PERKIN 2

Radical cations of perinaphthocyclopropanes. Conditions for the observation of 1,3-perinaphthadiyl radical cations†

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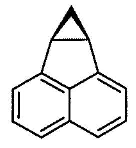
γ-Irradiation of 7,7a-dihydro-6b*H*-cycloprop[*a*]acenaphthylene (**1**) and its 7,7-dimethyl derivative (**2**) in haloalkane glasses at 77 K yields persistent parent radical cations of these compounds. On visible irradiation, $\mathbf{1}^{\cdot+}$ is transformed into the radical cation of phenalene, $\mathbf{3}^{\cdot+}$, which was also generated independently from neutral **3**. The transformation $\mathbf{1}^{\cdot+}\rightarrow\mathbf{3}^{\cdot+}$ presumably proceeds by opening of the central cyclopropane bond and subsequent H-shift in the resulting perinaphthadiyl radical cation which is, however, not observed. Surprisingly, the dimethyl derivative, $\mathbf{2}^{\cdot+}$, is also transformed into a phenalene radical cation by visible photolysis. In this case the mechanism is probably a different one, involving a distonic diyl cation obtained by cleavage of a lateral cyclopropane bond. In contrast to the above, the ring opening of the dicyclopropa[*a*,*g*]pyracyclene **4** radical cation proceeds stepwise, and the perinaphthadiyl cation intermediate can be observed. A second photochemical ring opening yields the radical cation of 2,7-dihydro-2,2,7,7-tetramethylpyrene that was generated independently from the neutral precursor.

The electronic absorption spectra of all observed radical cations are discussed in conjunction with the corresponding photoelectron spectra (where available) and with quantum chemical calculations.

1. Introduction

1,8-Naphthoquinodimethane[1] and its alkane-bridged derivatives, the 1,*n*-perinaphthadiyls¶ (**PD**, $n = 3,4$),[2–7] are non-Kekulé diradicals, each of which has a triplet ground state.[8] They have been characterized spectroscopically as persistent species in solid glasses or matrices and as transient intermediates in solution. Intramolecular stabilization of such triplet diradicals by bond formation, for example the ring closure of **PD** ($n = 3$) to perinaphthocyclopropane (7,7a-dihydro-6b*H*-cycloprop[*a*]acenaphthylene **1**), is inhibited by a "spin barrier", namely the requirement of triplet–singlet intersystem crossing at some point along the reaction path. That impediment is lost upon removal of an electron to form the radical cation doublet states of the reactants.

On the other hand, ionization tends to reduce the thermochemical driving force for bond formation; this is reflected in the fact that the ionization potential of the diradical (*e.g.* **PD**, $n = 3$) is generally much lower than that of the corresponding closed-shell product (**1**). Moreover, state symmetry may impose reaction barriers in radical cation interconversions that do not exist for their neutral counterparts. Thus, rearrangements of radical cations will often lead to products not formed from the parent neutral compounds, and this fact is increasingly exploited in reactions initiated by single electron transfer. For preparative purposes the reactive radical cation in termediates may be generated by chemical or electrochemical oxidation, photoinduced electron transfer or by inclusion in zeolites.[9]



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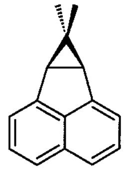

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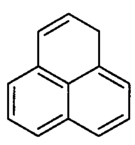

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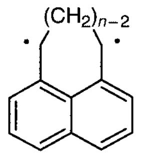

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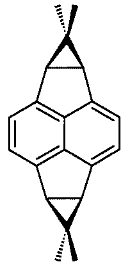

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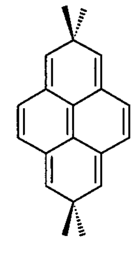

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We have recently been able to characterize the radical cation of 1,4-perinaphthadiyl[10] as an intermediate in the photochemical valence isomerization of perinaphthocyclobutane (cyclobut[*a*]acenaphthylene) radical cation to 1,8-divinylnaphthalene radical cation. Here we report on the photoreactions of perinaphthocyclopropane radical cations. Parent perinaphthocyclopropane (**1**), its 7,7-dimethyl derivative **2**, as well as the dicyclopropa[*a*,*g*]pyracyclene **4**,|| were ionized to their radical cations $\mathbf{1}^{\cdot+}$, $\mathbf{2}^{\cdot+}$ and $\mathbf{4}^{\cdot+}$ by γ-irradiation in Freon glasses.

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† Total energies and cartesian coordinates of the stationary points corresponding to the species in this study are available in ASCII format as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b002808h/

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¶ The IUPAC names for 1,3- and 1,4-perinaphthadiyls are 2,3-dihydro-1*H*-phenalene-1,3-diyl and 7,8,9,10-tetrahydrocyclohepta[*de*]naphthalene-7,10-diyl, respectively.

|| IUPAC name for **4**: 1,1,4,4-tetramethyl-1,1a,3b,4,4a,6b-hexahydrocyclopropa[*a*]cyclopropa[4,5]cyclopenta[1,2,3-*fg*]acenaphthylene.

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In the course of this work it proved necessary to look also at the radical cations of phenalene (**3**) and the 2,7-dihydropyrene **5**, which appeared as secondary photochemical products of the ring opening of $\mathbf{1}^{\cdot+}$ and $\mathbf{4}^{\cdot+}$, respectively. Although the ring opening of the central cyclopropane bond in $\mathbf{1}^{\cdot+}$ is calculated to be exothermic, a facile 1,2-H shift of the resulting **PD** radical cation leads directly to the more stable phenalene radical cation $\mathbf{3}^{\cdot+}$. Surprisingly, substitution of the apical position by two methyl groups does not protect $\mathbf{2}^{\cdot+}$ from decay to a dimethylphenalene radical cation. However, the second fused cyclopropane group in **4** leads to a kinetic stabilization of the corresponding **PD** radical cation, which can then be observed. Further photolysis leads to cleavage of the second cyclopropane ring and formation of the cross-conjugated polyene radical cation, $\mathbf{5}^{\cdot+}$.

2. Methods

Materials

Compounds **2**, **4**, and **5** were samples left from earlier work[2,5] and were purified by recrystallization before use. Compound **1** was synthesized according to the procedure of Wittig *et al.*[11]

Matrix isolation spectroscopy

Solutions of the precursors ($1–5 \times 10^{-3}$ M) in a mixture of Freons (equal parts of $CFCl_3$ and CF_2BrCF_2Br)[12,13] or *n*-butyl chloride–isopentane[14,15] were exposed to ≈0.5 Mrad of ^{60}Co γ-irradiation at 77 K. Electronic absorption (EA) spectra were recorded from 190 to 1500 nm with a Perkin-Elmer Lambda 900 instrument.

Photoelectron spectroscopy

Photoelectron (PE) spectra were recorded on a modified Perkin-Elmer PE16 spectrometer operated in preretardation (and hence constant resolution) mode under computer control.[16] Calibration was effected with a Xe–Ar mixture and the spectral resolution was 12 meV (digital resolution 2 meV).

