ккал моль$^{-1}$, відповідно). Низькобар’єрне перегрупування $\mathbf{10}^{+}$ у більш стабільний *син*-трициклооктадієнільний катіон-радикал $\mathbf{3}^{+}$ йде шляхом фрагментації, яка закінчується утворенням циклооктатетраєнільного катіон-радикала ($\mathbf{6}^{+}$). Експериментальне одноелектронне окиснення кубана в ацетонітрилі (фотоініційоване 1,2,4,5-тетраціанобензолом), разом із поверненням електрону до нестійкого катіон-радикалу показує, що $\mathbf{1}^{+}$ зазнає багатоступеневого перетворення у $\mathbf{6}^{+}$ більш ймовірно через $\mathbf{10}^{+}$ та $\mathbf{3}^{+}$, ніж через $\mathbf{2}^{+}$. Це було підтверджено окисненням *син*-трициклооктадієну (**3**), який, як і **1**, утворює **6** в умовах SET окиснення/перегруппування/відновлення. У той же час, кунеан (**2**) у аналогічних умовах окиснюється з утворенням семібульвалену (**9**). Перегрупування $\mathbf{1}^{+}$ у $\mathbf{6}^{+}$ через $\mathbf{3}^{+}$, яке спектрально досліджене при іонізації у вуглеводнево-скляній матриці домінує також і у розчині.



Scheme 1. Two pathways to cyclooctatetraene **6** from the cubane radical cation $\mathbf{1}^{\cdot+}$.

In the present paper we report high-level computational details for the transformation of $\mathbf{1}^{\cdot+}$ to $\mathbf{6}^{\cdot+}$, as well as experimental data on the behavior of cubane and some related C_8H_8 hydrocarbons under oxidative conditions in solution. Since Eaton pointed out that the difficulty in elucidating the intricacies of the rearrangements of $\mathbf{1}^{\cdot+}$ lies in the identification of the intermediates and products, we envisaged that combining an oxidative single-electron transfer (SET) step with back electron transfer (ET)[14] from the oxidant to the transient radical cations, would be a useful approach to this problem.

Results and Discussion

Although we have had positive experience[15, 16] with density functional theory (DFT)[17] for treating radical cations, the applicability of DFT to these species is still under a lot of discussion.[18–21] Therefore, we utilized both DFT (B3LYP/6-31G*) and Møller–Plesset (MP2/6-31G*)[22] second-order perturbation theory in combination with coupled-cluster single-point energies.[23–28] The slightly lower absolute BCCD(T) energies for the DFT structures favor the topology of the respective potential energy surfaces (PES) at B3LYP slightly.

The interconversion of the degenerate C_{2v} structures of $\mathbf{1}^{\cdot+}$ (Figure 1) via $\mathbf{TS}_{1\text{-}1}$ is associated with a sizable activation energy of 1.6 kcal mol^{-1} at 0 K. As a consequence, $\mathbf{1}^{\cdot+}$ undergoes dynamic Jahn–Teller averaging of static C_{2v} structures as suggested by Eaton et al.[10] A comparison of our BCCD(T)-computed and Eaton's published ESR[11] spectra of $\mathbf{1}^{\cdot+}$ (Figure 2) strongly supports this analysis. The computed spectra both for $\mathbf{1}^{\cdot+}$ and $\mathbf{TS}_{1\text{-}1}$ agree well with the neon-matrix ESR. The ESR spectra may be interpreted on the

