Electron-Transfer-Induced Rearrangements: Radical Cations of Bridged Bicyclobutanes

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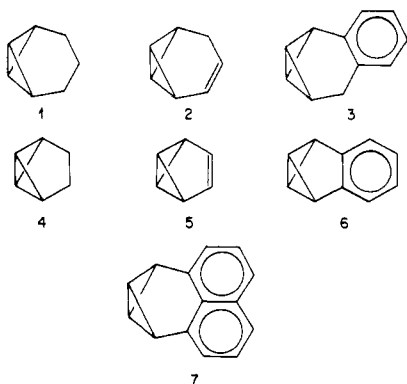Received December 14, 1984*

Abstract: The reaction of several bridged bicyclobutanes, **1–7**, with photoexcited electron acceptors gives rise to strong nuclear spin polarization effects. These results are interpreted in terms of two different types of radical cation intermediates in which spin and charge are localized either in the transannular bicyclobutane bond (A) or in a π orbital of the bridging moiety (B).

1, B = -(CH$_2$)$_3$-; **2**, B = -CH$_2$CH=CH-; **3**, B = CH$_2$(o-C$_6$H$_4$)-; **4**, B = -(CH$_2$)$_2$-;
5, B = -CH=CH-; **6**, B = -o-C$_6$H$_4$-; **7**, B = -[1,8]C$_{10}$H$_6$-

The chemical nature of the bridging unit determines the radical cation structures and influences the rearrangement pathways.

Bicyclobutanes have long intrigued chemists because of their unique structure and their unusual reactivity.[1] The central bond is formed by the overlap of nearly pure p orbitals, resulting in a rare negative ^{13}C–^{13}C coupling constant.[2] The unusual hybridization of the bridgehead carbon atoms (between sp and sp^2) manifests itself in a large ^{13}C–H coupling constant[3] and in a bridgehead acidity similar to that of acetylene.[4] The bicyclobutane system has a large strain energy (64 kcal/mol),[1] and the incorporation of an endo–endo bridge, as in derivatives **1–7**, places additional constraints on the framework. A variation of the bridging chain length causes corresponding changes in the dihedral angle between the cyclopropane rings ("flap angle") and in the transannular C–C bond length.[5]
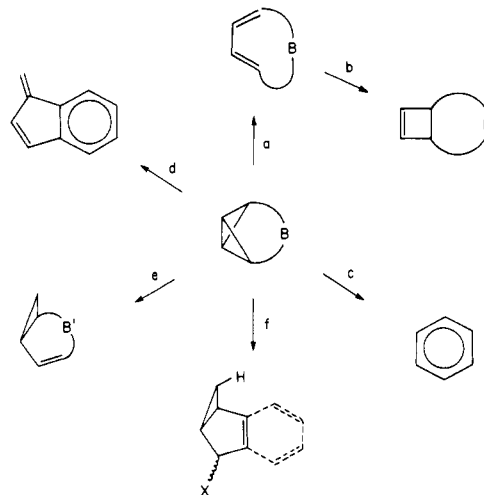

Table I. Molecular Orbitals of Bicyclobutane and Various Bridged Derivatives and Vertical Ionization Potentials (eV) Assigned to Them

	A_1	A_2	B_2	ref
bicyclobutane	9.1	11.2	>11.5	7
1	8.7	10.4	10.8	7
2	8.8	10.88	>11.8	28
4	9.4	10.2	11.5	7
5	9.8	10.8	>12.2	7,25
6	9.7	>11.1	>11.1	22
7	8.9	>10.2	>10.2	22

Scheme I

1, B = -(CH$_2$)$_3$-; **2**, B = -CH$_2$CH=CH-; **3**, B = -CH$_2$(o-C$_6$H$_4$)-;
4, B = -(CH$_2$)$_2$-; **5**, B = -CH=CH-; **6**, B = -o-C$_6$H$_4$-; **7**, B = -[1,8]C$_{10}$H$_6$-