Quantum chemical calculations

The geometries of all species were optimized by the B3LYP density functional method[17–19] as implemented in the Gaussian packages of programs,[20] using the 6-31G* basis set. For the C_{13} and C_{15} hydrocarbons, the stationary points were identified by second derivative calculations at the same level.

Two models were used in calculations of excited states: wherever possible we used the CASSCF/CASPT2 procedure[21] as provided in the MOLCAS program.[22] The active spaces were chosen such that the weight of the CASSCF wavefunction in the final CASPT2 wavefunction was between 60 and 65% for all states considered (a description of the active spaces for each molecule is given in the footnotes to Tables 1–3). As in previous cases of radical cations,[23] satisfactory agreement with experiment was obtained with the [C]3s2p1d/[H]2s ANO-L double zeta basis set;[24] therefore we saw no necessity to add higher angular momentum or diffuse functions. Transition moments were calculated on the basis of the CASSCF wavefunctions, using CASPT2 energy differences in the denominator.

For the C_{20} hydrocarbons, where CASPT2 calculations were not feasible due to excessive memory and CPU time requirements, we resorted to the semiempirical INDO/S-CI procedure[25] based on ROHF orbitals, whereby only singly excited configurations were taken into account. The INDO/S-CI calculations were performed with the ZINDO program.[26] Molecular orbitals were plotted with the MOPLOT program,[27] which gives a schematic representation of the MO's nodal structures in a ZDO-type approximation.[28]

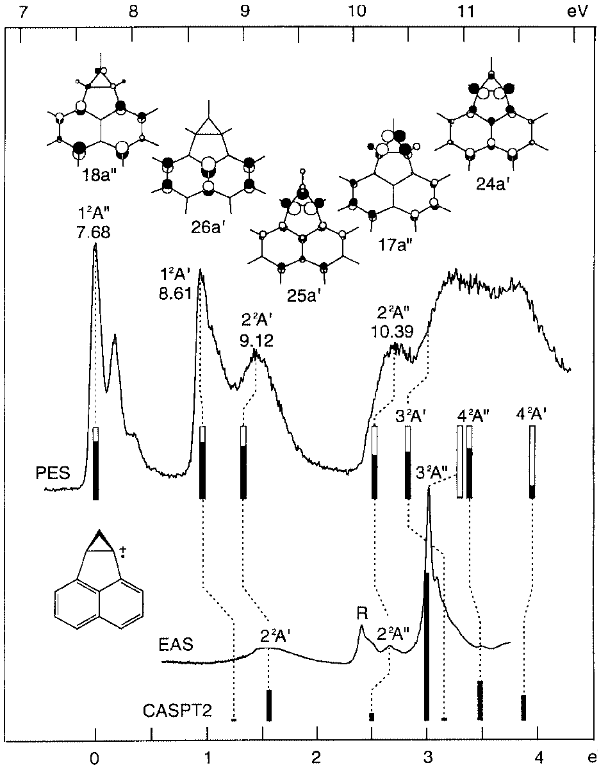

Fig. 1 Photoelectron spectrum (PES, upper trace) of cycloprop[*a*]acenaphthylene, **1**, and electronic absorption spectrum (EAS) of its radical cation, drawn on a common energy scale. The bars denote the results of the CASPT2 calculations listed in Table 1, where the height is proportional to the oscillator strength of the electronic transitions (EAS) and the black portion is proportional to the Koopmans character of the excited states (which is proportional to the intensity of PE bands).

3. Results and discussion

3.1. The radical cation of the cycloprop[*a*]acenaphthylene, $\mathbf{1}^{\cdot+}$

Fig. 1 shows the electronic absorption (EA) spectrum obtained after γ-irradiation of 7,7a-dihydro-6b*H*-cycloprop[*a*]acenaphthylene (**1**) in a Freon matrix at 77 K. It is shown on the same energy scale as the photoelectron (PE) spectrum and the results of the CASPT2 caculations, which are numerically listed in Table 1. The PE and EA spectra have similar appearances to those of acenaphthylene[29] and they match well with the theoretical predictions and with the qualitative expectations, as discussed below.

The first transition ($1^2A''\rightarrow1^2A'$), which is dipole forbidden in the parent naphthalene radical cation,[29] carries too little oscillator strength (*cf.* Table 1) to allow its detection in $\mathbf{1}^{\cdot+}$. This observation is in accord with the fact that the highest two occupied π-MO's of naphthalene are only slightly perturbed by the cyclopropane moiety. In contrast, the second excited state (third PE band) is well described by excitation (ionization) from the symmetric Walsh MO that is largely localized on the cyclopropane moiety. Loss of an electron from that MO leads to a pronounced weakening of the central bond. As a consequence, both the corresponding PE and EA bands are much broader than in other naphthalene derivatives and they also occur at lower energy. The energy and electronic structure of the $2^2A'$ state calculated by the CASSF/CASPT2 method do not change much on going from the optimized geometry of **1** to that of $\mathbf{1}^{\cdot+}$. The predicted energy is about 0.2 eV too low in both cases.

The next band (marked R) in the EA spectrum is not due to $\mathbf{1}^{\cdot+}$, as it appears with variable relative intensity in different samples. Its position (19500 cm^{-1} or 513 nm) coincides precisely with a strong peak in the excitation spectrum of the phenalenyl radical,[30] which we consider as a likely secondary product. The

Table 1 Excited states of the radical cation of 6b,7a-dihydro-7*H*-cycloprop[*a*]acenaphthylene ($\mathbf{1}^{\bullet+}$)

	Neutral equilibrium geometry					Radical cation equilibrium geometry				
		CASPT2					CASPT2			
States	PES[a] *E*/eV	*E*/eV	*K*(%)[e]	CASSCF[b] *E*/eV	CASSCF Configurations[d]	EAS[c] *E*/eV	*E*/eV	*f*[f]	CASSCF[b] *E*/eV	CASSCF Configurations[d]
$1^2A''$	(7.68)[g]	(0)	81	(0)	81% Ground conf.	(0)	(0)	—	(0)	80% Ground config.
$1^2A'$	0.93	0.96	79	0.72	79% 26a′→18a″	—	1.24	1.8×10^{-4}	1.10	78% 26a′→18a″
$2^2A'$	1.44	1.33	75	1.49	70% 25a′→18a″	1.55	1.56	0.0346	1.74	71% 25a′→18a″
					5% 24′a→18a″	(m)				
$2^2A''$	2.71	2.53	60	2.85	59% 17a″→18a″	2.66	2.50	0.0092	2.90	44% 17a″→18a″
					7% *18a″→19a″*	(w)				27% *18a″→19a″*
$3^2A'$	≈3	2.83	64	3.51	64% 24a′→18a″	—	3.16	6.7×10^{-5}	3.84	58% 24a′→18a″
										5% *18a″→27a′*
$3^2A''$	–	3.30	1	3.55	55% 18a″→19a″	3.02	3.00	0.1684	3.34	*38% 18a″→19a″*
					+ *doubly exc. conf.*	(s)				17% 17a″→18a″
										+ *doubly exc. conf.*
$4^2A''$	—	3.39	69	4.29	69% 16a″→18a″	(3.5)	3.49	0.0454	4.30	67% 16a″→18a″

