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RADICAL CATIONS OF CYCLOPENTADIENE DIMERS—FACETS OF AN INTRIGUING ENERGY SURFACE

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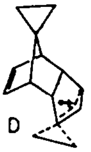
Abstract—The radical cations of various cyclopentadiene dimers can be generated by photoinduced electron transfer to strong electron acceptors. Nuclear spin polarization effects observed during these reactions provide insight into the radical cation structures. Three of the systems studied, *endo*-[4 + 2]- (**1**), *anti*-[2 + 2]- (**2**), and *exo*-[4 + 2]-dicyclopentadiene (**5**) give rise to unusual singly linked, delocalized radical cations, whereas the *anti*-[4 + 4]-dimer (**3**) and 1,3-bishomocubane (**4**) give rise to more conventional radical cations. The reactions of spiroheptadiene (**9**) and di(spiroheptadiene) (**10**) provide evidence for two different dimer radical cations, a doubly linked (D) and a singly linked (S) species. This finding supports a stepwise mechanism for the radical cation Diels–Alder reaction of **9**.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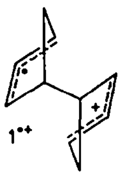
Recently we reported nuclear spin polarization results which support an unusual structure for the radical cation, $1^{\cdot+}$, of *endo*-dicyclopentadiene, **1**.[1] This radical cation assumes a structure which is fundamentally different from that of **1**: one carbon–carbon bond is completely broken; two carbon atoms are rehybridized; and the conjugation is extended. The structure of $1^{\cdot+}$ is also noteworthy because spin and charge are formally separated, and because it does not correspond to any minimum on the potential energy surface of **1**; indeed, it closely resembles a maximum on that surface, namely the transition state of the degenerate Cope rearrangement.[2]


$1^{\cdot+}$

The dissimilarity of the energy surfaces of radical cation and neutral diamagnetic precursor is unusual and has been established so far in only three additional systems: 1,1-diaryl-2-methylenecyclopropane,[3] a 5-methylenebicyclo[2.2.0]hex-2-ene derivative,[4] and several 4,8-bridged bicyclo[5.1.0]octa-2,5-dienes.[5] In each of these systems, the radical cations were assigned structures corresponding to maxima on the parent energy surfaces.

In contrast, the overwhelming majority of radical cations resemble more or less closely the structures of their neutral diamagnetic parent molecules. For example, aromatic hydrocarbons show minimal changes upon ionization. Other hydrocarbons may show noticeable changes in structural features such as bond length (e.g. norbornadiene or quadricyclane),[6] torsion angle (e.g. olefins),[7-10] or "flap" angles (e.g. bicyclobutane),[11,12] nevertheless a one-to-one correspondence between radical cations and their neutral precursors is maintained. Even for a select few radical cations whose singly occupied (SO) MO corresponds to a lowest unoccupied (LU) MO of the parent molecule (non-Koopmans states),[13,14] the connectivity of the carbon atoms remains largely unchanged. Finally, a sizable number of radical cations have been found to be unstable under the conditions of their generation; they undergo rearrangements to less strained radical cations.[12,15,16] We emphasize that the rearranged radical cations do not invalidate our conclusions, since in the majority of cases their structures correspond closely to the structures of less strained valence isomers of the parent molecules. Indeed, in all known cases, the rearranged radical cations generate rearranged products, whereas the non-vertical radical cations discussed here regenerate the starting material.

In view of the unusual radical cation structure of $1^{\cdot+}$, we have investigated several aspects of its potential energy surface. In this paper, we report results pertinent to the radical cations of four additional dicyclopentadiene isomers. Three of these are valence isomers which are directly related to **1**: the *anti*-[2 + 2]-dimer (**2**),† the *anti*-[4 + 4]-dimer (**3**),† and 1,3-bishomocubane (**4**), a photocyclization product of **1**. The

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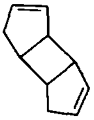
† The nomenclature and numbering system employed for the *cyclopentadiene dimers* are designed to emphasize the relation of the two monomer units in the dimer to each other. The carbons of one fragment are labeled 1–5, those of the other 1′–5′. Thus, in the *endo*-[4 + 2]-dimer, **1**, carbons 1 and 4 are bonded, respectively, to carbons 1′ and 2′. All *derivatives* are referred to by their customary designations.

fourth isomer is the *exo*-[4+2]-dimer, a stereoisomer, which may not be directly related to 1. In addition, we have studied the radical cation Diels–Alder reaction of spiro[2.4]hepta-4,6-diene and the electron transfer induced cycloreversion of di(spiroheptadiene).



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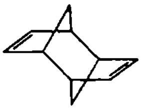

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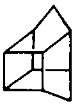

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In order to generate these radical cations, we have used photoinduced electron transfer reactions, and we have identified their structures on the basis of CIDNP results. This combination of techniques has been very successful, especially for the unambiguous identification of various strained-ring cations,[4-6,15-19] which all too often elude detection[20,21] because of their ready rearrangements, especially under the conditions of high-energy radiation.

PHOTO-INDUCED ELECTRON TRANSFER

A mild and versatile method for the generation of radical cation–radical anion pairs in solution is based on photoinduced electron transfer (PET). This method utilizes the fact that the oxidative power of an acceptor and the reductive power of a donor are substantially enhanced by photoexcitation. Thus, for donor-acceptor pairs with negligible or weak associative forces in the ground state, electronic excitation of either reactant may lead to the generation of radical ion pairs via electron transfer. We have utilized this method to generate a large number of radical cations derived from strained-ring hydrocarbon donors. The resulting radical ions have limited lifetimes since the pairs readily undergo intersystem crossing and electron return.

$$A \xrightarrow{h\nu} {}^{1}A^{*} \qquad (1)$$

$$^{1}A^{*} \xrightarrow{isc} {}^{3}A^{*} \qquad (2)$$

$$^{3}A + D \rightarrow {}^{3}\overline{A^{\dot{-}}D^{\cdot +}} \qquad (3)$$

$$^{3}\overline{A^{\dot{-}}D^{\cdot +}} \rightleftarrows {}^{1}\overline{A^{\dot{-}}D^{\cdot +}} \qquad (4)$$

$$^{1}\overline{A^{\dot{-}}D^{\cdot +}} \rightarrow A + D \qquad (5)$$

Scheme 1.