The molecular orbital description of bicyclobutane is also unusual. The HOMO (A_1) is bonding principally between the bridgehead carbons,[6] whereas the next two lower orbitals (A_2, B_2) are bonding in the perimeter (Table I).[7] The flap angle has a profound influence on the relative energies of these orbitals. Upon decreasing this angle, the gap between the two HOMO's (A_1, A_2) is diminished since the A_1 and B_2 orbitals decrease in energy, while the A_2 orbital increases in energy.[7] The symmetry of these orbitals affects the interaction with suitably disposed moieties in the bridging unit. For example, the olefinic orbitals of benzvalene interact with several of the bicyclobutane orbitals. The interaction of the A_2 orbital with the π^* orbital results in electron donation and causes a large downfield shift of the bridgehead protons.[8] The

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interaction of the B_2 orbital with the π orbital causes the latter to be raised further in energy making it the HOMO by a large margin.[7]

The unique bonding in bicyclobutane is rivalled by a palette of interesting rearrangements. The following discussion will be restricted to bridged bicyclobutanes. Upon thermolysis many bridged bicyclobutanes undergo rupture of a pair of bicyclobutane bonds leading to cyclic *cis,trans*-dienes (Scheme I, a). In most cases these intermediates undergo conrotatory ring-closure to yield bicyclic cyclobutenes (b).[9-11] Benzvalene (5) rearranges to benzene by a direct, allowed pathway (c),[12] whereas naphthvalene (6) gives rise to benzofulvene (d).[13] Protic acids attack the bicyclobutane system at the bridgehead position leading to the rupture of one bicyclobutane perimeter bond with retention of configuration. Under catalytic conditions Moore's hydrocarbon (1)[14] and dihydrobenzvalene (4)[9] rearrange to bicyclic vinyl cyclopropanes (e). In the case of homobenzvalene (2) the initially formed norcaradiene rearranges to cycloheptatriene.[15] Benzvalene and naphthvalene both add protic acids, giving bicyclic vinyl cyclopropanes (f), but rearrange under catalytic conditions (Ag⁺) to the respective aromatic isomers (c).[8,13]

Recently, Gassman and co-workers have shown that photoinduced electron-transfer oxidation of 1 gives an intermediate in which the bicyclobutane bridgehead bond is weakened.[16] CIDNP effects observed during these reactions have corroborated the formation of such a radical cation and have established its hyperfine coupling pattern.[17] We now present results for other bicyclobutane systems, 2–7, in which the structure of the bridging unit is varied in length and degree of saturation, and we examine the effect of the bridging group upon the structure and rearrangement of the radical cation intermediate. To this end we have applied the CIDNP technique to the photoreaction of these bicyclobutanes with strong electron acceptors such as chloranil. In all cases, the CIDNP effects originate in radical ion pairs, which are generated by electron transfer to triplet excited chloranil. The sign and magnitude of the hyperfine coupling constant (hfc) of a particular nucleus in the radical cation is reflected[18-25] in the signal direction and intensity observed for the same nucleus in the product. For the reactions discussed here, enhanced absorption indicates a negative hfc, whereas emission implies a positive hfc. In general, a negative hfc for a proton is evidence for positive spin density on the carbon to which it is bound. A positive proton hfc can be caused by hyperconjugation or homohyperconjugation with the unpaired spin. Accordingly, a positive hfc indicates spin density on a carbon one or two C–C bonds away from the nucleus in
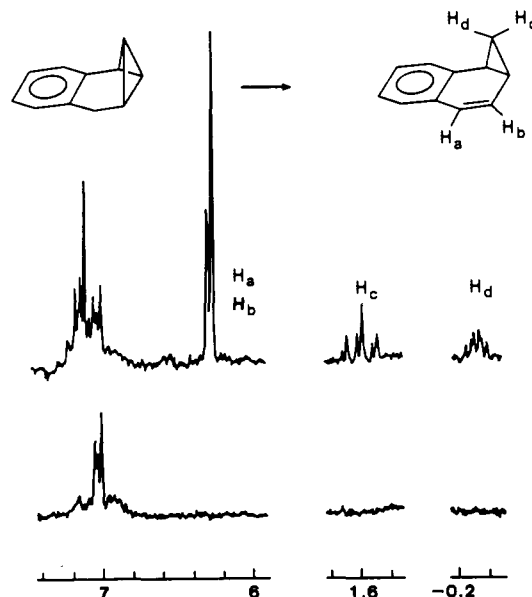

Figure 1. ¹H NMR spectra (90 MHz) of an acetone-d_6 solution containing 0.02 M chloranil and 0.02 M benzohomobenzvalene (3) in the dark (bottom) and during UV irradiation (top).

question.