[a] Photoelectron spectrum of **1** *cf.* Fig. 1. [b] Active space: 13 electrons in 4 occupied + 3 virtual MO's of a′ symmetry, and in 3 occupied + 2 virtual MO's of a″-symmetry. [c] Electronic absorption spectrum of $\mathbf{1}^{\bullet+}$, *cf.* Fig. 1. [d] In terms of single excitations between the MO's depicted in Fig. 1; excitations into virtual orbitals are in italics. [e] Percent Koopmans character, proportional to intensity of PE band. [f] Oscillator strength for electronic transition, computed on the basis of the CASSCF wavefunction, using the CASPT2 energy difference in the denominator. [g] First ionization potential of **1**, origin of energy scale for excited states.

next, weak band at 2.66 eV coincides with the 4th PE band and, according to the CASPT2 calculations, it is due to excitation to the second $^2A''$ state. At the geometry of neutral **1** this corresponds mostly to ionization from the 17a″ MO that is localized largely on the cyclopropane ring (antisymmetric Walsh MO). However, at the cation geometry, the HOMO→LUMO excitation begins to gain more importance. This configuration dominates the next excited state $3^2A''$ that gives rise to the intense peak at 3 eV in the EA spectrum of $\mathbf{1}^{\bullet+}$, and is characteristic of naphthalene cations. That state carries very little Koopmans character.†† Hence it is unlikely to contribute much intensity to the PE spectrum of **1**. The large hump between 10.5 and 12 eV is due to ionization from lower lying MO's such as 24a′ and 16a″. Note that the corresponding states, $3^2A''$ and $4^2A''$, are again predicted to be slightly too low in energy by the CASPT2 method.

3.2. The radical cation of 1*H*-phenalene ($\mathbf{3}^{\bullet+}$)

On irradiation with a cutoff filter transmitting at >540 nm, the EA spectrum of $\mathbf{1}^{\bullet+}$ changes to a new one that has a similar, yet distinct appearance (Figs. 2a and b), and turns out to be almost identical to that obtained on ionization of 1*H*-phenalene **3** (Fig. 2c), an isomer of **1**. Both spectra show the sharp peak at 19500 cm^{-1} that is indicative of the phenalenyl radical. In addition, the spectrum obtained from **3** shows a band at 25000 cm^{-1} (present as a shoulder in spectrum b of Fig. 2), which may be due to phenalenyl cation.[31] If the phenalenyl radical is formed, then it is to be expected that some of it would also become ionized, hence the 25000 cm^{-1} band of the phenalenyl cation is not unexpected.

To our knowledge, the PE spectrum of **3** has never been published and we therefore show it in Fig. 3, together with the EA spectrum of $\mathbf{3}^{\bullet+}$ from Fig. 2 and a schematic representation of the appropriate CASPT2 results. The spectra, and hence the electronic structure of $\mathbf{3}^{\bullet+}$, show very similar features to those of $\mathbf{1}^{\bullet+}$ (*cf.* Fig. 1), where the role of the cyclopropane Walsh MO's is taken over by the π-MO of the olefinic double bond in $\mathbf{3}^{\bullet+}$. Because ionization from a double bond entails smaller geometry changes than ionization from a cyclopropane σ-MO, the third PE band and the first EA band (electron loss or excitation from 5a″) are much sharper than in $\mathbf{1}^{\bullet+}$. At the neutral geometry (*cf.* bars under the PE spectrum) the higher excited states are again predicted to be too low in energy by the CASPT2 method. In contrast, the important intense peak at about 3 eV in the EA spectrum of $\mathbf{3}^{\bullet+}$ is right on the mark at the radical cation geometry. Note again from Table 2 the substantial changes in the electronic structure of the higher excited states on going from the neutral to the cation geometry of **3**.

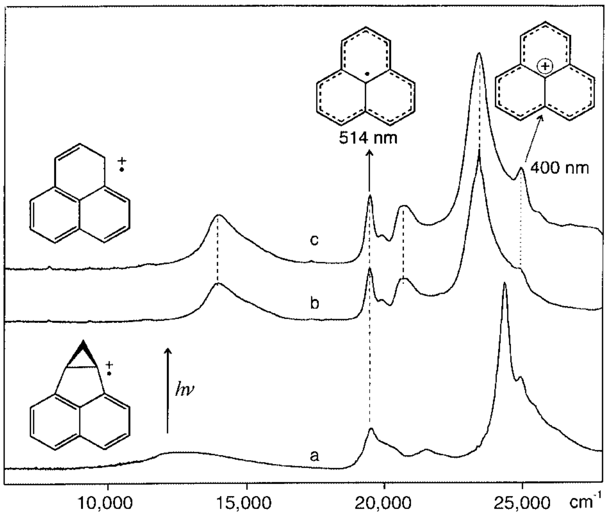

Fig. 2 Changes in the electronic absorption spectrum of $\mathbf{1}^{\bullet+}$ (spectrum a) on >540 nm irradiation (b). Spectrum (c) was obtained on ionization of phenalene, **3**, under the same conditions. The peaks at 19500 and 25000 cm^{-1} are attributed to the phenalenyl radical and cation, respectively.

In an effort to find the 1,3-perinaphthadiyl radical cation $\mathbf{PD}^{\bullet+}$ that should occur as an intermediate in the conversion of $\mathbf{1}^{\bullet+}$ to $\mathbf{3}^{\bullet+}$, we subjected solutions of **1** in butyl chloride–isopentane matrices to 254 nm irradiation, which resulted in the appearance of the characteristic sharp peaks of triplet 2,3-dihydro-1*H*-phenalene-1,3-diyl (**PD**) at 500–430 and at 340 nm.[32] Subsequent γ-irradiation of such samples gave, however, only mixtures of $\mathbf{1}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$ with no evidence for any additional species that might have gone undetected in the other experiments. Thus, we conclude that the perinaphthadiyl radical cation decays with very little, if any, activation to the more stable phenalene radical cation. Scheme 1 summarizes the findings from the above experiments.

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†† By Koopmans character we denote the percent weight of excited configurations that do *not* involve virtual MO's and hence contribute intensity to the PE spectrum (states which involve *only* excitations into virtual MO's do not give rise to PE bands).

