Review Article

From Cyclobutane (Four-Centre/Three-Electron) Radical Cations to the Mills–Nixon Effect†

Georg Geschedit,* a Horst Prinzbach, b Alwyn G. Davies a and Rainer Herges a

*Institute of Physical Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland, b Institute for Organic Chemistry and Biochemistry, University of Freiburg, Albertstrasse 21, 79104 Freiburg, Germany, c Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, UK and d Institute of Organic Chemistry, University of Braunschweig, Hagenring 10, 38106 Braunschweig, Germany


One-electron oxidation of pagodane-type molecules (2–9) leads to rather unusual radical cations. The corresponding EPR spectra are interpreted in terms of two different forms of four-centre/three-electron radical cations being embedded inside rigid polycyclic skeletons. With the help of quantum mechanical calculations these two forms have been assigned to an 'extended' and to a 'tight' structure representing two stages on the (Dsp) reaction coordinate of a [2+1] cycloadition. A cyclobutane moiety can change the ordering of the two highest occupied orbitals in the radical cation of an alternant hydrocarbon. This unexpected observation on the radical cation of binaphthylene (11) is traced back to the Mills–Nixon effect introduced in 1930.

Cyclobutanoid radical cations (four-centre/three-electron systems) have been attracting attention for some time. A great number of experimental1–3 and theoretical investigations4–8 have been carried out. Why are these four-centre/three-electron ions so popular? Is it because they can serve as illustrative models of the interface between experiment and theory?

The four-membered ring imposes a structure that deviates significantly from the ideal tetrahedral arrangement postulated for an sp3 carbon atom. The parent strained cyclobutane (1) has a puckered ring structure of D2h symmetry.9 This molecular symmetry leads to a degenerate pair of the highest occupied orbitals (HOMOs) and therefore the corresponding radical cation should be subject to Jahn–Teller distortions. A number of the theoretical investigations were directed towards the structural consequences for 1+*. Evidently 1+* is a very reactive species and thus for EPR studies it could only be generated by γ- or X-ray irradiation in freon matrices at low temperatures.2,10 The observed EPR spectra were interpreted in terms of a Jahn–Teller distorted structure at 4 K, which, however, is averaged at elevated temperatures. Alternatively, this symmetry reduction can also be attributed to matrix effects.

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Structurally modified four-centre/three-electron systems can be viewed as different stages on the reaction coordinate for the reaction ethene/ethene radical cation [2+1] cycloadition/reversion, a prototype for hole-catalysed pericyclic reactions.11,12

Is it possible to observe experimentally such [2+1] transition states? We have been pursuing this aspect by taking advantage of the availability of cage compounds of pagoda-type shape in which cyclobutane moieties are embedded in very rigid molecular skeletons. Originally, pagodane molecules were developed as key intermediates for efficient syntheses of dodecahedrane.13 ('Pagodane Route to Dodecahedrane').

In the parent [1.1.1.1]pagodane 2 the central paraalkylated cyclobutane is surrounded by fused cyclopanes (D3h symmetry), in the homologue [2.2.1.1]pagodane 3 two methylene groups are inserted so that the pagoda incorporates four cyclohexane units in one half whereas the other half remains composed of cyclopanes (C2v symmetry). When the 'upper' and the 'lower' halves of the cage are twisted by 90°, isopagodanes are created. Thus we attain [1.1.1.1]isopagodane 4 and [2.2.1.1]isopagodane 5. In tricyclo[1.1.3.02,5]hexadecane 6 the central four-membered ring is still paraalkylated, yet, because of the missing connections between the five-membered rings, the skeleton is rather flexible.
CYCLOBUTANE RADICAL CATIONS

[1.1.1.1]Pagodane (2) and [2.2.1.1]isopagodane (3) can be isomerised into [1.1.1.1]pagodadiene (6) and [2.2.1.1]isopagodadiene (8) in which two ethene moieties are fixed in a coplanar arrangement as in dodecahedra-1,6-diene (9). Whereas the distance between the two syneriplanar ethene parts in 7 and 8 amounts to ca. 280 pm, it is as much as ca. 350 pm in 9.14 To establish the interaction between the two ethene units, particularly in the case of 9, we have included the monoene 10 as a reference.