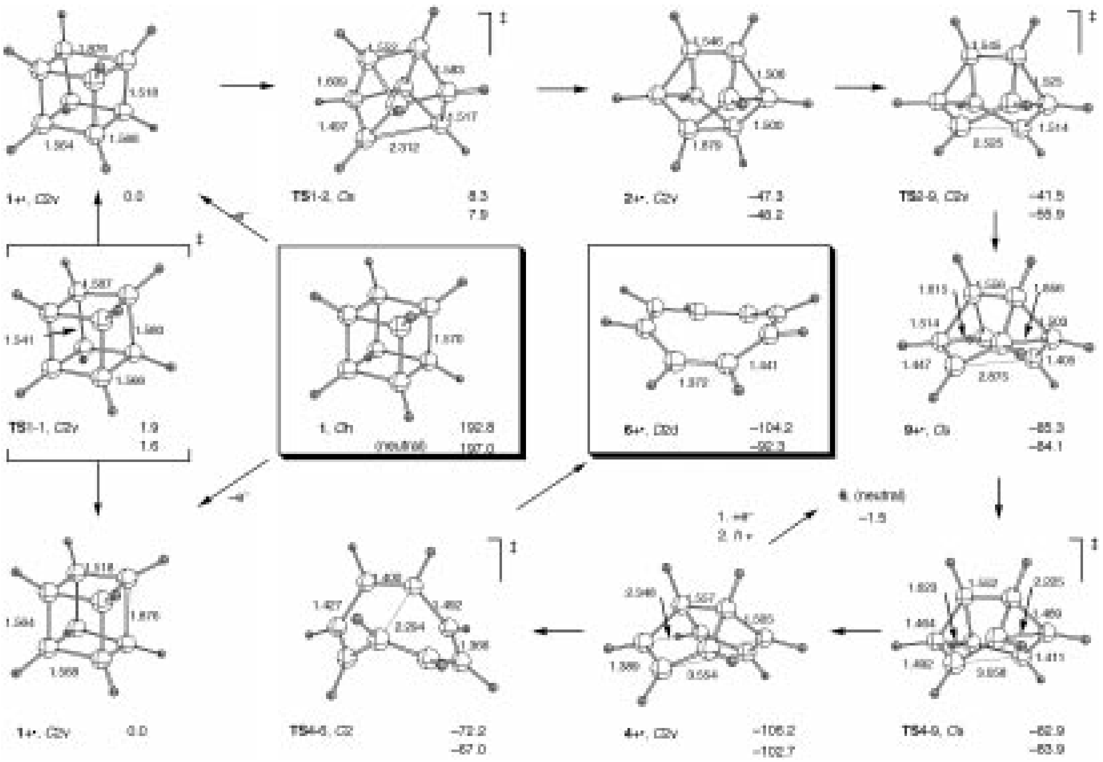


Figure 1. B3LYP/6-31G* optimized $C_8H_8^{\bullet+}$ structures relevant to the rearrangement of the cubane radical cation ($\mathbf{1}^{\bullet+}$); relative energies in kcal mol^{-1}; bond distances in Å; first entry: B3LYP/6-31G* + ZPVE; second entry: BCCD(T)/cc-pVDZ//B3LYP/6-31G* + ZPVE.

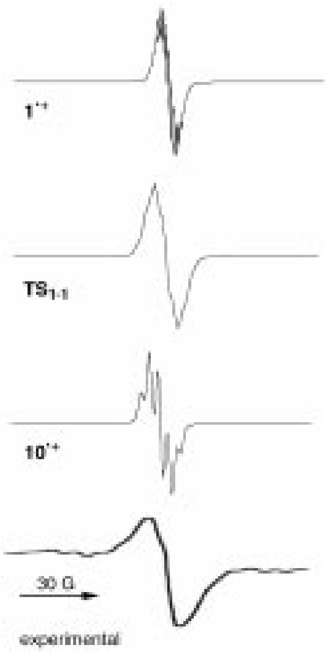
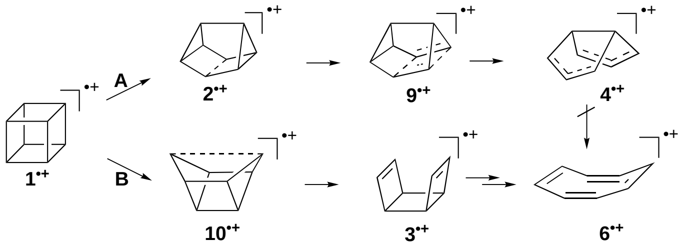


Figure 2. Comparison of the simulated ESR spectra for $\mathbf{1}^{\bullet+}$, $\mathbf{TS}_{1\text{-}1}$, and $\mathbf{10}^{\bullet+}$ (0 K) at BCCD(T)/cc-pVDZ with the experimental ESR spectrum for $\mathbf{1}^{\bullet+}$ (77 K, bottom, scanned from ref. [11] with permission). $\mathbf{TS}_{1\text{-}1}$ represents the averaged spectrum for rapidly interconverting, degenerate isomers of $\mathbf{1}^{\bullet+}$.

basis of the rapidly equilibrating minima of $\mathbf{1}^{\bullet+}$: as the ESR spectrum of $\mathbf{1}^{\bullet+}$ is already narrow and is dominated by a sine-shaped base peak, the averaged spectrum shows even less structure and resembles that of $\mathbf{TS}_{1\text{-}1}$.

