

than with bromide, and consequently the repulsive π -interaction in the fluoro compound is weaker, and less rate retardation is observed.⁴⁰

Acknowledgment. We are grateful to Prof. M. Pomerantz for assistance in calculating the carbocation structures, to Dr. T. Clark

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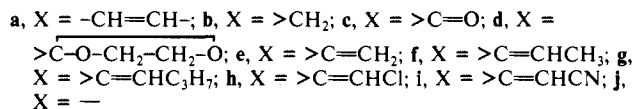
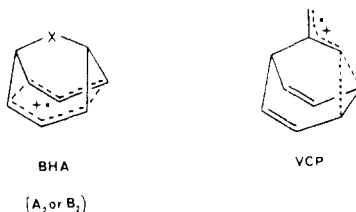
Supplementary Material Available: Optimized geometries and energies of transition states, ground-state molecules, and encounter complexes (3 pages). Ordering information is given on any current masthead page.

Radical Cations of Bridged Bicyclo[5.1.0]octa-2,5-dienes— Open-Shell Bis-Homoaromatic Systems

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Abstract: The radical cations of a series of bridged bicyclo[5.1.0]octa-2,5-dienes have been generated by photoinduced electron transfer to strong electron acceptors (chloranil, fluoranil) in solution. Chemically induced dynamic nuclear polarization effects observed during the reactions of simple bridged systems (**1b–d**,j) indicate that the intermediates are bis-homoaromatic (BHA)



systems of B₂ symmetry. These are the first homoaromatic radical cations of any structure type. Introduction of substituted *exo*-methylene groups as bridging units (**1e–i**) leads to a composite structure type with contributions from bis-homoaromatic structures of A₂ and B₂ symmetry and/or from a vinylcyclopropane structure (VCP) with an antisymmetric singly occupied molecular orbital.

The concept of homoaromaticity was pioneered by Winstein to account for the relative stability of molecules in which the cyclic conjugation of π orbitals is interrupted by an aliphatic fragment.¹ Homoaromatic systems have attracted much attention, and particularly mono- and bis-homoaromatic cations have emerged as a well-documented class of intermediates.^{2–4} There are considerably fewer, if any, examples of homoaromatic anions,^{5,6} while open-shell homoaromatic systems are unknown with the sole exception of the homocyclooctatetraene radical anion.^{7–9}

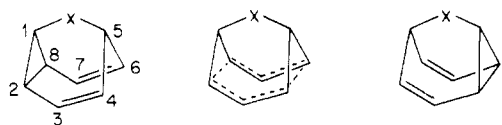
The concept of homoaromaticity has also been invoked to describe transition states of pericyclic reactions.¹⁰ For example, the degenerate Cope rearrangement of a series of bridged bicyclo[5.1.0]octa-2,5-dienes, bullvalene,^{11,12} barbaralane,¹² and semi-bullvalene,¹³ can be formulated through a transition state with a bis-homoaromatic array of orbitals. In the case of semi-bullvalene, this array is stabilized to the extent that the degenerate Cope rearrangement is fast on the NMR time scale even at -143°C ; it requires an activation energy of only 5.5 kcal/mol.¹⁴

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Theoretical considerations have been applied to formulate substitution patterns which might lower the activation energy even further and possibly lead to the ultimate in transition-state stabilization—a negative activation energy.^{10,15,16} However, these efforts have not met with success; to date no conclusive evidence has been reported for a bridged bicyclooctadiene system with a single bis-homoaromatic energy minimum. Even with electron-withdrawing substituents at positions 2, 4, 6, and 8 and electron donating substituents at positions 3 and 7, the semibullvalene system still possesses a double well potential surface.¹⁷

In the framework of the continuing general interest in organic radical cations^{18–23} and in the context of a research program focussed on radical cations with unusual structures,^{24–28} we have generated the radical cations of bridged bicyclooctadienes (**1b–j**) by photoinduced electron transfer to strong electron acceptors. Nuclear spin polarization (CIDNP) effects observed during these reactions suggest that the intermediate one-electron oxidation products are open-shell bis-homoaromatic radical cations, the first representatives of this hitherto elusive structure type.