When a four-ring moiety is part of a delocalised aromatic \( \pi \) system strain effects are not the only effects that need to be considered. The cyclobutadiene system represents the prototype of an antiaromatic compound with four \( \pi \) electrons. How does such a moiety affect the electronic structure of an aromatic alternating \( \pi \) system? This aspect will be dealt with in the second part of this report. As an illustrative example we have chosen bina-

although the radical anion of this compound has been known for many years, the corresponding radical cation became observable by EPR spectroscopy only recently. The purpose of this work is to establish different struc-

tures of the \( \text{C}_4 \) fragments depending on the strictly defined geometrical parameters in the cage compounds 2–9 and, in addition, to determine how a \( \text{C}_4 \) moiety can influence the structure of a delocalised \( \pi \)-system in one-electron oxidised stages. To this end we have generated the radical cations \( 2^+–11^+ \) and employed quantum chemical calculations at the Hartree–Fock \textit{ab initio} level to determine the geometries of the radical cations. The Fermi contact interactions necessary for the calculation of the hyperfine coupling constants were computed by \textit{ab initio} density functional theory methods (DFT)\(^{16–19}\) and semiempirical INDO\(^{20}\) procedures. As the frontier orbitals of 11 are of \( \pi \) type, Hückel orbitals\(^ {21}\) will also be discussed for that case.

Generation of radical cations

The radical cations of 2–10 could be generated by \( \gamma \)-irradiation (\(^{60}\)Co) in freon matrices\(^ {22,23}\) (\( \text{CFCl}_3\), \( \text{CF}_2\text{ClCCl}_2\text{F}\), \( \text{CF}_3\text{CCl}_3\)). In all matrices the hyperfine features of the corresponding EPR spectra were identical. Moreover, starting from 2, 3, 5, 6, 7 and 8 radical cations could also be detected upon electrolytic (helical Au anode)\(^ {24}\) or chemical oxidation [AlCl\(_3\)]\(^ {25}\), Ti\(^ {26}\) trifluoroacetate,\(^ {26}\) tris(4-bromophenyl)ammoniumyl hexachloroantimonate\(^ {27}\) in dichloromethane. The radical cation of 11 was produced by reaction with 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ) in a mixture of dichloromethane and trifluoroacetic acid.\(^ {28}\)

Cyclobutane-type radical cations in pagodane cages

EPR spectra. A common feature of the pagodane-type molecules is the presence of eight (6: 16) \( \beta \)-hydrogen atoms with respect to the central \( \text{C}_4 \) moiety (Fig. 1). If we assume that a predominant quantity of the spin population of the radical cations generated from 2–10 resides in the central part and the singly occupied orbitals centred at the corresponding carbon atoms have \( \pi \) character, the hyperfine coupling constants of the \( \beta \)-hydrogen atoms should mirror the structure of the four-centre/three-electron fragment.

![Fig. 1. \( \beta \) Protons in [1.1.1.1]pagodane.](attachment:image.png)
Indeed the EPR spectra of the radical cations of 2–10 are dominated by patterns caused by the hyperfine splittings of the β protons. Two examples are shown in Fig. 2. The EPR spectrum assigned to the radical cation of [2.2.1.1]isopagadiene (8⁺) consists of a quintet spaced by 1.63 mT. The coupling constants giving rise to the splittings within the five groups have been established by ENDOR spectroscopy and simulation.⁷⁹ Thus one set of four equivalent β protons has a hyperfine coupling constant, aₜ, of 1.63 mT, whereas the other set has to have an a₀ value that is markedly smaller. This experimental finding is consistent with expectation: if one set of β protons gives rise to a large a₀ indicating that it is oriented almost parallel to the z axis of a π orbital, the remaining four protons in the isopagadiane have to reside nearly perpendicular to the former ones, giving small a₀. The EPR spectrum of 6⁺ comprises nine equidistant line groups spaced 1.34 mT apart due to an a₁ of eight equivalent protons. This points to two sets of eight equivalent β hydrogen atoms where one set has an a₁ that gives rise only to a splitting within one group of lines and therefore is considerably smaller. Based on the calculations (Table 1), we assign the dominating a₁ to the β protons of one methylene group. Table 1 shows the a₁ obtained for the radicals 2⁺–10⁺. Evidently, under our experimental conditions, oxidation of the two [1.1.1.1]isopagadiene isomers 2 and 7 leads to the observation of identical EPR spectra indicating eight equivalent β protons.₅₀ Similarly, after one-electron oxidation of isomers 5 and 8 the same EPR signals are