In analogy to some other $C_8H_8^{\bullet+}$ species, $\mathbf{1}^{\bullet+}$ may eventually rearrange (pathway **A**, Scheme 2) to the cuneane radical cation, $\mathbf{2}^{\bullet+}$, and then to $\mathbf{4}^{\bullet+}$, which is the computed global minimum on this part of the $C_8H_8^{\bullet+}$ PES. Structure $\mathbf{4}^{\bullet+}$ may be considered as the "open form" of the semibullvalene radical cation, $\mathbf{9}^{\bullet+}$ (Figure 1);[29, 30] a barrier of 35.7 kcal mol^{-1} precludes the expansion of $\mathbf{4}^{\bullet+}$ to $\mathbf{6}^{\bullet+}$ (the reversible reaction is known).[13, 30–32]



Scheme 2. The two rearrangement pathways for the cubane radical cation ($\mathbf{1}^{\bullet+}$).

We also computed the C–C bond fragmentation pathway **B** for the cubane radical cation $\mathbf{1}^{\bullet+}$ (Scheme 2 and Figure 3). Breaking one of the C–C bonds in $\mathbf{1}^{\bullet+}$ leads to the secocubane-4,7-diyl radical cation, $\mathbf{10}^{\bullet+}$, which is a true and thus far unrecognized minimum on the $C_8H_8^{\bullet+}$ PES; $\mathbf{10}^{\bullet+}$ is 8.5 kcal mol^{-1} more stable than $\mathbf{1}^{\bullet+}$. The barrier for this C–C bond cleavage via $\mathbf{TS}_{1\text{-}10}$ (7.8 kcal mol^{-1}) is virtually the same as that for the isomerization of $\mathbf{1}^{\bullet+}$ to $\mathbf{2}^{\bullet+}$ via $\mathbf{TS}_{1\text{-}2}$ (7.9 kcal mol^{-1}). At the same time pathway **B** is more

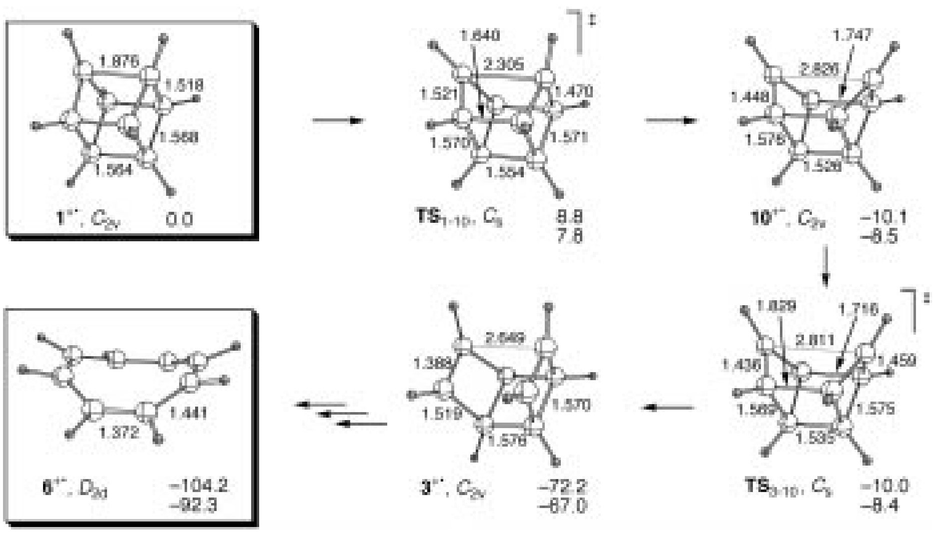
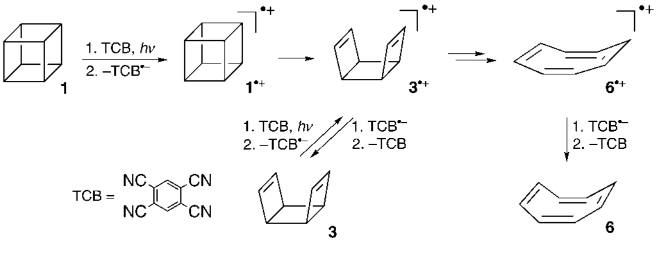


