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ON THE SINGLY BRIDGED STRUCTURE OF THE RADICAL CATION OF DICYCLOPENTADIENE

COMBINED STUDIES OF PHOTOELECTRON SPECTRUM, ELECTRONIC ABSORPTION SPECTRUM, AND MO CALCULATIONS

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Abstract—Supporting evidence for the ring-opened structure of the radical cation of dicyclopentadiene (DCP) proposed by Roth *et al.* is presented: geometry optimization procedures predict that the ring-opened structure is more stable than the ring-closed by about 0.4 eV for both the *exo*- and *endo*-DCP isomers and that the optimized geometries are symmetric with the C_1 and C_2 symmetries for the respective isomers. The allylic nature in the cyclopenta ring is clearly disclosed. The observed electronic absorption spectrum of the radical cations produced in a γ-irradiated rigid solution is inconsistent with the observed photoelectron spectrum of the parent molecules, but the discrepancy is removed by assuming that the observed electronic absorption spectrum is associated with the ring-opened structure.

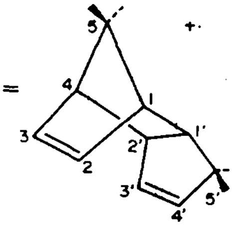
INTRODUCTION

This paper is intended to provide independent, circumstantial evidence for the singly bridged structure of the radical cation of dicyclopentadiene (DCP) proposed by Roth and Schilling as a result of their CIDNP studies.[1] The CIDNP technique is shown to be powerful to detect the radical cation of an electron donor whose conformation is significantly different from the parent molecule. In the cited literature Roth and Schilling demonstrated that when DCP and chloranil are chosen as electron donor (D) and acceptor (A), respectively, the following sequence of reactions are induced

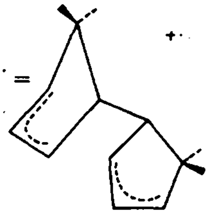
$$\begin{aligned} D+A &\xrightarrow{UV} D+{}^1A^* \xrightarrow{ISC} D \\ &+{}^3A^* \xrightarrow{ET} D^{+\cdot}+A^{-\cdot} \rightarrow \mathscr{D}^{+\cdot} \\ &+A^{-\cdot} \rightarrow {}^*D+A \end{aligned}$$

where ISC is intersystem crossing, ET is electron transfer, and *D is the nuclear spin polarized DCP molecule. The observed CIDNP pattern of the recovered *D suggests that the odd electron distribution during the charge separated stage must be allylic, i.e. the signs of the hfc constants of $H_{2,2'}$, $H_{3,3'}$, $H_{4,4'}$ are negative and those of $H_{1,1'}$, and $H_{5,5'}$ are positive which is compatible only with the singly bridged structure shown below.

$D^{+\cdot}$ =



$\mathscr{D}^{+\cdot}$ =



Our approach to the analysis of the radical cation is based on (a) comparison of the photoelectron spectrum (PES) of DCP with the electronic absorption spectrum (EAS) of the radical cation, which can be produced and stabilized in a γ-irradiated rigid solution at 77 K[2], and (b) reference to the result of MO calculations for the optimum geometry of the radical cation.

Comparison of the PES of molecules with the EAS of their radical cations is implemental to the assignment of the spectra if the molecular structure does not change appreciably upon ionization.[3] Conversely, any significant discrepancy between the two spectra may indicate that the geometry of the nascent radical cation immediately after ionization is not retained, and the geometry of the radical cation, whose EAS is observed, is different from that of the nascent one. An example of such a comparison to reveal the discrepancy has been reported for 1,4-dithia compounds.[4]

In this paper the radical cations of *exo*- and *endo*-DCP have been studied by our methods and it is concluded that the nascent, "vertical", radical cations are not stable but a bis-cyclopenta allylic structure is favored in agreement with the suggestion by Roth and Schilling.[1]