a, X = $-\text{CH}=\text{CH}-$; b, X = $>\text{CH}_2$; c, X = $>\text{C}=\text{O}$; d, X = $>\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}$; e, X = $>\text{C}=\text{CH}_2$; f, X = $>\text{C}=\text{CHCH}_3$; g, X = $>\text{C}=\text{CHC}_2\text{H}_5$; h, X = $>\text{C}=\text{CHCl}$; i, X = $>\text{C}=\text{CHCN}$; j, X = $-$

Method

The radical cations discussed in this paper were generated by photoinduced electron transfer, which has proved to be a gentle and versatile method for the generation of radical ions. Specifically, this method has allowed us to study numerous radical cations^{29–31} which do not survive the more forcing reaction conditions of radiolysis,^{32,33} for example, those of quadricyclane,²⁹ hexamethyl(Dewar benzene),³⁰ or benzvalene.³¹

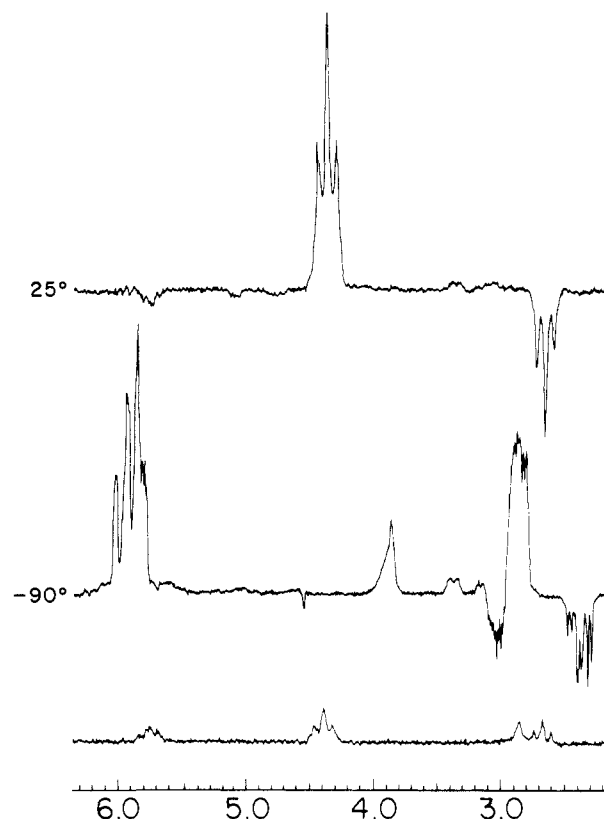


Figure 1. ^1H NMR spectra of acetone- d_6 solutions containing 0.02 M each of chloranil and barbaralane in the dark (bottom) and during UV irradiation at ambient temperature (top) and at -90°C (center).

The spin density distributions of these species are analyzed by the CIDNP technique. This method is based on the evaluation of transient, substantially enhanced NMR signals in absorption (A) or emission (E), which may be observed for some products of radical pair or radical ion pair reactions. The signal directions and intensities of these effects can be related to the signs and magnitudes of the hyperfine coupling (hfc) constants of individual nuclei in the paramagnetic intermediates. In turn, the hfc pattern can be interpreted in terms of carbon spin densities, revealing important structural features of the radical cations.

Experimental Section

The fluxional donor molecules were synthesized according to published procedures. Barbaralane (**1c**) was prepared by condensation of cyclooctatetraene dianion with dimethylcarbamoyl chloride followed by triplet sensitized rearrangement of the resulting trienone.³⁴ Barbaralane (**1b**) was prepared by reduction of barbaralane according to the Huang–Minlon modification of the Wolff–Kishner method.¹² The resulting C_8H_{10} hydrocarbon mixture was separated by gas chromatography (20% Carbowax). The main component was identified as bicyclo[3.2.2]nona-2,6,8-triene by comparison of its ^1H NMR spectrum with published data.³⁵ Barbaralane ethylene ketal (**1d**)³⁶ was prepared by condensation with ethylene glycol; *p*-toluenesulfonic acid was used as catalyst under azeotropic removal of water in refluxing benzene.