Figure 3. B3LYP/6-31G* optimized $C_8H_8^{\bullet+}$ structures relevant to the C–C bond cleavage of the cubane radical cation ($1^{\bullet+}$); relative energies in kcal mol^{-1}; bond distances in Å; first entry: B3LYP/6-31G* + ZPVE; second entry: BCCD(T)/cc-pVDZ//B3LYP/6-31G* + ZPVE.

favorable due to the substantial strain relief in the tricyclooctadiene radical cation $3^{\bullet+}$ (the C–C bond cleavage in $10^{\bullet+}$ that leads to $3^{\bullet+}$ proceeds via the low-lying $TS_{3\text{-}10}$ with $\Delta H_0^{\ddagger} <$ 1 kcal mol^{-1}). The ESR spectrum computed for $10^{\bullet+}$ (Figure 2) is clearly different from that of $1^{\bullet+}$. Thus, the break down of the cubane cage in $1^{\bullet+}$ occurs in a stepwise fashion. Despite extensive efforts, we were unable to locate a transition structure for the concerted $[2\pi + 2\pi]$ cycloreversion of $1^{\bullet+}$ to $3^{\bullet+}$.

Our computations show that pathway **A** is thermodynamically less favorable than **B** due to the substantial strain relief in $3^{\bullet+}$ compared with $2^{\bullet+}$ (18.8 kcal mol^{-1}). This is in agreement with results obtained for the ionization of **1** in hydrocarbon glasses under pulse radiolysis at 30 K,[12] where the intermediate bond-cleavage product $5^{\bullet+}$ (Scheme 1) as well as the final product radical cation $6^{\bullet+}$ were identified by electronic absorption spectroscopy. The unexpected product, radical cation $4^{\bullet+}$, which could formally be attributed to pathway **A**, was observed[12] under γ-irradiation of cubane. As we suspected that this was due to matrix effects or secondary reactions, we decided to study the SET oxidation of **1** with 1,2,3,5-tetracyanobenzene (TCB) in solution. When hydrocarbons are oxidized by photoexcited aromatics, back ET is a favored process,[33–38] and the transient radical cations may be trapped efficiently.

The photo-oxidation of **1** with TCB in acetonitrile at −40 °C gave cyclooctatetraene **6** (Scheme 3). At shorter reaction times substantial amounts of *syn*-tricyclooctadiene **3** were found together with **6**. Independent oxidation of **3** with TCB gave only **6**. Conversion of **1** to the neutral **6**, as well as to **3**, certainly involves SET oxidation followed by back ET: extended photo-irradiation of **1** or **3** in the absence of TCB did *not* give **6** and the starting hydrocarbons were recovered quantitatively.



Scheme 3. Photooxidation of cubane (**1**) and *syn*-tricyclooctadiene (**3**) with TCB.

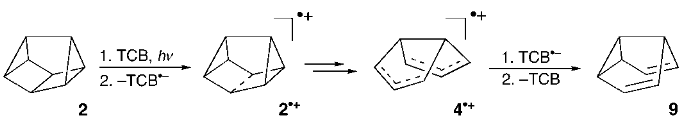
Thus, cubane may undergo an SET oxidation/photochemical rearrangement to cyclooctatetraene **6** via $3^{\bullet+}$. At the same time, the barriers for the isomerization of $1^{\bullet+}$ to $2^{\bullet+}$ and fragmentation of $1^{\bullet+}$ to $3^{\bullet+}$ are similar and two parallel processes cannot be excluded. Moreover, due to fast back ET, we cannot yet distinguish between pathways **A** and **B** (Scheme 2), because semibullvalene **9** may photochemically rearrange to cyclooctatetraene **6** (**A**):[14]

$$1^{\bullet+} \rightarrow 2^{\bullet+} \rightleftharpoons 4^{\bullet+} \xrightarrow{e^-} 9 \xrightarrow{h\nu} 6 \qquad \text{(A)}$$

$$1^{\bullet+} \rightarrow 10^{\bullet+} \rightarrow 3^{\bullet+} \rightleftharpoons 6^{\bullet+} \xrightarrow{e^-} 6 \qquad \text{(B)}$$

Trapping of the intermediates was attempted by anodic oxidation of **1** in acetonitrile, but only a mixture of quite a number of inseparable $C_8H_7NHCOCH_3$ isomers was observed (gas chromatography/mass spectrometry).