RESULTS AND DISCUSSION

Figures 1 and 2 collect compactly the information obtained in the present work for the *exo*- and *endo*-DCP isomers. At the upper left the observed PES are shown. The PES for *exo*-DCP has not been reported but the one for *endo*-DCP shown in Fig. 2 agrees well with the published spectrum.[5] The two peaks at 8.7 and 9.2 eV in Fig. 1 are associated with the vertical ionization from the two ethylenic units as will be

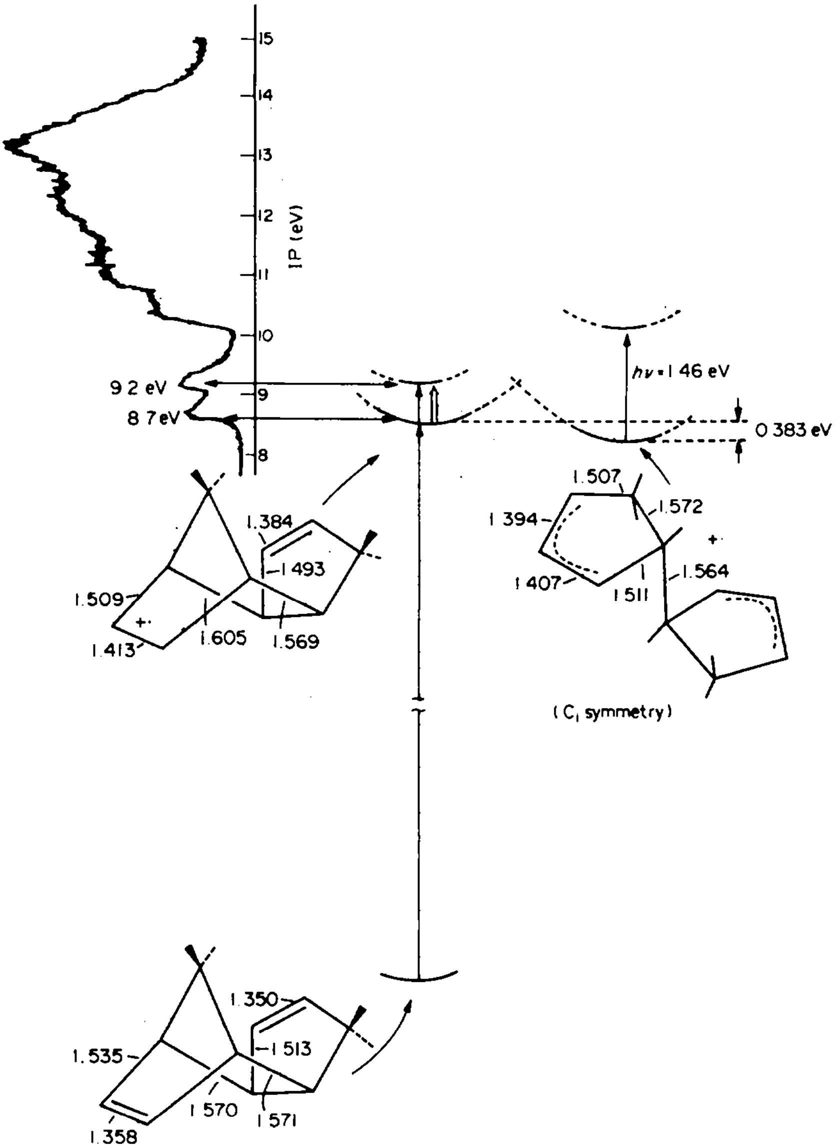


Fig. 1. Photoelectron spectrum of *exo*-DCP (upper left) and optimized geometries of the parent molecule, and the radical cations with ring-closed and ring-opened conformations.

discussed below. Although the separation is not so clear in Fig. 2, we regard the broad band at about 9 eV as comprising two close-lying peaks which are also associated with the ionization from the two double bonds in the parent molecule.

The parabolic curves in the central part of Figs 1 and 2 demonstrate schematically the potential minima of the parent molecules and their radical cations with the ring-closed structures. The molecular parameters given to the structural formulae and the potential minima of the radical cations are obtained by the procedures given below.