Experimental Section

Bicyclobutanes 2–7 were prepared according to literature methods. Benzvalene,[13] naphthvalene,[13] and naphtho[1,8]tricyclo[4.1.0.0²,⁷]heptene[11,26] were prepared by reaction of chloromethylene with cyclopentadienyl, indenyl, and phenalenyl anions, respectively. Naphthvalene and naphtho[1,8]tricyclo[4.1.0.0²,⁷]heptene were purified by chromatography (pentane) on Al₂O₃ (IV), whereas benzvalene was purified by preparative gas chromatography on a 6 ft × ³/₈ in. glass column packed with 5% didecyl phthalate and 1.25% triethanolamine on 60/80 Chromosorb G-AW. Dihydrobenzvalene was prepared by diimide reduction of benzvalene[27] and purified by gas chromatography on the above column. Homobenzvalene was prepared from benzvalene by the procedure of Christl and co-workers,[15] which involves dibromocarbene addition, ring-opening, and consecutive removal of the bromine atoms by LiAlH₄ and Na/NH₃ reduction. The resulting hydrocarbon was purified by gas chromatography. Benzohomobenzvalene was prepared from the dibromocarbene adduct of 1,4-dihydronaphthalene by treatment with *n*-BuLi[10] and purified by distillation.

The electron acceptor, chloranil (Eastman Organics), and the solvents, acetone-d_6 (Aldrich), acetonitrile-d_3 (Merck Sharp and Dohme), and nitromethane-d_3 (Aldrich) were used without further purification.

Samples containing 0.02 M each of chloranil and bicyclobutane were deaerated by purging with Ar for 3 min and irradiated through Pyrex in the probe of a Bruker WH90 FT NMR spectrometer with the collimated beam of an Osram 200W high-pressure mercury lamp.

Results

The CIDNP effects show a marked dependence on the bridging moiety. For bicyclobutane systems with a three-carbon bridge containing at least one methylene group, i.e., Moore's hydrocarbon (1),[17] homobenzvalene (2), and benzohomobenzvalene (3), polarization is observed prominently in rearrangement products. For 1 and 3, electron transfer results in a rearrangement to 2-norcarene (8)[17] and benzonorcaradiene (9), respectively. These products can be detected by NMR after several minutes of irradiation, and they show strong CIDNP effects during irradiation (Figure 1). Unlike 1, benzohomobenzvalene generates polarization in the rearrangement product exclusively. The polarized rearrangement product generated during the photoreaction of homobenzvalene has not been identified. However, norcaradiene and cycloheptatriene, both logical products on the CIDNP time scale, have been eliminated as viable candidates. With dihydrobenzvalene (4), in which the bridging chain is shortened, polarization is observed mainly in the starting material. The CIDNP effects are

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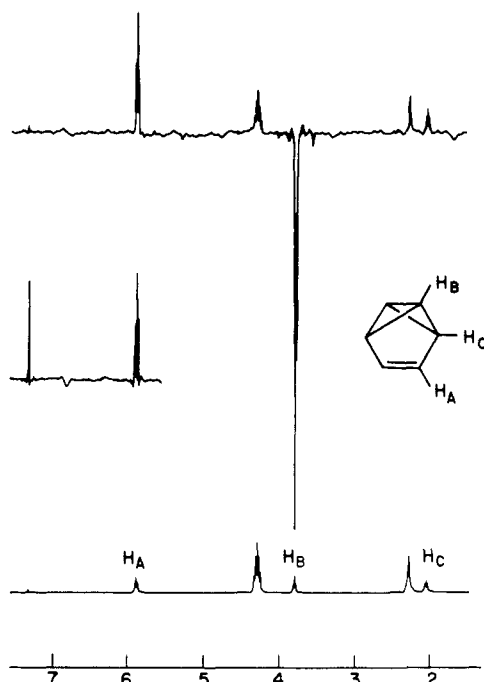
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Figure 2. ^{1}H NMR spectra (90 MHz) of a nitromethane-d_3 solution containing 0.02 M chloranil and ~0.1 M benzvalene (**5**) in the dark (bottom) and during UV irradiation at room temperature (middle) and at -30 °C (top).