Table 2 Excited states of the radical cation of 1*H*-phenalene ($3^{\cdot +}$)

	Neutral equilibrium geometry					Radical cation equilibrium geometry				
		CASPT2					CASPT2			
States	PES[a] *E*/eV	*E*/eV	*K*(%)[e]	CASSCF[b] *E*/eV	CASSCF Configurations[d]	EAS[c] *E*/eV	*E*/eV	*f*[f]	CASSCF[b] *E*/eV	CASSCF Configurations[d]
1^2A″	(7.45)[g]	(0)	78	(0)	78% Ground conf.	(0)	(0)	—	(0)	78% Ground config.
2^2A″	1.20	1.18	74	0.99	74% 6a″→7a″	—	1.44	4.0×10^{-4}	1.32	72% 6a″→7a″
3^2A″	1.77	1.64	68	1.82	68% 5a″→7a″	1.72 (m)	1.72	0.0465	1.93	68% 5a″→7a″ 4% *7a″→8a″*
4^2A″	2.65	2.46	44	2.81	44% 4a″→7a″ 17% *7a″→8a″*	2.56 (w)	2.42	0.0189	2.73	23% 4a″→7a″ *39% 7a″→8a″*
5^2A′	—	3.00	14	3.34	37% *7a″→8a″* 11% *7a″→9a″* 8% 4a″→7a″ 6% 3a″→7a″	2.89 (s)	2.86	0.1638	3.26	30% 4a″→7a″ 18% *7a″→8a″* 8% *7a″→9a″*
6^2A″	≈10.8	3.24	40	3.63	35% 3a″→7a″ 5% 4a″→7a″ 9% *7a″→10a″*	—	3.31	1.0×10^{-4}	3.63	33% 3a″→7a″ *15% 7a″→10a″* 7% *5a″→8a″*

[a] Photoelectron spectrum of **3** *cf*. Fig. 3. [b] Active space: 11 electrons in 6 occupied + 6 virtual MO's of a″ symmetry. [c] Electronic absorption spectrum of $\mathbf{3}^{\cdot +}$, *cf*. Fig. 3. [d] In terms of single excitations between the MO's depicted in Fig. 3; excitations into virtual orbitals are in italics. [e] Percent Koopmans character, proportional to the intensity of the PE band. [f] Oscillator strength for electronic transition, computed on the basis of the CASSCF wavefunction, using the CASPT2 energy difference in the denominator. [g] First ionization potential of **3**, origin of energy scale for excited states.

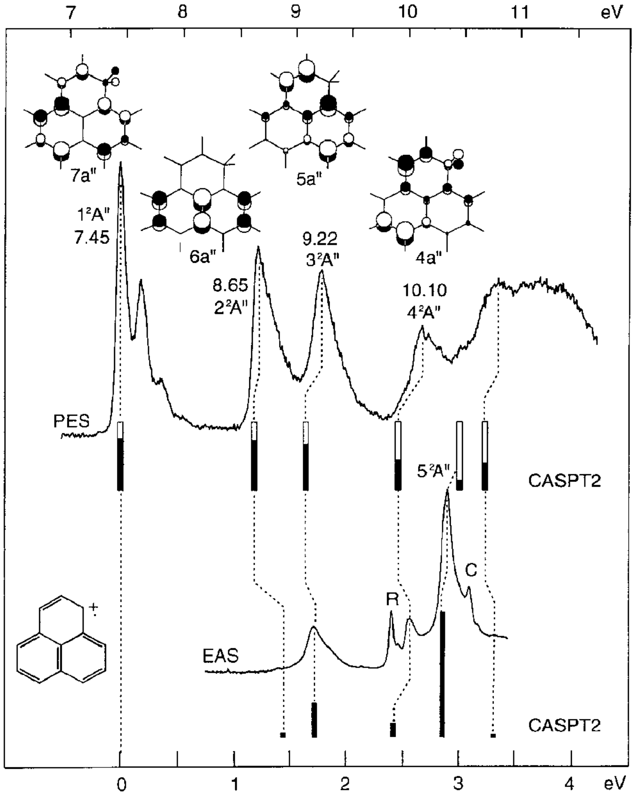
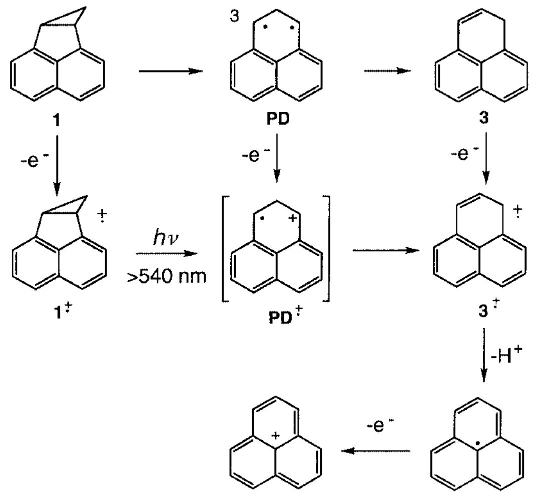


Fig. 3 Photoelectron spectrum (PES, upper trace) of phenalene, **3**, and electronic absorption spectrum (EAS) of its radical cation, drawn on a common energy scale. For the meaning of the bars, see the caption to Fig. 1.

3.3. The radical cation of the 7,7-dimethyl-7,7a-dihydro-6b*H*-cycloprop[*a*]acenaphthylene $\mathbf{2}^{\cdot +}$

The spontaneous decay to phenalene, which seems to render the observation of the diyl radical cation (**PD**$^{\cdot +}$) impossible, may occur by quantum mechanical tunneling, a mechanism that was proven to be operative in the case of the ^{3}**PD**.[4] In view of this, we thought that replacing the apical CH_2 by a CMe_2 group would increase chances of observing the diyl radical cation. Thus we subjected the dimethylcycloprop[*a*]acenaphthylene precursor **2** to ionization and subsequent photolysis.



Scheme 1 Summary of results obtained on ionization of **1** and **3**, respectively. See text for discussion.

Fig. 4 shows the spectrum of ionized **2** (b) and its conversion on >540 nm photolysis (c). For comparison, the spectra of $\mathbf{1}^{\cdot +}$ (a) and of $\mathbf{3}^{\cdot +}$ (d), as well as the CASPT2 predictions for $\mathbf{1}^{\cdot +}$ and $\mathbf{2}^{\cdot +}$ are also given. These calculations show that the ground state and the first two excited states of $\mathbf{1}^{\cdot +}$ are not affected much by methyl substitution. In contrast, the electronic transition to the 2^2A″ state is predicted to undergo a bathochromic shift of about 0.4 eV and the oscillator strength to increase by a factor of almost seven. The CASPT2 predictions are in excellent accord with experiment, which shows only a very small shift for the 1^2A″→2^2A' transition that appears as a broad shoulder in the spectrum of $\mathbf{2}^{\cdot +}$. In contrast, the small hump for the 1^2A″→2^2A″ transition in $\mathbf{1}^{\cdot +}$ shifts to lower energy by 0.5 eV and grows to a band of medium intensity. Finally, the intense 1^2A″→3^2A″ transition also shows a red shift that is in excellent accord with the CASPT2 prediction. Thus there can be no doubt that the spectrum in Fig. 4b is due to $\mathbf{2}^{\cdot +}$. Data for the excited states of $\mathbf{2}^{\cdot +}$ are given in Table 3.