(1) Since the molecular structures of the parent molecules are not available in the literature, computations using program QCPE No. 353 (MNDO with Davidon–Fletcher–Powell algorithm) to determine the optimum geometries of the parent molecules were carried out. Only the major bond lengths are shown in Figs 1–2.

(2) In order to reproduce the observed first two PES peaks at about 9 eV by Koopmans' theorem the energies of the highest (ε_1) and the penultimate (ε_2) occupied orbitals were calculated using program IMSPACK with the RHF-STO-3G approximation for the geometries determined in (1). The results are $\varepsilon_1 = -7.280$ and $\varepsilon_2 = -7.831$ eV for *exo*-DCP and $\varepsilon_1 = -7.418$ and $\varepsilon_2 = -7.638$ eV for *endo*-DCP, which are about 1.5 eV smaller than the observed ionization potentials of about 9 eV. However, the differences between ε_1 and ε_2 are comparable with the separations between the first and the second PES peaks of about 0.5 and ~0.1 eV for *exo*- and *endo*-DCP, respectively. Ignoring the discrepancy of about 1.5 eV above, the potential minima of the radical cations are vertically shifted to match the first two PES peaks.

(3) In order to see the extent of the deformation of the radical cations in their potential minima relative

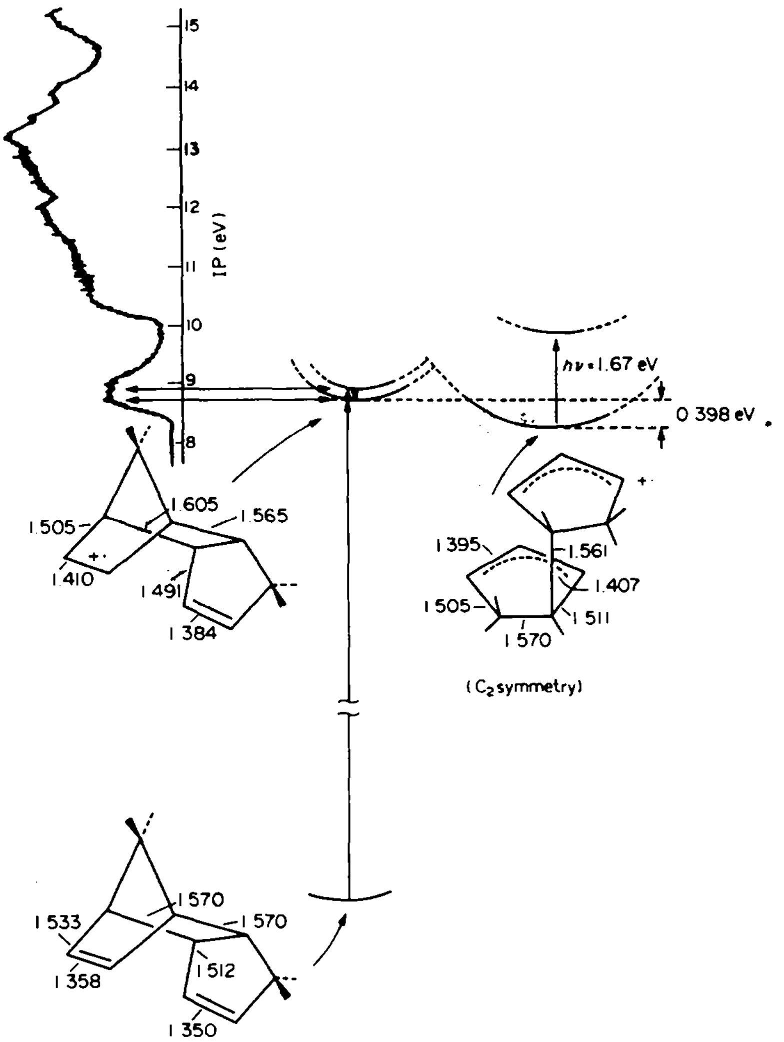


Fig. 2. Photoelectron spectrum of *endo*-DCP (upper left) and optimized geometries of the parent molecule, and the radical cations with ring-closed and ring-opened conformations.