weaker than those observed in the case of Moore's hydrocarbon, little, if any, polarization is observed for a rearrangement product, and no products can be detected after extensive irradiation.
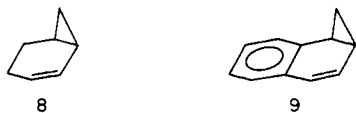
For benzvalene (**5**), naphthvalene (**6**), and "pleiavalene" (**7**), whose bridging units contain π systems but no methylene group, the CIDNP effects are markedly different from any described above. The photoreaction of **5** and **6** with chloranil gives rise to polarization for both the starting materials and the aromatic products, benzene and naphthalene, respectively (Figures 2 and 3). The tendency of these compounds to rearrange under electron-transfer conditions is altered relative to their thermal reactivity. Naphthvalene, which has a half-life of 31 h at 75 °C,[13] rearranges quantitatively within several minutes of irradiation. In contrast, benzvalene has a half-life of 0.2 h at 75 °C[28] but is rather impervious to the electron-transfer-induced photoreaction. Indeed, the rearrangement to benzene and the polarization of this product can be suppressed completely at lower temperatures (-30 °C, Figure 2). The photoreaction of **7** with chloranil, on the other hand, gives rise to weak polarization only for the starting material and not for the potential product, pleiadiene. This polarization is observed only at low substrate concentrations ($\sim 10^{-3}$ M), a common effect for polycyclic aromatic compounds.[29]

Discussion

The CIDNP results offer an insight into the structures of the intermediate radical cations. Of the molecules which show polarization for the reactants, two structurally distinct radical cations are indicated. The first of these has been demonstrated previously.[17] In Moore's hydrocarbon the hfc's (negative for the bicyclobutane bridgehead protons, positive for all others) identify the radical cation as one with positive spin density at the bridgehead carbons. The bicyclobutane central bond is, therefore,
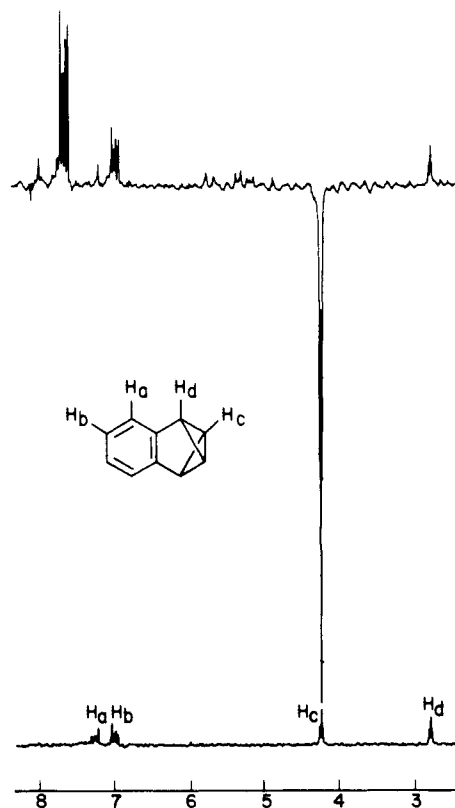
Figure 3. ^{1}H NMR spectra (90 MHz) of an acetonitrile-d_3 solution containing 0.02 M chloranil and 0.02 M naphthvalene (**6**) in the dark (bottom) and during UV irradiation (top).

weakened or broken in the radical cation. Dihydrobenzvalene (**6**) displays the same hfc pattern, indicating an analogous radical cation structure.