On photolysis at >540 nm, the EA spectrum of $\mathbf{2}^{\cdot +}$ is transformed into one that shows great similarity to that of the radical cation of phenalene (shown in Fig. 4d for comparison). This leads us to assign spectrum 4c to a dimethyl derivative of $\mathbf{3}^{\cdot +}$. Surprisingly, the photorearrangement of $\mathbf{2}^{\cdot +}$ is again

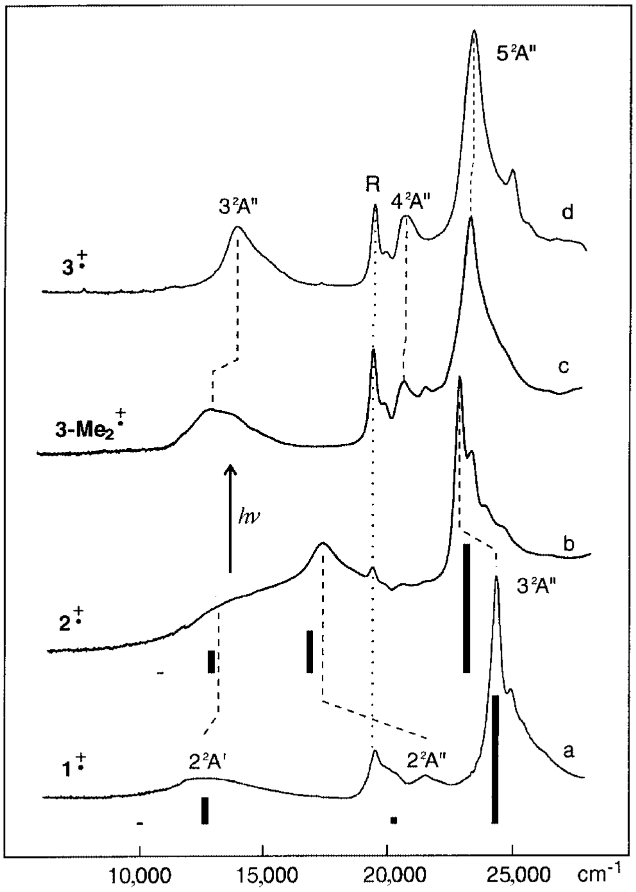


Fig. 4 Changes in the electronic absorption spectrum of $\mathbf{2}^{\bullet+}$ (spectrum b) on >540 nm irradiation (c). The spectra of $\mathbf{1}^{\bullet+}$ (a) and $\mathbf{3}^{\bullet+}$ (d) are shown for comparison.

accompanied by the formation of a strong peak at 19600 cm^{-1}, indicative of a phenalenyl radical (already present in small quantity after ionization of **2**) that is presumably formed by loss of a methyl radical. However, the spectrum 4c shows no features that could possibly be attributed to the diyl radical cation, **PD-Me$_2$**$^{\bullet+}$. Thus, methyl substitution did not have the desired effect of blocking the rearrangement to phenalene. If this rearrangement were to proceed through **PD-Me$_2$**$^{\bullet+}$, then this would imply a 1,2-methyl shift. The mechanism of this reaction shall be discussed in Section 4.

3.4. The radical cations of the dicyclopropa[*a*,*g*]pyracyclene, $\mathbf{4}^{\bullet+}$, and of 2,7-dihydro-2,2,7,7-tetramethylpyrene, $\mathbf{5}^{\bullet+}$

With little hope of seeing the elusive 1,3-perinaphthadiyl radical cation in the series of cycloprop[*a*]acenaphthylenes, we turned to the last member of the series, 1,1,4,4-tetramethyl-1,1a,3b,4,4a,6b-hexahydrocyclopropa[*a*]cyclopropa[4,5]cyclopenta[1,2,3-*fg*]acenaphthylene, **4**. After ionization, this compound gives an EA spectrum that looks qualitatively similar to that of $\mathbf{2}^{\bullet+}$ (see Fig. 5a). Unfortunately, CASSCF/CASPT2 calculations required too much effort for $\mathbf{4}^{\bullet+}$, so we resorted to the semiempirical INDO/S method to understand the electronic structure of this species. The good semiquantitative agreement between the calculated and the observed spectrum seems to indicate that this method works quite well in this case.

The first two excited states are predicted to be nearly degenerate because the second cyclopropyl group shifts the third occupied MO (25a′ in $\mathbf{1}^{\bullet+}$, *cf.* Fig. 1) very close to the purely naphthalene-based second occupied MO (26a′ in $\mathbf{1}^{\bullet+}$). The next excited state corresponds essentially to HOMO→LUMO excitation, whereas the one giving rise to the structured, intense band at 21000 cm^{-1} is predicted to be of highly mixed character. Thus, INDO/S predicts a different electronic structure for the third and fourth excited states than CASSCF does for $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, but that is most likely due to the different nature of the methods. In any event, a reliable assignment of all transitions in the spectrum (Fig. 5a) to $\mathbf{4}^{\bullet+}$ seems to be out of the question.

Table 3 Excited states of the radical cation of 7,7-dimethyl-7,7a-dihydro-6b*H*-cycloprop[*a*]acenaphthylene ($\mathbf{2}^{\bullet+}$) at the radical cation geometry

States	EAS[a] *E*/eV	CASPT2 *E*/eV	CASPT2 *f*[d]	CASSCF[b] *E*/eV	CASSCF Configurations[c]
1^2A″	(0)	(0)	—	(0)	80% Ground config.
1^2A′	—	1.34	8.1×10^{-5}	1.19	77% 26a′→18a″
2^2A′	1.67 (m)	1.59	0.0332	1.78	70% 25a′→18a″
2^2A″	2.14 (m)	2.08	0.0625	2.67	56% 17a″→18a″ *12% 18a″→19a″* 5% 16a″→18a″
3^2A″	2.84 (s)	2.86	0.1956	3.26	*52% 18a″→19a″* 6% 17a″→18a″ 6% 16a″→18a″
4^2A″	—	3.05	4.4×10^{-4}	3.76	54% 16a″→18a″ *6% 25a″→27a″* *5% 26a′→27a′*
3^2A′	—	3.23	0.0039	3.78	59% 24a′→18a″ *4% 18a″→27a′*

[a] EA spectrum of $\mathbf{2}^{\bullet+}$ *cf.* Fig. 5. [b] Active space: 13 electrons in 4 occupied + 3 virtual MO's of a′ symmetry, and in 3 occupied + 2 virtual MO's of a″ symmetry; [c] In terms of single excitations between the MO's depicted in Fig. 1; excitations into virtual orbitals are in italics. [d] Oscillator strength for electronic transition, computed on the basis of the CASSCF wavefunction, using the CASPT2 energy difference in the denominator.