to the parent molecules similar computations for the optimum geometries were carried out with the half-electron MNDO approximation combined with the DFP algorithm to obtain the molecular parameters shown in Figs 1–2. Again, only the major molecular parameters are shown but several points are worthy of note; the bond lengths of the double bonds are elongated as expected, but the extent of the elongation is larger for the C_2—C_3 than for the $C_{3'}$—$C_{4'}$ bond, which implies that the odd electron resides mainly in the region of the C_2—C_3 bond in the ring-closed radical cation in its ground electronic state. Of the two bridging single bonds, C_1—$C_{1'}$ and C_4—$C_{2'}$, the former changes little whereas the latter is lengthened. Other bond lengths not shown in the figures only change by less than 0.5%. Although the C_4—$C_{2'}$ bonds are significantly elongated as stated above, the whole structure should still be regarded as corresponding to the ring-closed radical cations. Although all the bond angles obtained by the computations are omitted in Figs 1–2, the cyclopenta rings remain definitely bent as in the neutral molecules. Because of this relatively small structural change as a whole the first optical transition energy of the radical cations, indicated by the open arrows in Figs 1–2, should be expected not far from the ΔIP ≅ 0.5 eV for *exo*-DCP and about 0.2 eV for *endo*-DCP. As described in the Experimental we surveyed carefully the expected spectral region but found that the first absorption bands actually appear in the region of about 1.5 eV (Fig. 3).

Therefore, we abandoned the view that the radical cations remained ring-closed in the optical measurement, and tried to find other local minima. In reference to the symptom of the weakening of the C_4—$C_{2'}$ bond upon ionization as mentioned above we initiated the geometry optimization procedure under the assumption that carbon atoms C_4 and $C_{2'}$ were unlinked. Ultimately converged geometries with this assumption are shown on the right of Figs 1 and 2. There are several points to note.

(1) Both *exo*- and *endo*-DCP converged to symmetric bis-cyclopenta allylic structures with C_i and C_2 symmetries, respectively.

(2) The cyclopenta rings are almost planar within ±2°, and the bond lengths of C_2—$C_{3'}$, $C_{2'}$—$C_{3'}$,