In contrast, the results for benzvalene and naphthvalene indicate completely different radical cation structures. A detailed analysis will be given for naphthvalene since it provides more information than does benzvalene. The most prominent feature of the CIDNP effects (Figure 3) is the strong emission of the bridgehead protons (H_c). Of the aromatic protons, those adjacent to the substituted aromatic positions, H_a, show little, if any, effect, whereas the remaining protons, H_b, display enhanced absorption. These results are consistent with a naphthvalene radical cation in which the unpaired spin occupies an orbital resembling the HOMO of **6**. Photoelectron spectroscopy data and semiempirical calculations[30] have been interpreted as evidence that the HOMO of **6** is, in essence, an o-xylene-type HOMO with B_2 symmetry. Electron density resides at the substituted aromatic carbons, and, to a lesser extent, on the carbons bearing H_b. The positive hfc for H_c results from a strong homohyperconjugative interaction with the π spin. The remaining bicyclobutane protons, H_d, show little polarization because of their orthogonal orientation relative to the partially occupied π orbital. The naphthalene polarization is complementary to the naphthvalene polarization and supports the same structure for the naphthvalene radical cation. Enhanced absorption is observed only for the β protons, whereas the α protons show little polarization. This polarization pattern differs from that induced in the naphthalene radical cation under analogous conditions. The photoreaction with chloranil gives rise to enhanced absorption mainly for the α protons (Figure 4). This pattern is fully compatible with the ESR spectrum of the radical cation in which the hfc of the α protons (5.5 G) is nearly 3 times as large as that of the β-protons (2.1 G).[31] The results observed in the naphthvalene isomerization are consistent with formation of a

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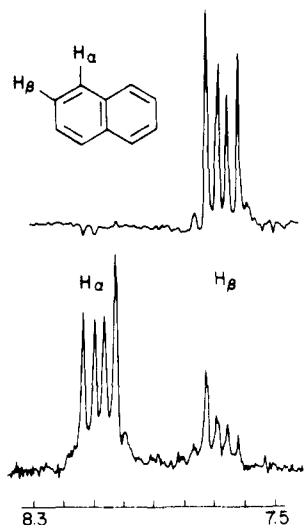
Figure 4. ^{1}H NMR spectra (90 MHz) of acetone-d_6 solutions containing 0.02 M chloranil and 0.003 M naphthalene (bottom) and 0.02 M naphthvalene (top), respectively, during UV irradiation.

naphthalene radical cation after diffusive separation of the naphthvalene$^+$·–chloranil$^-$· pair. The β protons of naphthalene originate as the H$_b$ and H$_c$ protons of naphthvalene and display the polarization (enhanced absorption) complementary to the sum of the H$_b$ and H$_c$ polarizations.

This line of reasoning applies equally well to benzvalene. The negative hfc derived for the ethylenic protons (H$_a$) is consistent with a radical cation in which spin and charge occupy an orbital resembling the HOMO of **5**. Photoelectron spectroscopy and theoretical modeling.[7,32] indicate that the HOMO of **5** is essentially the π orbital possessing B_2 symmetry. The bicyclobutane bridgehead protons (H$_b$) show a strong homohyperconjugative interaction, and the remaining protons show little effect because of their orientation. The benzene polarization (enhanced absorption at room temperature) could be consistent with either a rearrangement of benzvalene radical cation after diffusive separation or with reaction of any benzene contaminating the sample. The analogy with the results observed for naphthvalene and the suppression of this effect at lower temperatures are taken as evidence that the benzene polarization indeed originates in the benzvalene radical cation.

"Pleiavalene" (**7**) also displays effects indicative of a π-radical cation. Enhanced absorption is observed mainly for the two α protons of the naphthalene nucleus. In contrast to the effects induced in benzvalene and naphthvalene, no polarization is observed for the bicyclobutane bridgehead protons. These results are fully compatible with the molecular orbital description of **7**.[30] The HOMO of **7** is a naphthalene HOMO of A_2 symmetry with electron density largely in the α positions. The failure to observe bridgehead polarization can be explained by the substantial energy gap (>2.65 eV) between the two orbitals of naphthalene and bicyclobutane and by an unfavorable geometry for orbital overlap.