It is an important feature of this method that for a given donor the exothermicity of the electron transfer reaction can be adjusted by variation of the solvent (polarity) and of the acceptor (reduction potential, excited-state energy). For example, in most cases the exothermicity can be adjusted readily between 0.2 and 1.0 eV, i.e. the reaction can be changed from a marginally exothermic to a strongly exothermic one.

THE CIDNP METHOD

Radical cations generated by photoinduced electron transfer can be studied conveniently by an indirect method complementary to the ESR technique. Chemically induced dynamic nuclear polarization (CIDNP) is based on transient enhanced NMR signals, in absorption (A) or emission (E), shown by some products of radical reactions.[22,23] The first CIDNP effects were reported in 1967, and their potential as a mechanistic tool for radical pair reactions was soon recognized. Nuclear spin polarization effects were discovered in reactions of neutral radicals. However, we were able to establish that similar effects could be induced in radical ions as well.[24]

The theory underlying this effect depends critically on two selection principles: the nuclear spin dependence of intersystem crossing in a radical pair, and the electron spin dependence of the rates of radical pair reactions. Combined, these selection principles cause a "sorting" of nuclear spin states into different products and result in characteristic non-equilibrium populations in the nuclear spin levels of geminate reaction products (whose formation is allowed for singlet pairs but spin forbidden for triplet pairs) and in complementary non-equilibrium populations in the spin levels of free-radical ("escape") products (whose formation is electron spin independent). The transitions between these levels will be in the direction towards restoring the normal Boltzmann population; their intensities will depend on the extent of non-equilibrium population. The observed effects are optimal for radical pairs with lifetimes in the nanosecond range. On a shorter time scale, hyperfine induced intersystem crossing is negligible, whereas on a longer time scale the spin polarization decays due to spin lattice relaxation in the radicals.

The quantitative theory of CIDNP[25-28] is developed to a stage where the intensity ratios of CIDNP spectra can be computed on the basis of reaction and relaxation rates and the characteristic parameters of: the radical pair (initial spin multiplicity, μ); the individual radicals (electron g factors, hyperfine coupling constants, a); and the products (spin—spin coupling constants, J). On the other hand, the patterns of signal directions and intensities observed for different nuclei of a reaction product can be interpreted in terms of the hyperfine coupling constants of the same nuclei in the radical cation intermediate.

The ^{1}H hfcs are related to carbon spin densities by different mechanisms of interaction. For π radicals, there are two principal mechanisms involving either an exchange interaction or hyperconjugation. Protons attached directly to carbon atoms bearing positive spin density have negative hfcs because of the preferred exchange interaction between the unpaired π spin density and the carbon σ electron (Fig. 1(a)).

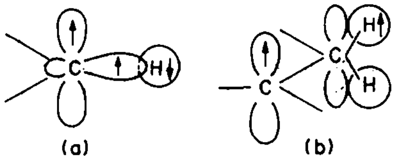


Fig. 1. (a) Preferred configuration of electron spins in the σ orbital connecting a hydrogen atom to an sp^2 hybridized carbon atom bearing unpaired π spin density. (b) "Molecular π orbital" consisting of two carbon p_z orbitals and an H_2 "group orbital" generated by hyperconjugative interaction of an sp^2 hybridized C atom bearing unpaired spin with a CH_2—R group.

Positive hfcs on the other hand, are usually observed for protons which are one C—C bond removed from a carbon bearing positive spin density. The positive sign is due to a hyperconjugative interaction which delocalizes the π spin density on carbon into an H_n "group orbital" (cf. Fig. 1(b)).

In summary, the patterns of CIDNP signal directions and intensities observed for diamagnetic products can be related to signs and magnitudes of ^1H hfcs of paramagnetic intermediates. The hfcs, in turn, can be interpreted in terms of carbon spin densities and these reveal important structural features of the intermediates. Combined with PET as a method of radical ion generation the CIDNP technique has provided the key to elucidating mechanistic details of reactions such as the photoreduction of carbonyl compounds by amines,[29,30] or the electron transfer sensitized isomerization of olefins.[17,31] In addition, the polarization patterns observed in many systems have provided insight into many short-lived radical cations which previously had eluded detection or identification by any other technique.

MATERIALS

endo-Dicyclopentadiene (**1**, Aldrich, Milwaukee, WI 53233, U.S.A.), the *exo*-isomer (**5**, Wiley Organics) and 3,4-dihydrodicyclopentadiene (**8**, Wiley Organics, Columbus, OH 43220, U.S.A.) were purified by gas chromatography (6 ft × 3/8 in 20% SE-30, 80°). The electron acceptor, chloranil (Eastman Kodak, Rochester, NY 14650, U.S.A.), and the solvents employed in the CIDNP experiments, acetone-d_6 (100%D, Aldrich) and acetonitrile-d_3 (99.7%D, Aldrich), were used without purification.

endo-*Dicyclopentadiene-d_2* (**1**-d_2). Dicyclopentadienone, prepared from α-1-hydroxydicyclopentadiene[33] by chromic acid oxidation,[11] was reduced by lithium aluminum deuteride in diethyl ether to produce β-1-hydroxydicyclopentadiene-d_1[32] in 46% yield. Treatment of this alcohol with an equimolar amount of thionyl chloride in an ether solution containing 1 equivalent of pyridine[34] at 0° generated α-1-chlorodicyclopentadiene-1-d_1, b.p. 50°/0.1 Torr, in 21% yield. The chloride (0.5 g, 0.003 M) was treated with 2 equivalents of $LiAlD_4$ (60 mg, 1.5 mM) in boiling diethyl ether[35] for 18 h. The mixture was quenched with a saturated aqueous Na_2SO_4 solution, and the resulting hydrocarbon was isolated by distillation (b.p. 60°/0.5 Torr) and purified by preparative gas chromatography (6 ft × 3/8 in 20% SE-30, 80°) yielding 42 mg (12%) **1**-d_2. MS: m/z (rel. intensity) 134 (16), 68 (94), 66 (100). ^1H-NMR (500 MHz, $CDCl_3$, δ): 1.28 (d, 1H), 1.30 (m, 0.2H), 2.08 (dm, 0.2H), 1.45 (dt, 1H), 2.69 (m, 1H), 2.74 (s, 1H), 2.84 (s, 1H), 3.19 (m, 1H), 5.46 (s, 1H), 5.48 (m, 0.5H), 5.92 (m, 1H), 5.96 (m, 1H).