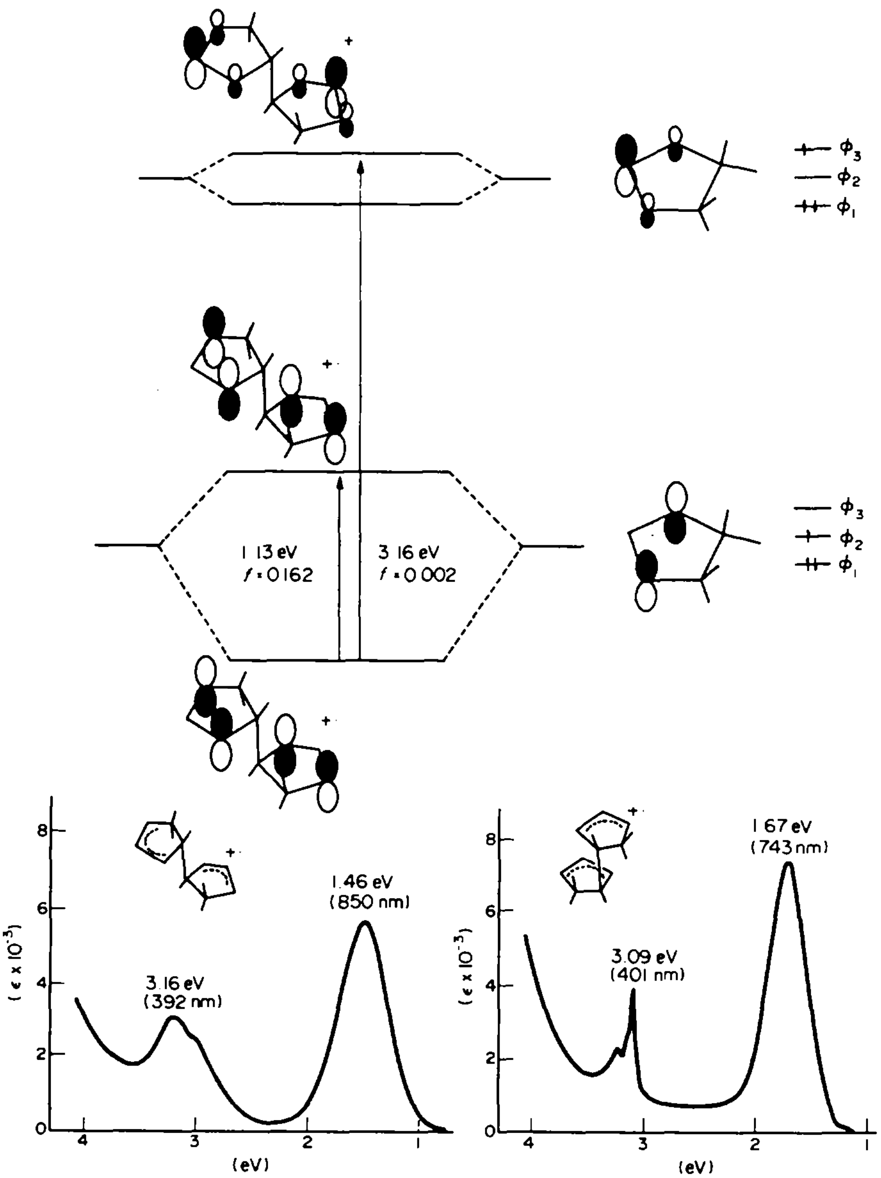


Fig. 3. Optical absorption spectra of the radical cations derived from *exo*- (lower left) and *endo*-DCP (lower right) in their ring-opened conformations. Essentially the same spectra were obtained regardless of whether the samples were irradiated and measured at 77 or at 4 K. The energy diagram in the center shows schematically the first two electronic transitions calculated for the radical cation derived from *exo*-DCP in its ring-opened conformation. The symbols $\phi_1 \sim \phi_3$ represent the three allylic MOs.

C_3—$C_{4'}$, and $C_{3'}$—$C_{4'}$ are typical of the allylic bond whereas the rest of the C—C bonds are typical single bonds.

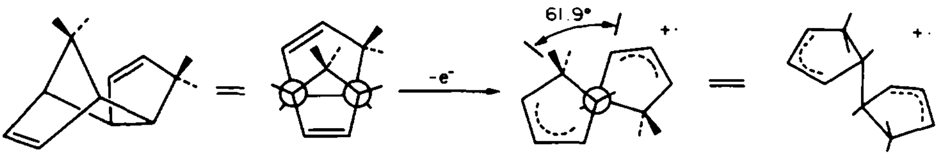
(3) The dihedral angles of C_5—C_1—$C_{1'}$—$C_{2'}$ are 61.9° and −62.9° for *exo*- and *endo*-DCP, respectively, as shown in Eqs (1) and (2).

(4) The total energies of the ring-opened radical cations are −1438.218 and −1438.260 eV for *exo*- and *endo*-DCP, respectively, whereas those of the ring-closed ones are −1437.835 and −1437.862 eV. Thus, the ring-opened radical cations are more stable than the others by about 0.4 eV for both isomers.

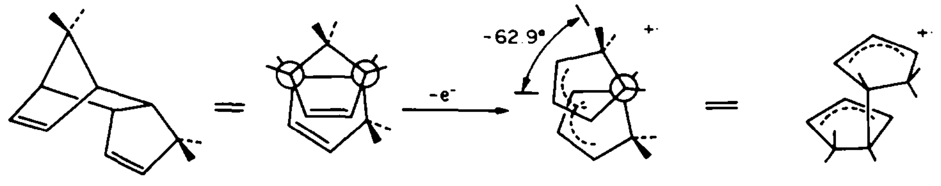
The above result suggests that the ionized DCP molecules somehow surmount a small potential barrier connecting the two minima in Figs 1 and 2, and relax as the ring-opened radical cations. The decisively allylic character of the ring-opened structures determined as above is consistent with the conclusion of the CIDNP study.[1]

We expected that the ring-opened structures may also account for the observed EAS of the radical cations which are shown in Fig. 3.