9-Methylenebarbaralane (**1e**) and derivatives (**1f–i**) were prepared via Wittig reactions with barbaralane. For the preparation of **1e**,³⁷ **1f**,³⁸ and **1i** the Wittig reagents were generated in situ from the corresponding triphenylphosphonium bromide salts and *n*-BuLi. **1i**: colorless liquid; ^1H NMR (CDCl_3) δ 5.70 (br t, 6.5 Hz, 2 H), 5.08 (s, 1 H), 4.49 (br t, 6.6 Hz, 2 H), 4.10 (br t, 6.7 Hz, 2 H), 3.49 (dt, 6.9 and 2.6 Hz, 1 H), 3.04 (dt, 6.6 and 2.6 Hz, 1 H); IR (neat) 3040, 2210, 1610, 790, 750, 735

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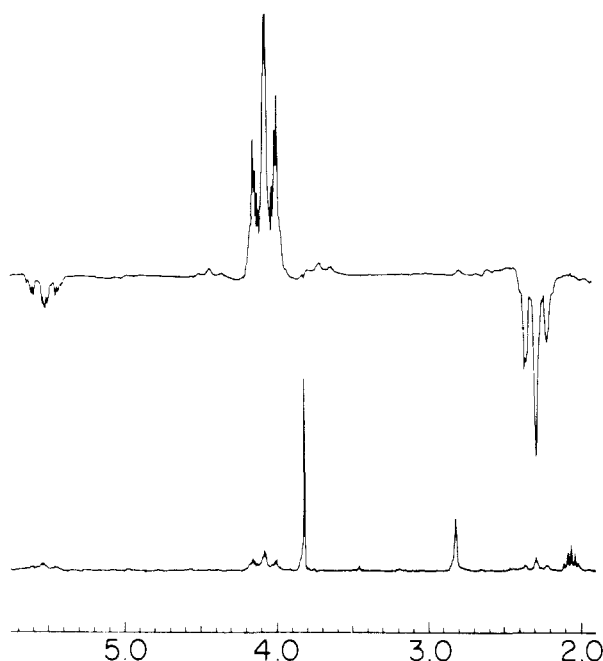


Figure 2. ^1H NMR spectra of acetone- d_6 solutions containing 0.02 M each of chloranil and barbaralane ethylene ketal in the dark (bottom) and during UV irradiation (top).

cm^{-1} . (Chloromethylene)triphenylphosphorane was prepared either through condensation of chlorocarbene with triphenylphosphine,³⁹ or through deprotonation of (chloromethyl)triphenylphosphonium chloride (Aldrich). Reaction of barbaralane with the latter reagent produced **1h** in good yield and purity, whereas some butylidenebarbaralane (**1g**) was isolated with **1h** in the reaction with the former reagent. The formation of **1g** is ascribed to an exchange reaction of the chloromethylene Wittig reagent with *n*-butyllithium. Compounds **1g** and **1h** were separated by gas chromatography (6 ft column; 20% SE-30; 150 °C; retention times at 120 mL/min: **1g**, 23 min; **1h**, 20 min). **1g**: colorless liquid; ^1H NMR (CDCl_3) δ 5.67 (br t, 7.0 Hz, 2 H), 5.28 (t, 7.1 Hz, 1 H), 4.71 (br t, 7.1 Hz, 2 H), 3.61 (br t, 6.6 Hz, 2 H), 3.07 (dt, 3.0, 6.9 Hz, 1 H), 2.81 (dt, 3.0, 6.5 Hz, 1 H), 2.01 (dt, 7.1, 7.4 Hz, 2 H) 1.35 (tq, 7.4, 6.6 Hz, 2 H), 0.87 (t, 6.6 Hz, 3 H). **1h**: colorless liquid; ^1H NMR (CDCl_3) δ 5.89 (s, 1 H), 5.70 (m, 2 H), 4.98 (br t, 7.2 Hz, 2 H), 3.41 (m, 3 H), 2.99 (br t, 6.7 Hz, 1 H); IR (neat) 3040, 1610, 800, 765, 740 cm^{-1} .

All donors were sublimed at 0.05 torr or purified by gas chromatography (20% SE-30) prior to use. The electron acceptor, chloranil (Eastman Organic Chemicals), was used without purification, as were the deuterated solvents, acetone- d_6 (99.9%, Aldrich) and acetonitrile- d_3 (99.7%, MSD Isotopes).

Samples containing 0.02 M each of the fluxional donor molecules and an acceptor were purged with Ar for 2 min and irradiated in Pyrex tubes in the probe of a Bruker WH 90 Fourier transform NMR spectrometer with the collimated beam of an Osram 200-W high-pressure mercury lamp. Pulse angles of 15 to 90° were employed, without any apparent changes in the CIDNP patterns.