anti - [2+2] - *Dicyclopentadiene* (anti - *tricyclo*[5.3.0.0^{2,6}]*deca*-3,9-*diene*, **2**). This was prepared by benzophenone photosensitized dimerization of cyclopentadiene.[36] The product mixture contained predominantly *endo*- and *exo*-dicyclopentadiene. The [2+2]-dimer was enriched by heating the mixture under reflux resulting in the preferential retro-Diels–Alder reaction of the [4+2]-dimers. The residue was distilled under vacuum (b.p. 63°/0.1 Torr) and the resulting 1 : 1 mixture of [2+2]- and [4+2]-dimers was separated by gas chromatography (6 ft × 3/8 in 20% SE-30, 100°, 100 ml min^{-1}).

anti - [4+4] - *Dicyclopentadiene* (anti - *tricyclo*[4.2.1.1^{2,5}]*deca*-3,7-*diene*, **3**). This was prepared according to the method of Grimme *et al.*[37,38] 1,3-Bishomocubane (pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decane, **4**) was prepared by acetone photosensitized cyclization of **1**[39] and recrystallized from methanol (m.p. 134–136°).

Pentacyclo[5.3.0.0^{2,5}0.^{3,9}.0^{4,8}]*deca*-6,10-*dione bis-ethylene ketal*. Cyclopentenone (Aldrich) was brominated with N-bromosuccinimide, and the product was dehydrobrominated with triethyl amine. The resulting cyclopentadienone rapidly dimerized.[40] The dimer was cyclized by direct irradiation[41] and the resulting diketone converted to the bis-ethylene ketal by condensation with ethylene glycol.[42]

Spiro[2.4]hepta-4,6-diene (**9**) was prepared by reaction of sodium cyclopentadienide with 1,2-dibromoethane[43] and purified by GC (10 ft × 3/8 in 10% carbowax, 130°). *endo*-Di(spiroheptadiene) (**10**) was generated by thermal dimerization of **9**.[43]

EXPERIMENTAL

Samples containing 2×10^{-2} M of an electron acceptor and typically the same concentration of an electron donor in acetone-d_6 or acetonitrile-d_3 were deoxygenated by purging with argon for 1 min. They were irradiated through Pyrex with a collimated beam of a 200 W Osram high-pressure mercury lamp in the probe of a Bruker WH90 Fourier Transform NMR spectrometer. A pulse angle of 90° was employed to minimize the total acquisition time when it could be shown that the polarization patterns and relative intensities were the same as those obtained with pulse angles as low as 30°.

In cases where steady-state irradiation resulted in substantial conversion, the samples were irradiated with the frequency-tripled output of a Quantel Nd/YAG laser (355 nm, 13 ns pulse width, 30–40 mJ pulse^{-1}). The 0–15 V signal coincident with lasing was fed into a NIC 293 pulse programmer to trigger the NMR experiment. The optical pulse and the 90° radio frequency pulse were separated by a variable delay between 10 and 100 μs. The different delays did not alter the CIDNP effects. A total of 16 sweeps were accumulated for each experiment. The results were compared with the polarization from a single sweep to ensure the absence of appreciable conversion.

RADICAL CATIONS OF CYCLOPENTADIENE DIMERS

In view of the unusual structure of the radical cation $1^{\cdot +}$, we have investigated several aspects of its potential energy surface: we have examined the electron transfer induced isomerization of **1**-d_2 and have addressed the question of conformational mobility in $1^{\cdot +}$; we have studied the radical cation of 1,3-bishomocubane in order to assess its potential interconversion with $1^{\cdot +}$; we investigated the radical cation of *exo*-dicyclopentadiene and considered its interconversion with the *endo*-radical cation; and lastly, we have evaluated the relevance of $1^{\cdot +}$ and substituted derivatives for the mechanism of the radical cation Diels–Alder reaction.[44–48]

Electron transfer induced isomerization of dicyclopentadiene

The CIDNP results, on which the assignment of the singly linked structure ($1^{\cdot +}$) is based, provide no information on one structural feature, namely the degree of overlap between the two allylic moieties. An examination of molecular models suggests two limiting cases. In one possible structure the groups may be sufficiently close to form a six-carbon five-electron fully delocalized (aromatic) array; this structure resembles the transition state for the thermal degenerate Cope rearrangement of **1**. The alternative structure has two separate allylic moieties bearing the positive charge and the unpaired spin, respectively. However, in either structure carbons 4 and 2′ and carbons 2 and 4′ are equivalent and can couple with equal probability. Accordingly, the involvement of the singly linked radical cation $1^{\cdot+}$ requires that the electron transfer induced reaction of a labeled dicyclopentadiene should lead to a statistical distribution of that label over both cyclopentene fragments. This type of equilibration was established in the thermal interconversion of α-1-hydroxydicyclopentadiene and *syn*-8-hydroxydicyclopentadiene reported by Woodward and Katz.[32].

In order to further support the structure of the radical cation, $1^{\cdot+}$, we have synthesized 5′-dideuterio-*endo*-[4+2]-dicyclopentadiene and studied its reaction with photoexcited chloranil. The results confirm that the electron transfer reaction causes a rapid degenerate isomerization. While the dark spectrum (Fig. 2) of $1\text{-}d_2$ shows the characteristic features of the 5′-protons only weakly, the CIDNP spectrum shows equal intensities for the protons in the 5- and 5′-positions. However, the relative intensities in the two positions are diminished by a factor of two relative to all other enhanced signals. Apparently the deuterium labeled $C_{5'}$ and the diprotio-C_5 are readily equilibrated.