At the moment practicable MO calculations to analyze the optical spectrum of molecules as large as DCP are limited to those of the level of CNDO/S. Therefore, reference to such a calculation should be done with reservation. Nevertheless, the CNDO/S cal-



(1)



(2)

culation made for the ring-opened radical cations of DCP gave apparently reasonable results as shown in Fig. 3 for the *exo*-DCP system. The ground state is found to be characterized almost purely by the single configuration in which the odd electron occupies the MO constructed from the in-phase combination of the non-bonding allylic orbital, ϕ_2, schematically shown on the right of the energy diagram (the CI coefficient was 0.989). The first excited state is found to be expressed predominantly by the out-of-phase combination of ϕ_2 (CI coefficient being 0.969). The transition energy and the oscillator strength are calculated as 1.13 eV and $f = 0.162$, which may be compared with the observed 1.46 eV ($\lambda_{max} \cong 850$ nm in Fig. 3) and $\varepsilon = 6 \times 10^3$. The observed second absorption band at 392 nm (3.16 eV) happens to be identical with the calculated transition energy of 3.16 eV with $f = 0.002$, although the agreement must be coincidental. The character of the second transition can be described in terms of extensive interactions of configurations characterized by $\phi_2 + \phi'_2 \rightarrow \phi_3 - \phi'_3$, $\phi_1 + \phi'_1 \rightarrow \phi_2 + \phi'_2$, and $\phi_1 + \phi'_1 \rightarrow \phi_2 - \phi'_2$ (the orbital pattern at the top of Fig. 3 corresponds to $\phi_3 - \phi'_3$). Here, ϕ_1 and ϕ_3 stand for the bonding and antibonding allylic orbitals, and the primed orbitals belong to the counterpart moiety of the two allylic units.

Similar calculations at the CNDO/S level were carried out for the ring-opened radical cation of the *endo*-isomer. In this case, however, the calculated first transition energy of 0.61 eV with $f = 0.074$ is in poor agreement with the observed values of 1.67 eV ($\lambda_{max} = 743$ nm) with $\varepsilon = 7 \times 10^3$. As for the second transition the calculation gives 3.06 eV with $f = 0.005$ which happens to be close to the observed energy of 3.09 eV ($\lambda_{max} = 401$ nm). All in all, we consider that the CNDO/S calculations are semiquantitatively significant within a factor of two.

In conclusion, this paper shows that the apparent discrepancy between the PES of the parent molecules and the EAS of the radical cation can be reconciled by assuming an extensive rearrangement of the vertical radical cation. It is also shown that the calculation for the optimum geometry can provide a guide to infer the rearranged structure. The approaches adopted in this work should be complementary to the CIDNP method since the former gives plausible detailed structural information of the non-vertical radical cation.

EXPERIMENTAL

exo-Dicyclopentadiene was synthesized from the *endo*-isomer by the procedure given in the literature.[6] Photoelectron spectra were measured as described previously.[7] The radical cations of both *exo*- and *endo*-DCP were produced by γ-irradiation of frozen solns of Freons at 77 and 4 K.[2] The optical spectra of the irradiated solns were measured using 1.5 mm thick Suprasil or Infrasil cells. The latter, combined with a Cary 17I spectrophotometer, enabled us to extend the accessible wavelength to 3000 nm. The difference spectra before and after irradiation by a dose of typically $1 \sim 2 \times 10^3$ J kg^{-1} were associated with the radiation-induced radical cations of the DCPs.[8] The extinction coefficient of the electronic absorption was determined by the procedure described previously.[9]

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