![Image](image_url)

*Fig. 2. EPR spectrum of 6⁺ (top: solvent, CH₂Cl₂; counterion: ClO₄⁻; T=203 K; the insert on the right hand side shows the central line at an enhanced resolution; the simulations are indicated below the experimental spectra) and 8⁺ (bottom left: solvent, CH₂Cl₂; counterion: SbCl₅⁻; T=203 K) and the ENDOR spectrum of 8⁺ (the line marked with # is the ‘mirrored’ ENDOR line belonging to a₁=1.63 mT).*

### Table 1. Experimental and theoretical a₁ assigned to the β protons of pagodane-type radical cations. The theoretical values in agreement with the experimental values are in italics.

<table>
<thead>
<tr>
<th>Radical cation</th>
<th>a₁ (exp.)/mT</th>
<th>a₁ (calc.)/mT</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1.1.1.1]Pagodane</td>
<td>0.95/1.76</td>
<td>1.544</td>
</tr>
<tr>
<td>[2.2.1.1]Pagodane</td>
<td>0.95/1.76</td>
<td>1.544</td>
</tr>
<tr>
<td>[1.1.1.1]Isopagodane</td>
<td>0.95/1.76</td>
<td>1.544</td>
</tr>
<tr>
<td>[2.2.1.1]Isopagodane</td>
<td>0.95/1.76</td>
<td>1.544</td>
</tr>
<tr>
<td>[3.3.3.3]</td>
<td>0.95/1.76</td>
<td>1.544</td>
</tr>
<tr>
<td>Dodecadiene-1,6-diene</td>
<td>0.95/1.76</td>
<td>1.544</td>
</tr>
<tr>
<td>Dodecahedraene</td>
<td>0.95/1.76</td>
<td>1.544</td>
</tr>
</tbody>
</table>

**INDO///UHF/3-21G* UB3LYP/6-31G*// UHF/3-21G***

<table>
<thead>
<tr>
<th>Radical cation</th>
<th>a₁ (exp.)/mT</th>
<th>a₁ (calc.)/mT</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1.1.1.1]Pagodane</td>
<td>0.95/1.76</td>
<td>1.544</td>
</tr>
<tr>
<td>[2.2.1.1]Pagodane</td>
<td>0.95/1.76</td>
<td>1.544</td>
</tr>
<tr>
<td>[1.1.1.1]Isopagodane</td>
<td>0.95/1.76</td>
<td>1.544</td>
</tr>
<tr>
<td>[2.2.1.1]Isopagodane</td>
<td>0.95/1.76</td>
<td>1.544</td>
</tr>
<tr>
<td>[3.3.3.3]</td>
<td>0.95/1.76</td>
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<tr>
<td>Dodecadiene-1,6-diene</td>
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</tr>
<tr>
<td>Dodecahedraene</td>
<td>0.95/1.76</td>
<td>1.544</td>
</tr>
</tbody>
</table>
detected (see Fig. 2). In these two cases the EPR spectra mirror the molecular symmetry of the parent compounds, i.e., \( D_{1h} \) (2, 7) and \( C_{2v} \) (5, 8). On the other hand, the EPR spectra of the radical cations generated from 4 and 6 indicate a decrease in symmetry compared with their neutral progenitors: whereas 4 and 6 have \( D_{2d} \) symmetry the hyperfine data of the radical cations represent \( C_{2v} \), that is, the two molecular halves are no longer equivalent pointing to a distortion of the central cyclobutane moiety. The radicals \( 3^+ \), \( 9^+ \) and \( 10^+ \) indicate an unaltered symmetry compared with their neutral counterparts. It is noteworthy that for the monoene \( 10^+ \), the \( \alpha_{\beta} \) of the four equivalent \( \beta \) protons is twice the size of that detected for the diene \( 9^+ \) (eight equivalent protons). \(^{35}\)