Conformational considerations

One of the intriguing aspects of the unusual radical cation derived from dicyclopentadiene is its conformation. The fact that $1^{\cdot+}$ is generated from 1 and that it regenerates the starting material upon electron return does not rule out conformational mobility. On the other hand, the potential existence of an "aromatic" structure with five delocalized π-electrons may dictate conformational rigidity.

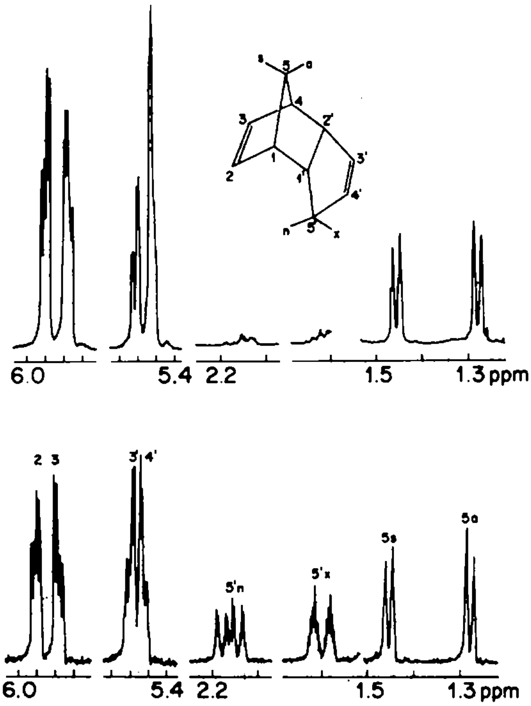


Fig. 2. ¹H-NMR spectra (500 MHz) of 0.02 M chloroform-d_1 solutions of *endo*-dicyclopentadiene (bottom) and endo-dicyclopentadiene-d_2 (top). The labels s, a, n and x designate, respectively, the *syn*, *anti*, *endo*, and *exo* protons in the 5 and 5′ positions.

In an attempt to evaluate conformational rigidity in this system, we selected two alternative precursors for the non-vertical radical cation $1^{\cdot+}$: the *anti*-[2+2]- and the *anti*-[4+4]- cyclopentadiene dimer. Although the thermal dimerization of cyclopentadiene yields the *endo*-[4+2]-isomer almost exclusively, the valence isomers are accessible by alternate routes. The *anti*-[2+2]-dimer is prepared by triplet-photosensitized dimerization,[36] whereas the *anti*-[4+4]-dimer requires a more elaborate synthetic scheme.[37,38] The radical cations of these isomers and their relation to $1^{\cdot+}$ are of particular interest.

The reaction of the *anti*-[2+2]-dimer with photoexcited chloranil gave rise to a CIDNP spectrum (Fig. 3(b)) which very closely resembles that produced during the analogous reaction of the *endo*-[4+2]-isomer (Fig. 3(a)). This observation indicates the involvement of the same radical cation, $1^{\cdot+}$, and its conversion to 1. More importantly, the failure to observe any polarization for the starting material, 2, indicates that the product formed upon electron return is independent of the geometry of the precursor. This result may reflect either the existence of a single prefered radical cation conformation or a similarly prefered mode of coupling for the biradical or zwitterion which may be an intermediate in the formation of 1 from $1^{\cdot+}$ upon electron return. In order to understand these factors more clearly, a brief discussion of the conformational profile of $1^{\cdot+}$ (and of the corresponding biradical or zwitterion) appeared useful.

The conformation of the doubly allylic intermediates can be characterized by the dihedral angle of an appropriately chosen reference system of carbon atoms. We have chosen the dihedral angle between the C_1—C_2 and the $C_{1'}$—$C_{2'}$ bonds, which constitute an internally consistent reference system. This structure has six exceptional conformations, each pair separated by a rotation of approximately 60° (Fig. 4). Two of the maxima, those at 0° and near −140°, contain one pair of eclipsed carbon–carbon bonds. Based on n-butane as a model,[49] these conformers should lie as much as 4 kcal mol^{-1} above the adjacent minima. The third maximum (~110°) contains two pairs of eclipsed carbon–carbon bonds giving rise to a strain energy estimated near 8 kcal mol^{-1}. Of the three maxima, the 0° conformer corresponds to an isomer on the parent energy surface, namely the *anti*-[2+2]-dimer.

The three minima near −70°, 55°, and 160° correspond to staggered conformations. Their relative energies should be nearly equal since all have two or three gauche interactions. Of the three minima, only one is closely related to a potential recombination product (and a potential point of entry): the conformation with a dihedral angle of ~55° appears well suited to regenerate the *endo*-[4+2]-dimer and, in turn, should be readily accessible from this dimer. In contrast, the minimum with a dihedral angle of −70° requires a rotation of at least 120° through at least one eclipsed conformation to reach the minimum corresponding to 1. Of the three potential points of entry onto the radical cation surface, one each correspond to a maximum and a minimum, whereas the *anti*-[4+4]-dimer falls between the minimum with a dihedral angle of 160° and the eclipsed conformation near one of 110°.