On photolysis at >640 nm (>15500 cm^{-1}) the spectrum of $\mathbf{4}^{\bullet+}$ is completely transformed into one which has barely any absorption in the visible, but a very strong band in the near UV ($\nu_{\max} = 23000$ cm^{-1}). This spectrum looks similar to that of 7,8,9,10-tetrahydrocyclohepta[*de*]naphthalene-7,10-diylium,[10] which is reproduced for reference purposes as a dashed line. On this basis we assign spectrum 5b to the 1,3-perinaphthadiyl radical cation $\mathbf{6}^{\bullet+}$ obtained by opening one of the cyclopropane rings in $\mathbf{4}^{\bullet+}$. The results of the INDO/S calculations on $\mathbf{6}^{\bullet+}$ were, however, not in sufficiently good agreement with experiment to warrant an assignment of the excited states of this compound.

Finally, photolysis at 450 nm leads to cleavage of the remaining cyclopropane ring in $\mathbf{6}^{\bullet+}$ to yield the radical cation of 2,7-dihydro-2,2,7,7-tetramethylpyrene, $\mathbf{5}^{\bullet+}$. This assignment is confirmed by independent generation of $\mathbf{5}^{\bullet+}$ through ionization of **5** (spectrum d in Fig. 5). There are some differences between the two spectra c and d above 20000 cm^{-1}. The spectrum obtained from $\mathbf{4}^{\bullet+}$ contains a band at 19600 cm^{-1}, close to the position of the sharp peak of the phenalenyl radical, which indicates that such a species is also formed in the case of $\mathbf{4}^{\bullet+}$. Conversely, the spectrum recorded after ionization of **5**, which does not show the latter band, contains a peak at 21500 and a broader band at 22900 cm^{-1}. The latter band coincides with the main peak of $\mathbf{6}^{\bullet+}$ and may indicate formation of this compound by ring closure of $\mathbf{5}^{\bullet+}$ (note that the small hump at 19000 cm^{-1} is also visible in spectrum 5d). We have no explanation for the 21500 cm^{-1} peak that could have arisen from an impurity in the sample of **5**. Above 24000 cm^{-1} spectrum 5d becomes ill defined due to strong absorption of **5**.[5]

Despite deficiencies in the excited state calculations on these big molecules, the observed reaction sequence $\mathbf{4}^{\bullet+} \rightarrow \mathbf{X}^{\bullet+} \rightarrow \mathbf{5}^{\bullet+}$ provides strong evidence for the assignment of $\mathbf{X}^{\bullet+}$ to $\mathbf{6}^{\bullet+}$.

4. Mechanistic considerations

The most ready explanation of the outcome of the

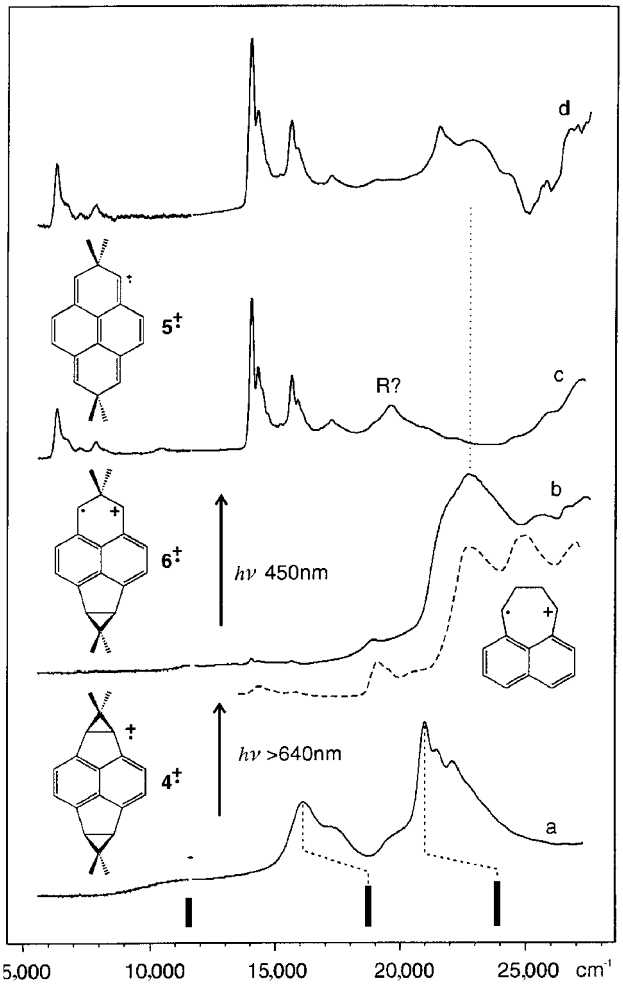
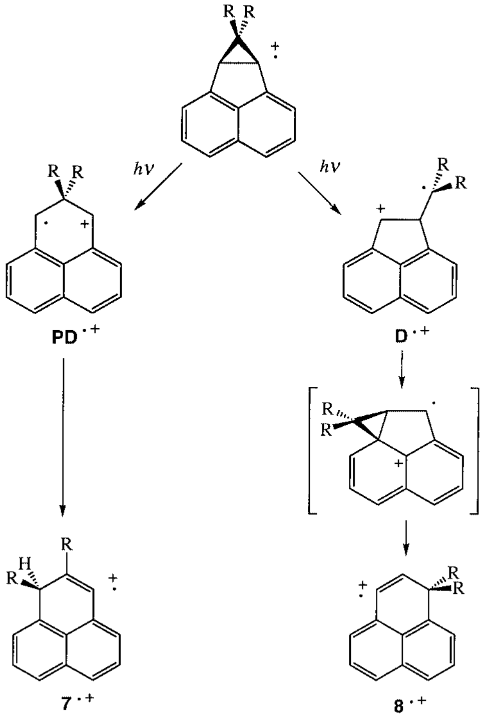


Fig. 5 Changes in the electronic absorption spectrum of ionized **4** (spectrum a) on >640 nm irradiation (b) and on subsequent 450 nm irradiation (c). Spectrum (d) was obtained by ionization of 2,7-dihydro-2,2,7,7-tetramethylpyrene, **5**, under the same conditions. The dashed line represents the spectrum of the 1,4-perinaphthadiyl radical cation obtained previously from cyclobut[*a*]acenaphthylene.

experiments described above is that rearrangement of **PD**$^{\bullet+}$ to the phenalene radical cation occurs by migration of a hydrogen atom in the case of the parent compound and by migration of a methyl group in the case of the dimethyl derivative. In fact, precedent exists for such rearrangements in cyclopentane-1,3-diyl radical cations where both hydrogen atoms and methyl groups were found to migrate to the trivalent carbon centers on warming to 105 K.[33]

However, in cyclopentane-1,3-diyl radical cations, charge and spin are formally localized on the two divalent carbon atoms, whereas in the present perinaphthadiyl radical cations they are delocalized throughout the π-system of the naphthalene moiety. Wagner–Meerwein type rearrangements require a localization of the charge in the p_π-AO adjacent to the migrating σ-bond. This can easily be achieved in alicyclic 1,3-diyl radical cations,[34] but in aryl substituted ones it entails a loss of resonance of the benzylic type. Hence such diyl radical cations as **PD**$^{\bullet+}$ are expected to offer more resistance to Wagner–Meerwein shifts.