**Calculations and discussion.** According to quantum mechanical calculations the pagodane radical cations prefer either a cyclobutane-like, ‘tight’ or a diene-like, ‘extended’ arrangement (Fig. 3). The ‘tight’ and ‘extended’ geometries of pagodane radical cations were optimised by UHF \( \textit{ab initio} \) 3–21G* calculations and the \( \alpha_{\beta} \) values were determined by the semiempirical INDO\(^{20,34}\) and the Becke three-parameter hybrid method with HF, using the LYP functional (B3LYP). \(^{35}\) These calculations were performed with the use of GAUSSIAN 94. \(^{36,37}\)

In Fig. 4 the experimental and the calculated \( \alpha_{\beta} \) ascribed to the \( \beta \) protons in the molecular moiety consisting only of cyclopentane units are compared. The calculated values for the ‘tight’ and the ‘extended’ isomers are distinctly different. The almost perfect fit of the theoretical and experimental \( \alpha_{\beta} \) for the diene-like structure is associated with the disagreement for the cyclobutane isomer and \textit{vice versa} (Fig. 4). Thus the correlation of the calculated and experimental data should allow the distinction between the two structures. Based on Fig. 4 (see also Table 1) it can be deduced that the radical cations of 2/7, 5/8, 6 and 9 prefer the ‘extended’, whereas 4/2 \(^+\) and 2\(^+\) favour the ‘tight’ configuration.

The two isomeric geometries (Fig. 3) possess two distinct irreducible representations of the symmetry. When we take into account a [1.1.1.1]pagodane or [1.1.1.1]isopagodane (or 6) with \( D_{2h} \) or \( D_{2d} \) symmetry,
the central four-centre moiety can be regarded as a square ($D_{4h}$). Based on this assumption, the singly occupied orbital ‘tight’ isomer can be denoted as $b_{2g}$ whereas the ‘extended’ one represents a $b_{3u}$ orbital (Fig. 5).

**Binaphthylene and the Mills–Nixon Effect**

In the above section it was demonstrated that a hydrocarbon skeleton can influence the structure of an embedded four-centre/three-electron radical cation. In this section we focus on the consequences of a cyclic $C_4$ fragment upon the behaviour of a one-electron oxidised alternating $\pi$ system.

It is well established that an alternating $\pi$ system obeys the pairing principle. That is, each bonding orbital of energy $\alpha + \pi$ possesses an antibonding counterpart of energy $\alpha - \pi$ with the same absolute values of the orbital coefficients.\(^{21,38}\) The $\alpha$ of protons adjacent to the $\pi$ centres are proportional to these coefficients. Thus the radical cation of an alternating $\pi$ system with a singly occupied HOMO should have very similar $\alpha$ values to those of the radical anion with a singly occupied LUMO. An early example of this is biphenylene (12).\(^{39,40}\) Figure 6 indicates the $\alpha$ of 12\(^{+}\) and 12\(^{-}\) and indeed the hyperfine data are very similar.

One-electron reduction of binaphthylene (11) leads to an EPR spectrum with $\alpha$ values in very good agreement with those predicted from the Hückel LUMO of 11. However treatment of 11 with DDQ in trifluoroacetic acid–CH$_3$Cl$_2$ gave an EPR signal which had a completely different pattern and was considerably narrower than that of 11\(^{-}\) (Fig. 7). The ENDOR spectrum of 11\(^{+}\) indicates three coupling constants of 0.173, 0.061, and 0.044 mT each due to four protons (the latter $\alpha$ is not resolved in the EPR spectrum). It is noteworthy that, according to the Hückel model, the two pairs of frontier orbitals, i.e., the HOMO/HOMO–1 and LUMO/LUMO–1 are almost degenerate ($\Delta E = 0.039\beta$). Therefore even small perturbations of 11 (11\(^{+}\), 11\(^{-}\))

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**Fig. 6.** Hyperfine data of 12\(^{-}\) and 12\(^{+}\).