To elucidate this point further and to differentiate between pathways **A** and **B**, we oxidized cuneane (**2**) with TCB; only semibullvalene **9** was formed, apparently after back ET to $4^{\bullet+}$ (Scheme 4). Hydrocarbon **9** was stable under these conditions and could be isolated.



Scheme 4. Photooxidation of cuneane (**2**) with TCB.

The observed SET rearrangement of **2** to **9** after electron recapture is clearly different from that of cubane **1**. Thus, the rearrangement of the cubane radical cation $1^{\bullet+}$ in solution indeed initially follows fragmentation to $3^{\bullet+}$, rather than isomerization to $2^{\bullet+}$. This is similar to the behavior of **1** under pulse radiolysis in hydrocarbon glasses at 30 K, in which pathway **B** is apparently followed.[12] We can therefore conclude that $2^{\bullet+}$ is *not* involved in the cubane radical cation rearrangements and that **1** follows the same reaction pattern for oxidation in matrix conditions and in solution.

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Conclusion

As predicted by Eaton et al., the cubane radical cation $\mathbf{1}^{\bullet+}$ equilibrates with its degenerate isomers (we computed a barrier of 1.6 kcal mol^{-1}). As the barrier for the rearrangement of $\mathbf{1}^{\bullet+}$ to $\mathbf{10}^{\bullet+}$ is sizable (about 7.9 kcal mol^{-1}) Eaton must have observed the ESR spectrum of $\mathbf{1}^{\bullet+}$.

The first step in the rearrangement of $\mathbf{1}^{\bullet+}$ is either isomerization to the cuneane radical cation, $\mathbf{2}^{\bullet+}$ (pathway **A**) or C–C bond breaking to the secocubane-4,7-diyl radical cation, $\mathbf{10}^{\bullet+}$ (pathway **B**—the first C–C bond cleavage). The latter is followed by rearrangement to the *syn*-tricyclooctadiene radical cation, $\mathbf{3}^{\bullet+}$ (low-barrier second C–C bond cleavage). Pathway **B** is favored thermodynamically because $\mathbf{3}^{\bullet+}$ is 18.8 kcal mol^{-1} more stable than $\mathbf{2}^{\bullet+}$. While pathway **A** terminates with the reduction of the bicyclooctadienediyl radical cation $\mathbf{4}^{\bullet+}$ to semibullvalene **9**, pathway **B** gives the cyclooctatetraene radical cation $\mathbf{6}^{\bullet+}$. We identified the two pathways based on the structural analysis of the isolated neutrals.

As only **9** was found in the oxidation of **2** with photoexcited TCB, and as the oxidation of **1** leads exclusively to **6** (via **3**), $\mathbf{1}^{\bullet+}$ must follow pathway **B**. Hence, $\mathbf{2}^{\bullet+}$ is probably *not* involved in the rearrangement of $\mathbf{1}^{\bullet+}$ to $\mathbf{6}^{\bullet+}$.

Thus, the C–C bond fragmentation of cubane, which was spectroscopically observed recently for the ionization of **1** in the solid state, takes place similarly in solution.

Computational methods: The B3LYP and MP2 methods with 6-31G* basis set were used as implemented in Gaussian 98[39] for geometry optimizations and harmonic vibrational frequency analyses (NIMAG = 0 for minima and 1 for transition structures). The reaction pathways along both directions from the transition structures were followed by the intrinsic reaction coordinate[40] method. Coupled-cluster single-point energies utilizing Brueckner-type orbitals [BCCD(T)][41, 42] with a cc-pVDZ basis set[43, 44] and zero-point B3LYP and MP2 vibrational energies (ZPVE, unscaled) were used to improve the energies. Unless noted otherwise, our final energies refer to BCCD(T)/cc-pVDZ//B3LYP/6-31G* + ZPVE; the MP2 results are available in the Supporting Information.