Given these conformational features it is not sur-

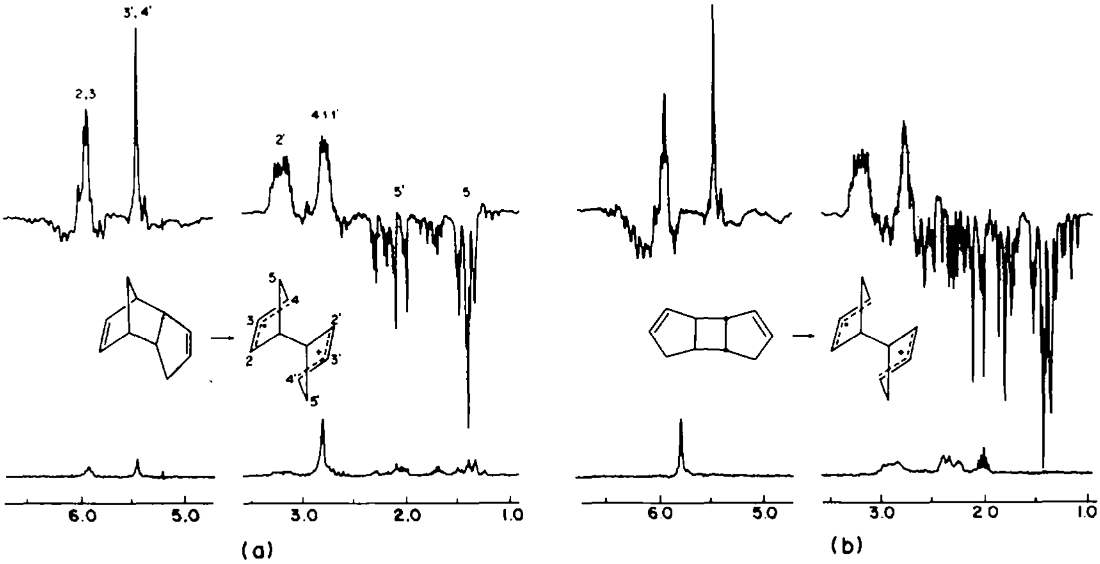


Fig. 3. A comparison of the ¹H CIDNP spectra (90 MHz) obtained by UV irradiation of acetone-d_6 solutions containing 0.02 M chloranil as an electron acceptor and 0.02 M of an electron donor, either *endo*-[4+2]-dicyclopentadiene (a) or the *anti*-[2+2]-dimer (b).

prising that the *endo*-[4+2]-dimer failed to rearrange upon electron transfer, whereas the *anti*-[2+2]-dimer isomerized readily. Both observations are compatible with limited conformational mobility, but insufficient to prove it. A more definitive answer could be expected from the third isomer investigated, the *anti*-[4+4]-dimer, if it formed a singly linked radical cation. However, the results observed for this isomer proved to have no bearing on the problem of conformational mobility. The CIDNP effects observed for 3 (Fig. 5) indicate positive electron spin density only for the olefinic carbons and, therefore, rule out carbon–carbon bond cleavage in the radical cation. The doubly linked intermediate may owe its comparative stability to its symmetry, which allows for the ready delocalization of spin and charge through the two doubly allylic links, an element of stabilization unavailable for the doubly linked radical cations derived from 1 and 2.[22]

The radical cation of exo-*dicyclopentadiene* (5)

The structures originally considered, and ruled out, for the radical cation of *endo*-dicyclopentadiene (1) included doubly linked localized "monoolefin" rad-

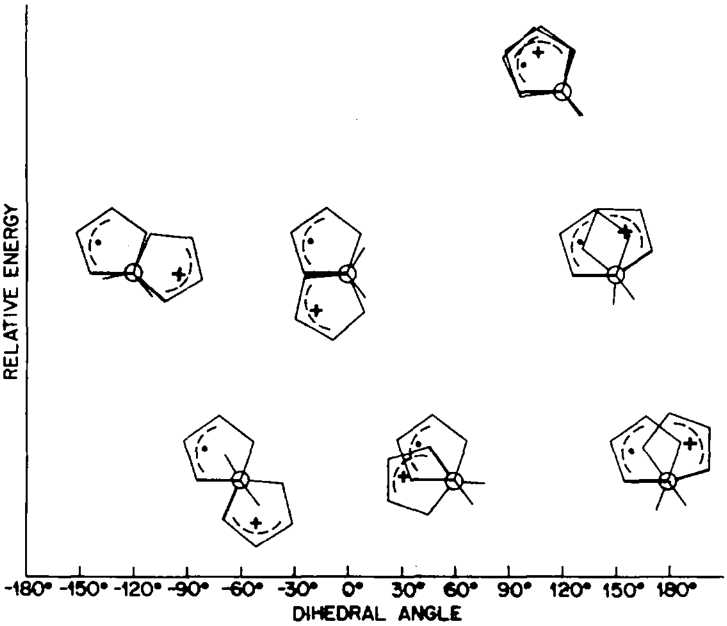
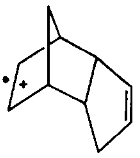


Fig. 4. Selected conformers of the singly linked radical cation $1^{\cdot+}$ accessible by oxidation of 1 and 2. In addition to minima near 55°, 160°, and −70°, and maxima near 0°, 110°, and −140°, the figure shows one non-extremum conformation corresponding to the possible point of entry from the *anti*-[4+4]-dimer (3).

Fig. 5. ^{1}H-NMR spectra (90 MHz) of an acetone-d_6 solution containing 0.02 M each of *anti*-[4+4]-dicyclopentadiene (**3**) and chloranil in the dark (bottom) and during UV irradiation (top).

ical cations (e.g. **6**) and a delocalized "diolefin" radical cation (**7**). The latter species can be ruled out because the two olefinic moieties of **1** do not interact appreciably as documented by the photoelectron spectrum.[50] Accordingly, the formation of **1**$^{\cdot+}$ is thought to proceed via ring opening of a short-lived localized radical cation. The driving force for the rearrangement should lie in the release of ring strain and in the extension of conjugation.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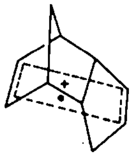
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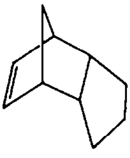
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In an attempt to further support this hypothesis we studied the PET reaction of a monoolefin, **8**, related to **1** and of the *exo*-isomer, **5**. The monoolefin upon reaction with photoexcited chloranil gave rise to the following nuclear spin polarization effects: enhanced absorption was observed for the olefinic protons and emission for the allylic protons. This pattern is compatible with a localized radical cation. However, the polarization is weak suggesting that the radical cation is short lived. The existence of this localized monoolefin radical cation strongly suggests that a similarly short-lived and localized radical cation might be derived from *exo*-dicyclopentadiene. Ring opening of this species could, once again, generate a doubly allylic radical cation, with a spin density distribution similar to **1**$^{\cdot+}$. These considerations are borne out by the strong CIDNP effects observed during the photoreaction of chloranil with **5** (Fig. 6). As in the reaction of the *endo*-isomer, the observation of enhanced absorption for two allylic protons indicates that the doubly allylic carbon–carbon bond is broken.