The CIDNP effects observed in systems that exhibit polarization for a rearranged product but not for the starting material provide some understanding of the rearrangement. First, the rearrangement must be faster than geminate recombination (1–10 ns) since the CIDNP effects observed are identical with those generated in the product radical cations under comparable conditions.[29] Second, these rearrangements are electron-transfer induced and not acid catalyzed. This assignment is based on several lines of reasoning. The acid-catalyzed rearrangement of **1** and **3** could, in principle, be induced by adventitious or photogenerated acid. The former reaction must be eliminated since it would be expected to occur in the dark whereas the observed rearrangement requires irradiation. The light-induced acid catalysis would involve hydrogen abstraction by the photoexcited quinone from the solvent
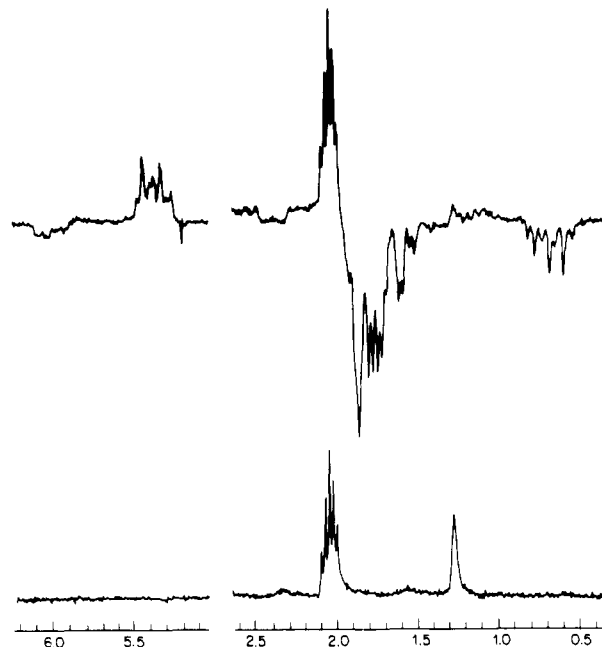

Figure 5. ^{1}H NMR spectra (90 MHz) of an acetone-d_6 solution containing 0.02 M chloranil, 0.02 M Moore's hydrocarbon (**1**), and 0.005 M pyridine in the dark (bottom) and during UV irradiation (top). The polarized species observed is 2-norcarene (**8**).

and generation of the corresponding hydroquinone. In this scheme the proton initiating the rearrangement originates in the solvent. Therefore, deuterium incorporation would be expected in deuterated solvents with exchangeable protons (deuterons). No such incorporation is observed. Moreover, light-induced acid catalysis would involve a slow buildup of rearranged material which would then enter the reaction cycle as an electron donor/quencher. However, low concentrations (2 × 10^{-3} M) of **8** and **9** do not give rise to sufficiently strong polarization to account for the effects observed during the reactions of **1** and **3**. Furthermore, the addition of a base such as pyridine failed to inhibit the rearrangement (Figure 5), whereas such a treatment is known to inhibit the acid-catalyzed rearrangement during the electrochemical oxidation of **1**.[33] Finally, no rearrangement of **4** to bicyclo[3.1.0]hex-2-ene is observed under these reaction conditions.

Several observations can be brought to bear on the mechanism of the rearrangement of these bicyclobutane derivatives under our reaction conditions. First, all rearrangements are those of radical cations, and they appear to traverse unique reaction coordinates. The "relative rate" of rearrangement for the bicyclobutane radical cations with at least one methylene linkage in the bridge parallels the relative rates of the thermal rearrangements,[9] which decreases in the order **2** > **1** > **4**. Under electron-transfer conditions **2** exhibits polarization largely for a rearranged species, **1** exhibits polarization for the rearranged species or the starting material depending on the solvent employed, and **4** exhibits polarization largely for the starting material. The products, however, are more reminiscent of the acid-catalyzed rearrangements (vide supra). Since in the case of **1** and **4** a radical cation with a broken central bond exists, it is likely that this is the primary species along the reaction coordinate. A cyclobutyl–cyclopropylcarbinyl type rearrangement then gives an edge-weakened bicyclobutane, and a subsequent 1,3-hydride shift produces the radical cation of the final product. This type of rearrangement appears to have very specific geometrical requirements since it occurs readily for radical cations with a three-carbon bridge but not for those with a two-carbon bridge.