Experimental Section

All NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz (^{1}H NMR) or 75 MHz (^{13}C NMR) in $CDCl_3$ solutions. The chemical shifts are given on the δ scale in ppm; internal standard: HMDS. All compounds show adequate IR and distortionless enhancement by polarization transfer ^{13}C NMR spectra. The GC/MS analyses were carried out by using a HP 5890 Series II gas chromatograph (column HP Ultra1 50 m × 0.2 mm × 0.33 mm film: cross linked methyl silicone) with a HP 5971A mass detector. A standard 150 W UV lamp (maximum emission 300 nm) was used for the photochemical experiments.

Photo-oxidation of cubane 1 with TCB: Method **A**: A solution of **1** (104 mg, 1.0 mmol) and TCB (151 mg, 0.8 mmol) in acetonitrile (120 mL) was irradiated under argon at −40 °C with a 150 W lamp (maximum emission at 300 nm) for 10 h. Acetonitrile was removed in vacuo (200 mbar), the residue was then diluted with water (10 mL) and extracted with 2-methylbutane (5 × 30 mL). The combined extracts were washed with water and brine, and were dried over Na_2SO_4. The solvent was removed at atmospheric pressure by using a Vigreux column (200 mm). Separation of the residue on a silica gel column (40 cm × 1.5 cm, Merck Kieselgel 60, 0.063–0.1 mm) with 2-methylbutane as eluant gave 41 mg (39 %) of **1**, 18 mg of **3** (17 %), and 35 mg of **6** (34 %), which are identical from NMR and MS data to standard samples.

The reaction was carried out as above for 2 h. The ^{1}H NMR ($CDCl_3$) of the reaction mixture shows the signals of the cubane **1**: 4.03 (s, 91 %), cyclooctatetraene **6**: 5.80 (s, 3 %), and *syn*-tricyclooctadiene **3**: 3.21 (m), 6.02 (m), 6 %.

Photo-oxidation of syn-tricyclo-octadiene 3[45] with TCB: A solution of **3** (52 mg, 0.5 mmol) and TCB (75 mg, 0.4 mmol) in acetonitrile (60 mL) was irradiated as in **A**. The ^{1}H NMR of the reaction mixture shows the signals of **3** (54 %) and **6** (46 %).

Photo-oxidation of cuneane 2[46] with 1,2,3,4-tetracyanobenzene (TCB): A solution of **2** (52 mg, 0.5 mmol) and TCB (75 mg, 0.4 mmol) in acetonitrile (60 mL) was irradiated for 4 h as in **A**. Column chromatography gave 41 mg (79 %) of semibullvalene **9**. ^{1}H NMR ($CDCl_3$): $\delta = 5.25$ (m, 2H), 4.25 (m, 4H), 3.04 (m, 2H)—identical to as previously described.[47]

Electro-oxidation of cubane 1: A mixture of **1** (104 mg, 1.0 mmol) in acetonitrile (75 mL) and NH_4BF_4 (150 mg, 1.4 mmol) was placed into a glass cell with Pt electrodes and subjected to direct current at 2.4 V anode potential for 36 h. The reaction mixture was diluted with water (5 mL), the acetonitrile was evaporated and worked up as described in **A**; 68 mg of **1** were recovered. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (20 mL), washed with water and brine, and dried, and the solvents were removed in vacuo. The residue (47 mg) was purified by flash chromatography on silica gel (diethyl ether/methanol 10:1) and analyzed by GC/MS (HP 5890 Series II GC with HP 5971A MSD, capillary column HP Ultra1, 50 m × 0.2 mm × 0.33 m film, $T = 80-200$ °C, 10 °C min^{-1}, mass selective detector) and showed the following main peaks characteristic for isomeric monoacetamides: 24.74 min (161, 8 %; 118, 100 %; 104, 3 %; 91, 36 %; 65, 9 %); 25.33 min (161, 15 %; 138, 11 %; 118, 100 %; 91, 27 %); 25.69 min (161, 4 %; 118, 100 %; 91, 30 %); 26.35 min (161, 1 %; 118, 100 %; 102, 15 %; 91, 27 %).

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