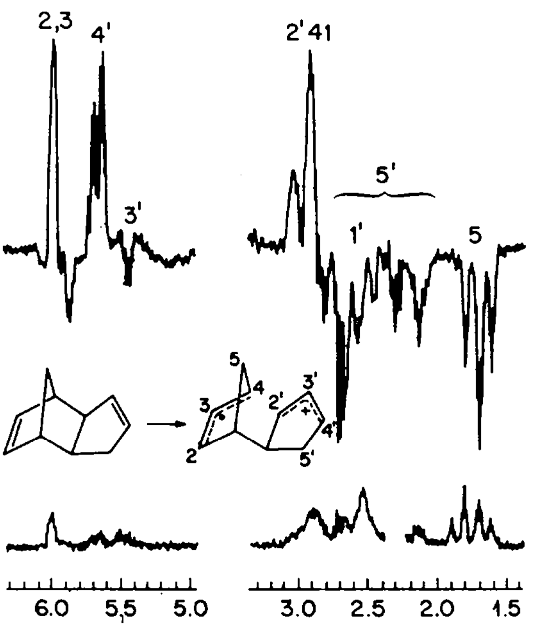
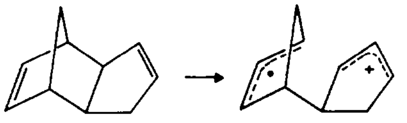
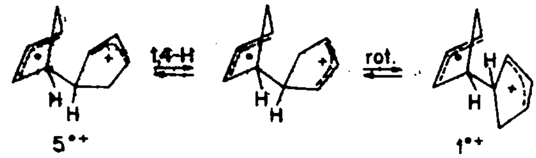


Fig. 6. ^{1}H-NMR spectra (90 MHz) observed during the UV irradiation of an acetone-d_6 solution containing 0.02 M each of chloranil and *exo*-[4+2]-dicyclopentadiene (**5**, top) and of the same solution in the dark (bottom).


5 5•+

The radical cation **5**$^{\cdot+}$ has a conformational profile similar to that of **1**$^{\cdot+}$ with three possible points of entry. In addition to the *exo*-[4+2]-dimer, the *syn*-[2+2]- and the *syn*-[4+4]-dimers could produce this intermediate upon electron transfer. It is interesting to discuss the connection between the potential energy surfaces of **1**$^{\cdot+}$ and **5**$^{\cdot+}$ and pathways that may interconvert the radical cations. The two tertiary carbons of **1**$^{\cdot+}$ have the same absolute configuration; in essence, **1**$^{\cdot+}$ is a racemic radical cation. On the other hand, **5**$^{\cdot+}$ is a *meso* radical cation having tertiary carbons of different absolute configurations.

The interconversion of **1**$^{\cdot+}$ and **5**$^{\cdot+}$ can be envisioned via a single or two successive 1,4-hydrogen shifts or by equivalent sequences of deprotonation and protonation. Neither of these processes can be ruled out *a priori*. We note that hydrogen migrations in radical cations have been suggested to account for the rearrangement of a trimethylene bridged bicyclobutane to the norcarene radical cation.[11] Similarly, radical cations have appreciable carbon acidities and their deprotonation by a semiquinone base (the geminate counterion of **5**$^{\cdot+}$) is quite reasonable.



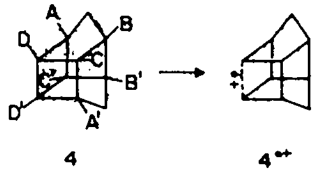
The radical cations of 1,3-*bis-homocubane and derivatives*

While three of the potential precursors of $1^{\cdot+}$ require cleavage of one carbon–carbon bond, the photocyclization product of 1, 1,3-bishomocubane (4), is a more remote precursor. Nevertheless, in view of the growing number of radical cations that undergo ring opening or fragmentation it appeared interesting to probe whether the radical cation of 4 might undergo successive (or simultaneous) cleavage of three carbon–carbon bonds to generate $1^{\cdot+}$.

Reaction of the parent system and of the bis-ethylene ketal with photoexcited chloranil gave rise to weak CIDNP effects, which rule out any involvement of $1^{\cdot+}$ and any ring opening $4 \rightarrow 1$. Nevertheless, these results are interesting, because they give insight into a class of radical cations about which little is known. The positions of spin and charge can be derived from the polarization pattern.

The 90 MHz ^{1}H-NMR spectrum of the parent system has four discrete features: two broad signals (2.65 and 2.85 ppm) represent eight methine protons whereas two AB doublets represent the methylene groups. The methine signals appear in emission indicating that at least some of these protons are coupled to the unpaired spin. The location of spin density is narrowed down by the finding that the methylene protons fail to show any polarization. This observation rules out appreciable spin density at the four carbons adjacent to the methylene groups.

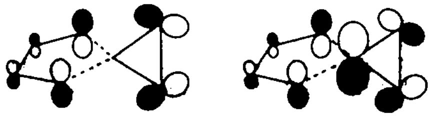
Similar conclusions can be derived from the CIDNP effects observed for the *bis*-ketal. One methine signal (2.85 ppm) appears in emission whereas the other (2.45 ppm) shows enhanced absorption. The downfield signal is assigned to the four protons (H_A, H'_A, H_B, H'_B) adjacent to the ketal moieties. Accordingly, only four carbon atoms on the bicyclohexane fragment remain as possible locations of the unpaired electron spin density. An examination of the structure indicates that most of the strain energy should be located in this fragment. It should be released to a significant extent by weakening (or breaking) the bond common to the two four-membered rings (C_D—C'_D). Our data cannot rule out some delocalization of spin and charge onto centers C_C and $C_{C'}$. However, it is quite clear that only one of the links between the monomer units is weakened (or broken) and that the other three remain unaffected. The barrier separating $4^{\cdot+}$ from $1^{\cdot+}$ or from complete fragmentation must be substantial.