Therefore we think that a 1,2-methyl shift is not a very likely decay pathway for **PD-Me**$_2{}^{\bullet+}$. However, the question arises if **PD**$^{\bullet+}$ (or **PD-Me**$_2{}^{\bullet+}$) is a necessary intermediate in the rearrangement of **1**$^{\bullet+}$ (or **2**$^{\bullet+}$) to the radical cation of phenalene (or dimethylphenalene). In principle, an alternative pathway *via* cleavage of a *lateral* cyclopropane bond, leading to a different diyl radical cation, **D**$^{\bullet+}$, is also conceivable. **D**$^{\bullet+}$ could then proceed to rearrange by a retro-di-π-methane-type sigmatropic rearrangement to phenalene.



Scheme 2 Different pathways leading from cycloprop[*a*]acenaphthylene to phenalene. The designations **7**$^{\bullet+}$ and **8**$^{\bullet+}$ pertain to the compounds with R = CH$_3$.

Table 4 Excited states of the radical cations of 2,2- (**7**$^{\bullet+}$) and 2,3-dimethylphenalene (**8**$^{\bullet+}$) at the radical cation geometries

		7$^{\bullet+}$		**8**$^{\bullet+}$	
	EAS[a]	CASPT2[b]		CASPT2[b]	
States	*E*/eV	*E*/eV	f^c	*E*/eV	f^c
$1^2A''$	(0)	(0)	—	(0)	—
$2^2A''$	—	1.39	4.3×10^{-4}	1.47	5.0×10^{-4}
$3^2A''$	1.60 (m)	1.60	0.0447	1.58	0.0473
$4^2A''$	2.57 (w)	2.42	0.0157	2.41	0.0233
$5^2A''$	2.90 (s)	2.80	0.1602	2.81	0.1755
$7^2A''$[d]	—	3.56	0.0160	3.61	0.0415
$8^2A'$	—	3.64	0.0493	3.71	0.0217

[a] EA spectrum of the radical cation of dimethylphenalene, *cf.* Fig. 5b. [b] CASSCF calculation with an active space of 11 electrons in 12 MO's (of a″ symmetry in the case of **7**$^{\bullet+}$). [c] Oscillator strength for electronic transition, computed on the basis of the CASSCF wavefunction, using the CASPT2 energy difference in the denominator. [d] The transition to the 62A″ state at around 3.3 eV carries an oscillator strength of less than 10^{-3}, hence it is not listed.

For R = CH$_3$, the two pathways depicted in Scheme 2 lead to different products. Since we only have optical spectra at our disposal we examined whether these would allow us to distinguish between the two products. Unfortunately, this does not appear to be the case. In Table 4 we list the CASSCF/CASPT2 predictions for the radical cations of 2,2- and 2,3-dimethylphenalene (**7**$^{\bullet+}$ and **8**$^{\bullet+}$, respectively). These calculations show that different arrangements of the methyl groups lead to only very minor shifts in the electronic transitions.

Since the experimental tools at our disposal did not allow us to distinguish between the two mechanistic alternatives, we turned to theory. We used the B3LYP/6-31G* method to study the relative stabilities of the different intermediates that are involved in the rearrangement of ionized **2**, and to characterize their frontier molecular orbitals. First, we focussed on the

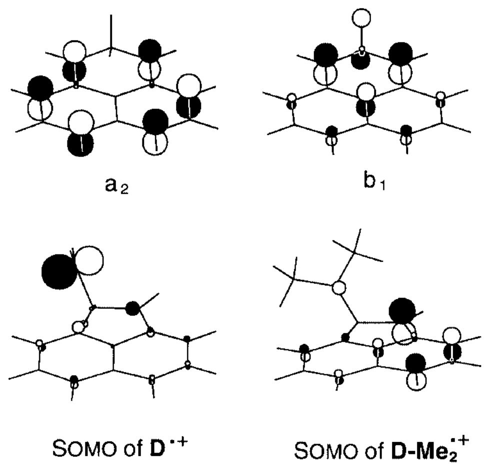


Fig. 6 Frontier MOs of **PD**$^{\bullet+}$ (upper half) and of the diyl radical cation, **D**$^{\bullet+}$, obtained by cleavage of a lateral cyclopropane bond of **1**$^{\bullet+}$ or **2**$^{\bullet+}$. See text for discussion.

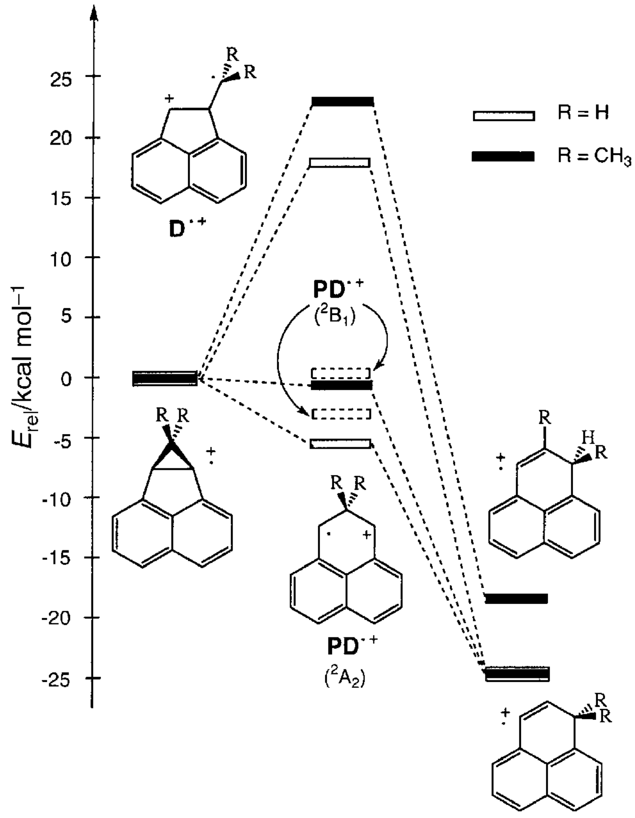


Fig. 7 Relative energies of cycloprop[*a*]acenaphthylene radical cations, diyl radical cations **PD**$^{\bullet+}$ (in their $^2A_2$ and $^2B_1$ states) and **D**$^{\bullet+}$, as well as phenalenes according to B3LYP/6-31G* calculations.