The rearrangements of **5** and **6** are different since the bicyclobutane central bond is not likely to be involved. Instead, pairs of non-adjacent bicyclobutane bonds are cleaved. This mode of

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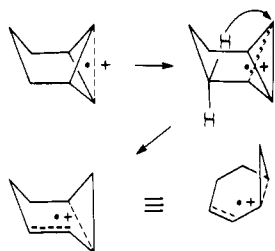
reaction is caused by the weakening of the B_2 perimeter bonds by electron donation to the half-filled π orbitals. The ability of these radical cations to regenerate their neutral precursors indicates that significant barriers exist for aromatization. Such barriers have been implicated for the benzvalene radical cation in the gas phase.[34]   The electron-transfer-induced rearrangement of naphthvalene and the thermal rearrangement follow dramatically different pathways as shown by the dramatically different products.

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Conclusion

CIDNP effects observed upon reaction of bridged bicyclobutanes with triplet chloranil are interpreted in terms of two different radical cation types. One structure type involves a weakened bicyclobutane central bond, whereas the other is a π-radical cation. The latter is observed in benzvalene and naphthvalene where the energy of the π-bonding HOMO is raised because of the molecular symmetry. The former radical cation type is observed in Moore's hydrocarbon and dihydrobenzvalene. The two types of radical cations undergo different rearrangements. A skeletal rearrangement and a 1,3-H shift are observed in the case of Moore's hydrocarbon and of benzohomobenzvalene, whereas bicyclobutane–butadiene ring-openings are observed in benzvalene and naphthvalene. The field of radical cation rearrangements, which traverse unique reaction coordinates, constitutes an important, emerging field of organic chemistry.

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Molecular Orbital Effects on the Structure of Cyclopropane Radical Cations

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Abstract: The interaction of photoexcited electron acceptors with selected cyclopropane derivatives results in electron transfer and generates radical ion pairs. Nuclear spin-polarization effects observed during these reactions allow an insight into the structures of the intermediates. The radical cations can assume two different structure types, which are derived either from the $^2A_1$ or the $^2B_2$ cyclopropane radical cation. Spiro[cyclopropane-1,9′-fluorene] gives rise to a radical cation, **12,** in which two cyclopropane bonds are weakened ($^2B_2$). In contrast, 2,3-benzo-5,6-cyclopropanorbornene has a radical cation, **16,** in which a single cyclopropane bond is weakened ($^2A_1$). These structures can be rationalized on the basis of frontier molecular orbital considerations.

In the framework of the continuing general interest in radical cations,[1–4] those derived from strained ring hydrocarbons are attractive targets because they can assume a variety of interesting structure types.[5–8] The relative energies of their accessible states are subject to substituent effects, and in selected cases, appropriately chosen substituents can alter the ordering of states. For example, cyclopropane radical cations can assume either a "trimethylene" structure in which one C–C bond is weakened (type A) or a structure resembling a π complex, i.e., with two weakened C–C bonds (type B).[5] A recent ab initio calculation of the cyclopropane radical cation[9] suggests that the lowest energy surface has low-lying saddle points corresponding to the general structure types $^2A_1$ and $^2B_2$. The minima are of lower symmetry and have
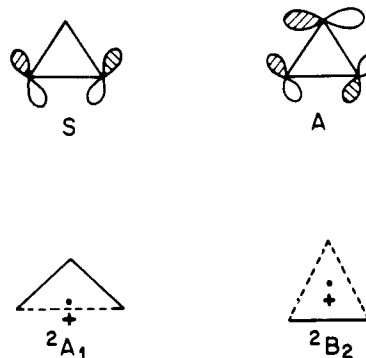
geometries intermediate between $^2A_1$ and $^2B_2$. The structures of substituted cyclopropane radical cations are logically derived from the two degenerate highest occupied molecular orbitals (HOMOs)

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