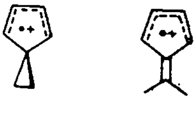
Radical cations of di(spiroheptadiene) (**10**) *and the electron transfer induced dimerization of spiro*[2.4] *heptadiene* (**9**)

The oxidative dimerization of diolefins resulting in cycloadducts of the [4+2] type (cation radical Diels–Alder reaction) has been the focus of much interest recently.[44–48] Especially the mechanism of this reaction and its synthetic utility have been investigated intensively. The results unambiguously support a radical ion chain mechanism.[44] However, only limited experimental evidence is available concerning the key step of the dimerization, i.e. the addition of the radical cation to the parent olefin. Is this addition a stepwise or a concerted reaction, and, if it is concerted, does the radical cation serve as the "diene" component ([3+2]cycloaddition) or as dienophile ([4+1]cycloaddition)? The observed retention of dienophile stereochemistry tends to support a concerted mechanism,[44] whereas the existence of the singly linked doubly allylic radical cation $1^{\cdot+}$ derived from *endo*-dicyclopentadiene might be construed as evidence for a stepwise mechanism.[1] No experimental evidence has as yet been reported that would differentiate the [3+2]- from the [4+1]cycloaddition type. However, orbital symmetry arguments have been adduced in favor of the [4+1]cycloaddition type.[46,47] In the following section we describe a system which shows with special clarity that the cycloaddition and the complementary cycloreversion have a stepwise component.

We have been interested in the effects of MO symmetry on the structures of radical cations derived from molecules containing a cyclopropane moiety.[51,52] In this context, the radical cation of spiro[2.4]hepta-4,6-diene appeared particularly interesting because the HOMO of the butadiene fragment cannot interact with either the symmetrical (S) or the antisymmetrical (A) HOMO of the cyclopropane fragment. Accordingly, we have studied the electron transfer reaction of 9 with photoexcited electron acceptors such as chloranil.



The electron transfer reaction of spiro[2.4]heptadiene with chloranil resulted in strong polarization for the reactant and its [4+2]-dimer (Fig. 7, top). The monomer polarization suggests a butadiene-like radical cation, which lacks appreciable interaction with the cyclopropane fragment. In essence, the spiroheptadiene radical cation has a spin density distribution similar to a series of fulvene radical cations[53] studied in our laboratory.



The dimer polarization is significant since it constitutes evidence for a rapid radical cation Diels–Alder reaction. The polarization pattern unambiguously identifies a dimer radical cation with appreciable spin

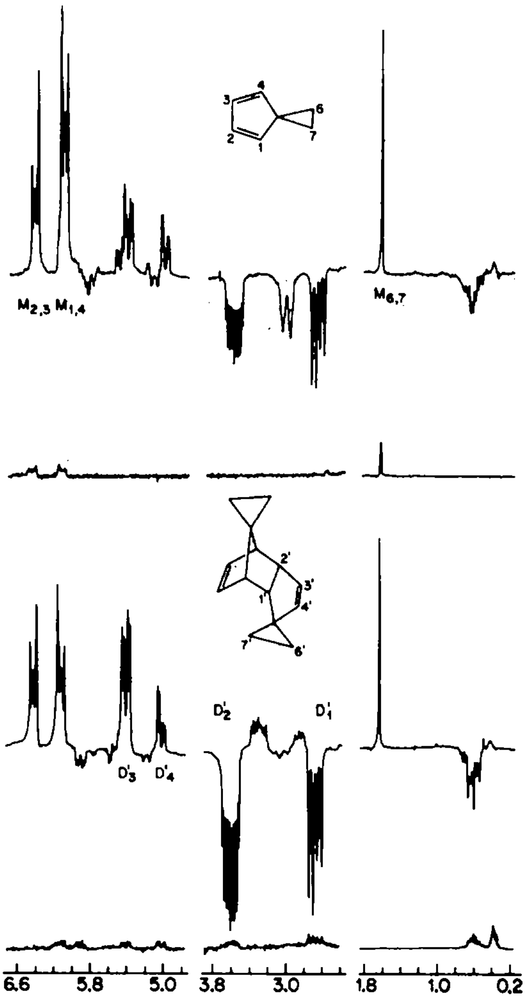


Fig. 7. ^{1}H-NMR spectra (90 MHz) observed during the UV irradiation of acetone-d_6 solutions containing 0.02 M of chloranil and spiroheptadiene (**9**) or di(spiroheptadiene) (**10**).

density only on two carbons of the dienophile fragment. This finding establishes the existence of a doubly linked (D) dimer radical cation in which spin and charge are localized in the vinylcyclopropane moiety. The same radical cation is implicated in the electron transfer reaction of the dimer (Fig. 7, bottom). The monomer polarization generated in the dimer reaction also originates in the doubly linked radical cation (D), further underscoring its significance.

In view of these considerations it is tempting to interpret the results shown in Fig. 7 as evidence for a concerted mechanism with the radical cation as dienophile, i.e. a [4 + 1]cycloaddition. However, such a conclusion is not strictly justified. This caveat follows from a limiting feature inherent in the CIDNP technique. Nuclear spin polarization effects typically reflect the electron spin density distribution of the intermediate, which is present during the spin sorting process, i.e. 1–10 ns after the generation of the original radical pair. In contrast, the structures of short-lived (10–1000 ps) radical precursors and longer lived (10–1000 ns) radical successors will not be reflected in the polarization of the ultimate diamagnetic products. Accordingly, the above results merely establish the existence of the doubly linked radical cation D, and the fact that it suffers cycloreversion (→→**9**) or reduction by the counter ion (→**10**). They cannot rule out the prior (**9** → D) or subsequent (**10** → D) involvement of a singly linked intermediate, S. Therefore, the results must be considered inconclusive as far as the (detailed) mechanism of the radical cation Diels–Alder reaction (and its cycloreversion) are concerned.

A change in experimental conditions to pulsed laser excitation allows a more detailed insight into this mechanism. Under these conditions the reaction of the dimer still produces a polarization pattern supporting the involvement of D (Fig. 8, top). However, the reaction of the monomer provides evidence for a different dimer radical cation. The nature of this intermediate is most clearly indicated by the enhanced absorption signals of H_4 and H'_2 (Fig. 8, bottom), which are characteristic for a singly linked radical cation (S).