1,3-perinaphthadiyl cations, which distinguish themselves by two very close lying electronic states that can be thought to arise by ionization from the symmetric (a_2 in C_{2v}) or the antisymmetric singly occupied MO (b_1 in C_{2v}) of the triplet biradical. In the case of the seven-membered ring analogue (formed by ring-opening of cyclobut[*a*]acenaphthylene) the "symmetric" state had been found to lie about 10 kcal mol^{-1} below the "antisymmetric" one. This situation is reversed in the present case, because the symmetric MO is destabilized through hyperconjugation with the central CH_2 (or CMe_2) group (*cf.* Fig. 6, top part). The ring opening to the more stable "antisymmetric" form of **PD**$^{\bullet+}$ is exothermic by 5.5 kcal mol^{-1} in **1**$^{\bullet+}$, but by only 0.7 kcal mol^{-1} in **2**$^{\bullet+}$ (hence, it could just as well be slightly endothermic in that case).

The differences in electronic structure between the parent compound and its dimethyl derivative are more important in the other diyl radical cation, **D**$^{\bullet+}$ in Scheme 2, where the charge and the spin bearing moieties are *reversed* by methyl substitution. In the parent compound the spin is largely localized on the exocyclic CH_2 group (and the charge in the naphthyl part). On the other hand, more than 50% of the charge is on the CMe_2 group in the dimethyl derivative, while the spin is distributed over the α-naphthyl moiety (*cf.* the two SOMOS in Fig. 6, lower part). Actually, only the dimethyl derivative of **D**$^{\bullet+}$ is a true intermediate on the B3LYP/6-31G* potential energy surface. All attempts to locate a minimum for parent **D**$^{\bullet+}$ led to collapse back to **1**$^{\bullet+}$.[35]

The thermochemistry for lateral cleavage of the cyclopropane ring is not strongly affected by dimethyl substitution (see Fig. 7). However, the occupation of the p-AO at the CH_2 (or CMe_2) group is of great importance with regard to the subsequent sigmatropic shift. Migration of a vicinal C–C-bond to that center can only take place easily if the center is cationic, as is the case in **D-Me**$_2{}^{\bullet+}$. Hence, whatever **D**$^{\bullet+}$ may be formed on photolysis of **1**$^{\bullet+}$ will decay back to the starting compound, whereas **D-Me**$_2{}^{\bullet+}$ can proceed to phenalene by a sigmatropic shift. In contrast, parent **PD**$^{\bullet+}$ can decay very easily by 1,2-H shift to phenalene, whereas **PD-Me**$_2{}^{\bullet+}$ is protected from that rearrangement. Thus, it could well be that both diyl radical cations are formed in both cases, but that differences in the activation energies for their decay to phenalene result in a change in mechanism on going from the parent compound to the dimethyl derivative.

In **4**$^{\bullet+}$, however, the case is different. The most stable state of the corresponding **PD**$^{\bullet+}$ is the "symmetric" one ($^2A'$), 7 kcal mol^{-1} below **4**$^{\bullet+}$ and 1.7 kcal mol^{-1} below the $^2A''$ state (this is due to the fact that the antisymmetric diyl SOMO is lifted above the symmetric counterpart by strong interaction with the antisymmetric Walsh MO of the cyclopropane ring on the opposite side). The evident similarity of the spectrum attributed to the **PD**$^{\bullet+}$ obtained from **4**$^{\bullet+}$ to that of the seven-membered ring analogue, which has also a "symmetric" ground state, testifies to that assignment. Perhaps the $^2A''$ state is less prone to undergo the retro-di-π-methane rearrangement (or the 1,2-methyl shift) responsible for the decay to the phenalene radical cation than **PD-Me**$_2{}^{\bullet+}$ in its $^2A_2$ state (corresponding to $^2A''$ in C_s). This may account for the fact that the **PD**$^{\bullet+}$ obtained from **4**$^{\bullet+}$ is stable at 77 K, in contrast to that from the closely analogous one arising from **2**$^{\bullet+}$.

5. Conclusions

We have subjected two cycloprop[*a*]acenaphthylenes and a dicyclopropa[*a*,*g*]pyracyclene derivative to ionization by γ-irradiation of Freon matrices at 77 K. Under these conditions all three compounds retain their structure, *i.e.* the parent radical cations can be observed. The electronic structure of the two acenaphthylenes is discussed by comparison with the photoelectron spectra and on the basis of CASSCF/CASPT2 quantum chemical calculations.

On subsequent irradiation with visible light, all three radical cations undergo rearrangements. In the case of the acenaphthylene derivatives, the products are the corresponding phenalene radical cations, whereas the cyclopenta[*fg*]acenaphthylene derivative undergoes a simple cleavage of the central bond of one of the cyclopropane rings to yield a 1,3-perinaphthadiyl cation similar to that obtained on ring opening of cyclobut[*a*]acenaphthylene radical cation.[10] In a second photochemical step, the 1,3-perinaphthadiyl cation **6**$^{\bullet+}$ undergoes cleavage of the second cyclopropyl moiety to give the radical cation of the 2,7-dihydropyrene, **5**$^{\bullet+}$.

Theoretical considerations suggest that the photorearrangements of parent cycloprop[*a*]acenaphthylene and its 7,7-dimethyl derivative to the corresponding phenalene derivatives occur by different pathways, *i.e.* by cleavage of the *central* cyclopropane bond followed by a 1,2-H shift in the parent compound, and by cleavage of a *lateral* cyclopropyl bond followed by a Wagner–Meerwein shift in the dimethyl derivative. The reasons for this mechanistic divergence lie in the changes of the electronic structure of the primary diyl cations on alkylation. Attachment of a second cyclopropyl ring in the dicyclopropa[*a*,*g*]pyracyclene derivative results in a stabilization of the "symmetric" state of the 1,3-perinaphthadiyl cation which is, therefore, observed as an intermediate.

By combination of experiment and theory, we have been able to sort out an intriguing mechanistic puzzle and to show how small changes in the substitution pattern of certain radical cations can have severe repercussions in their reactivity.

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34 In fact, recent calculations have shown that the rearrangement of the (puckered) cyclopentane-1,3-diyl to cyclopentene radical cations involve a (planar) intermediate with localized spin and charge which is more stable than the corresponding delocalized species and which decays nearly spontaneously by H- or Me-shift (L. Blancafort, W. Adam, D. Gonzàlez, M. Olivucci, T. Vreven and M. A. Robb, *J. Am. Chem. Soc.*, 1999, **121**, 10583).
35 The geometry of parent $\mathbf{D}^{\bullet +}$ was obtained by separate optimizations of the radical saturated at the α-naphthyl position and the cation with a CH_3 instead of the radical bearing CH_2 group, and by combination of the structures of these two species.