**Fig. 7.** EPR spectra of 11\(^{+}\) (top) and 11\(^{-}\) (bottom).
may lead to reversed ordering of the energetically almost equivalent orbitals.\textsuperscript{15}

In 1930 Mills and Nixon\textsuperscript{41} proposed that when a small ring is annelated to a benzene ring, bond localisation may occur. Later Finnegan and Streitwieser\textsuperscript{42,43} suggested that the angle strain is relieved by rehybridisation. More p-character is induced into the formal single bonds of the cyclobutane moiety whereas the s character is increased in the adjacent benzene-ring bond. This results in bond alternation and in the polarisation of charges as shown in Fig. 8. When these effects are applied to the Hückel orbitals of 11 the ‘paired’ orbitals HOMO–1 (b\textsubscript{2g}) and LUMO +1 (b\textsubscript{1u}) are destabilised whereas the related pair HOMO (a\textsubscript{u}) and LUMO (b\textsubscript{1u}) are stabilised. For the unoccupied orbitals this Mills--Nixon effect leads to further separation of the two lowest unoccupied orbitals (Fig. 9), but switching is induced for the two highest occupied orbitals. This results in the breakdown of the pairing principle, i.e., the HOMO–1 (b\textsubscript{2g}) becomes the singly occupied orbital in 11\textsuperscript{+}, and indeed the hyperfine data derived from this orbital are in very good agreement with the experimental data (Table 2). Similar results are also obtained when the geometry of 11 and its radical ions is calculated by \textit{ab initio} 3–21G calculations and the spin densities are determined with the INDO\textsuperscript{44} method.\textsuperscript{15}

Conclusions

When planar C\textsubscript{4} units of rectangular shape are embedded in rigid polycyclic hydrocarbon skeletons two different states of four-centre/three-electron radical cations can be distinguished. These two structures can be regarded as snapshots within a [2 + 1] cycloadition (or two Jahn–Teller variants of a D\textsubscript{2h} cyclobutane radical cation). Whereas the ‘extended’ structure resembles an early stage, the ‘tight’ structure corresponds to the product on the reaction coordinate.

The dynamics of the interconversion of valence isomeric radical cations are the subject of further studies. Moreover, we are attempting to gain more insight into the peculiarities of the hydrocarbon cages being responsible for the through-cage electron delocalisation.

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**Fig. 9.** Frontier orbitals of 11 and the influence of the Mills--Nixon effect on their ordering.

**Table 2.** Experimental and Hückel calculated \(a_d\) of the radical ions of 11.

<table>
<thead>
<tr>
<th>Species</th>
<th>Method</th>
<th>(a_d(1,6,7,12)/mT)</th>
<th>(a_d(2,5,8,11)/mT)</th>
<th>(a_d(3,4,9,10)/mT)</th>
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</thead>
<tbody>
<tr>
<td>11\textsuperscript{−}</td>
<td>Experiment</td>
<td>0.423</td>
<td>0.157</td>
<td>0.090</td>
</tr>
<tr>
<td>11\textsuperscript{−}</td>
<td>Hückel–McLachlan (LUMO)</td>
<td>−0.40</td>
<td>−0.20</td>
<td>−0.06</td>
</tr>
<tr>
<td>11\textsuperscript{+}</td>
<td>Experiment</td>
<td>0.061</td>
<td>0.004</td>
<td>0.173</td>
</tr>
<tr>
<td>11\textsuperscript{+}</td>
<td>Hückel–McLachlan (HOMO)</td>
<td>−0.40</td>
<td>−0.20</td>
<td>−0.06</td>
</tr>
<tr>
<td>11\textsuperscript{+}</td>
<td>Hückel–McLachlan (HOMO – 1)</td>
<td>+0.07</td>
<td>+0.03</td>
<td>−0.14</td>
</tr>
</tbody>
</table>
The tenor of the second part of this review is that a four-ring fragment is able to distort the structure of alternant hydrocarbons in a way that can be rationalised with such an 'antique'\textsuperscript{45} model as the Mills–Nixon effect.\textsuperscript{41} Although this explanation also can be applied to radical cations of benzylicyclobutenes,\textsuperscript{46} additional experimental evidence is desirable. In particular the study of radical cations generated from bicycloannelated benzenes, which seem to possess localised bonds even in the neutral state, is an intriguing task.\textsuperscript{47–49}

Acknowledgements. This work was supported by the Swiss National Science Foundation and the Deutsche Forschungsgemeinschaft. We are indebted to Rohit Batra (Basel) for his help with the DFT calculations and to our coworkers whose names are quoted in the references.

References