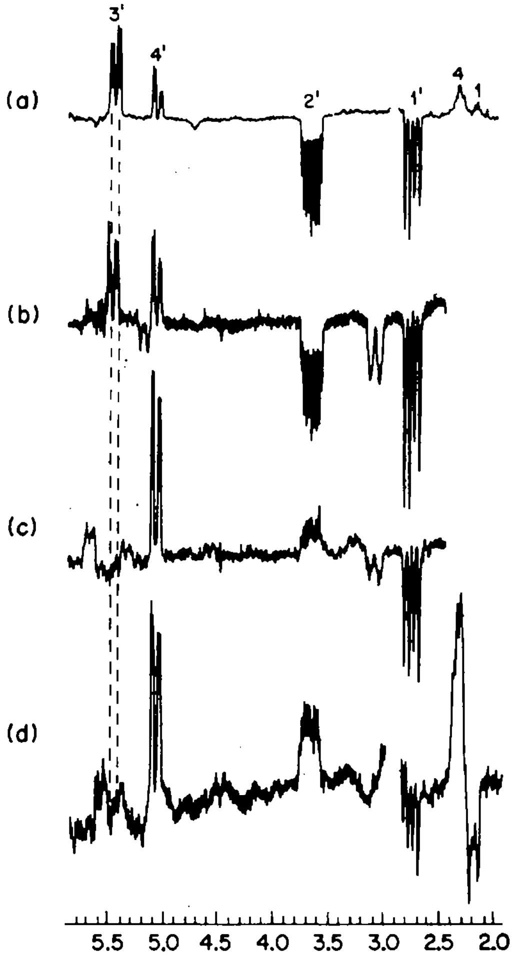


Fig. 8. ^{1}H-NMR spectra (90 MHz) observed 100 μs after excitation of chloranil solutions (0.02 M) with the frequency tripled output (355 nm) of a Nd/YAG laser: (a) acetone-d_6 solution containing 0.01 M di(spiroheptadiene), 16 laser pulses; (b) acetonitrile-d_3 solution containing 0.005 M spiroheptadiene, 4 × 16 laser pulses; (c) acetonitrile-d_3 solution containing 0.1 M spiroheptadiene, 4 × 16 laser pulses; (d) acetone-d_6 solution containing 0.1 M spiroheptadiene, 4 × 16 laser pulses.

The substantial differences between steady-state (Fig. 7, top) and time-resolved CIDNP results (Fig. 8, bottom) require comment. The typical advantage of time-resolved CIDNP spectroscopy lies in the ability to "isolate" CIDNP effects due to "early" pair recombination (100 ns–10 μs, depending on the available time resolution) from all other CIDNP effects.[54–56] However, in the system discussed here, this feature appears to be of secondary importance. Rather, the fact that the time resolved laser experiment minimizes the conversion of monomer to dimer, appears to be crucial. This feature prevents the dimer from entering the reaction cycle as a competing electron donor and eliminates the resulting strong dimer polarization (cf. Fig. 7, bottom).

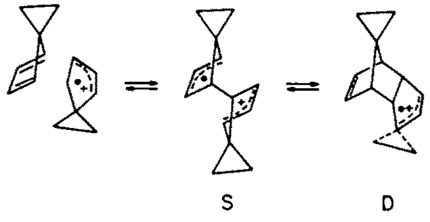
The spectra shown in Fig. 8 clearly support the involvement of two dimer radical cations, S and D, following the generation of the monomer radical cation, $\mathbf{9}^{\cdot+}$. The high monomer concentration used in these experiments favors the rapid interception of $\mathbf{9}^{\cdot+}$ by a monomer molecule (Eq. 6) and, likewise, the rapid interception of the doubly linked radical cation (Eq. 8). In contrast, the analogous reaction of S to form a singly linked biradical or zwitterion (Eq. 7) is less favorable, causing S to be the polarization determining intermediate.

$$\mathbf{9}^{\cdot+} + \mathbf{9} \rightarrow \mathrm{S} \qquad (6)$$

$$\mathrm{S} + \mathbf{9} \rightarrow \mathrm{S}^{2\cdot\pm} + \mathbf{9}^{\cdot+} \qquad (7)$$

$$\mathrm{D} + \mathbf{9} \rightarrow \mathbf{10} + \mathbf{9}^{\cdot+}. \qquad (8)$$

This sequence of reactions is further supported by the observation that variations in the reaction conditions (monomer concentrations, solvent polarity) lead to CIDNP effects, which can be explained as composites of polarization (Fig. 8, (b) and (c)) induced in S and D. Accordingly, a non-concerted contribution to the radical cation Diels–Alder reaction of **9** is clearly established, although a competing concerted mechanism cannot be eliminated. We note that the difference between a truly stepwise and a non-synchronous concerted reaction is subtle. However, our results unambiguously require the existence of the stepwise mechanism with S as an intermediate, and cannot be explained by a non-synchronous concerted process.



S D

CONCLUSION

The results discussed in this contribution once again emphasize the profound effect of steric and electronic factors on radical cation structures. In the case of dicyclopentadiene, **1**, the singly linked radical cation is favored because of its extended delocalization of spin and charge. For the *anti*-[2+2]-dimer, the relief of ring strain further facilitates rupture of the doubly allylic bond. For di(spiroheptadiene), on the other hand, the doubly linked radical cation D is stabilized by delocalization of spin and charge into the cyclopropane moiety. However, the singly linked species, S, remains accessible. The doubly linked radical cation of *anti*-[4+4]-dicyclopentadiene owes its stability to its symmetry, which allows delocalization over the two π bonds. The bis-homocubane radical cations have spin and charge in one strategic bond, whose weakening allows the maximum relief of strain; they fall far short of complete "unzipping" to $\mathbf{1}^{\cdot+}$.

All these assignments are based on unique insights provided by CIDNP results. This technique has been similarly successful in delineating mechanistic details of the radical cation Diels–Alder reaction. We hope to elucidate additional interesting radical cations with the help of this useful technique.

Acknowledgements—The authors are indebted to several colleagues who contributed to the work discussed here: to F. C. Schilling, who recorded the 500 MHz ^{1}H-NMR spectra; to W. D. Reents who analyzed the mass spectrum of $\mathbf{1}$–d_2; to Professor W. Grimme for a generous gift of hydrocarbon **3**; and to S. H. Bertz for helpful discussions.

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