Preparative photoreactions were carried out with solutions containing the same concentrations (0.02 M) of barbaralane derivatives as used for the CIDNP experiments; acetone (Fisher, AR) was substituted for acetone- d_6 . The solutions were purged with N_2 for 5 min and irradiated with a 450 W Hanovia lamp through a pyrex filter for 5 h.

Results

The electron-transfer reactions of all barbaralane derivatives with photoexcited quinones give rise to exceedingly strong CIDNP effects. These are conveniently divided, according to their appearance, into three categories. The first group of derivatives is comprised of barbaralane and its ethylene ketal. The reactions of these donor molecules give rise to strongly enhanced absorption for the protons in positions 2, 4, 6, and 8, strong emission for those in positions 1 and 5, and weak emission for H_3 and H_7 (Figures 1 and 2). In addition, the ketal showed net emission for the sharp singlet of the methylene protons (Figure 2).

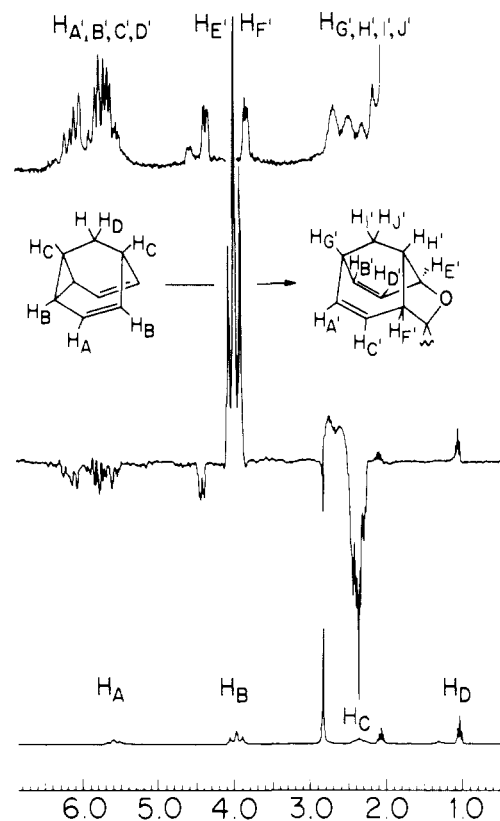
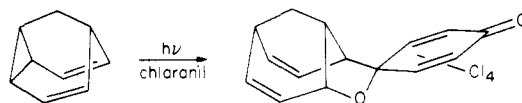


Figure 3. ^1H NMR spectra of acetone- d_6 solutions containing 0.02 M each of chloranil and barbaralane in the dark (bottom) and during UV irradiation (center). The top trace shows a spectrum of the [6 + 2] cycloadduct formed during 5 min of irradiation.

The photoreaction of chloranil with barbaralane was carried out at temperatures (−68 to −90 °C) sufficiently low to suppress the rapid degenerate interconversion of the valence tautomers. At these temperatures the protons $\text{H}_{2,8}$ and $\text{H}_{4,6}$ and H_1 and H_5 , which are magnetically equivalent at room temperature, become magnetically distinct (Figure 1). However, the polarization of $\text{H}_{2,8}$ and $\text{H}_{4,6}$ (enhanced absorption) and of H_1 and H_5 (emission) remains similar in direction as well as intensity, demonstrating their similarity in the paramagnetic intermediate.

The electron-transfer reaction of barbaralane (**1b**) results in a similar polarization pattern for the starting material. However, in addition, this reaction gives rise to a complementary set of enhanced signals, which are interpreted in terms of a chloranil adduct (Figure 3). The emission signals at 4.4 ppm (and at 3.8 ppm) are ascribed to aliphatic protons at the junction with the chloranil fragment; the emission signals between 5.6 and 6.2 ppm indicate the presence of olefinic protons; and the enhanced absorption signals between 2.5 and 2.7 ppm are assigned to be two bridgehead protons originating as H_1 and H_5 . These data can be interpreted formally in terms of a [6 + 2] cycloadduct, an assignment which rests primarily on the presence of four olefinic protons and of two additional signals with unusual chemical shifts typical for chloranil cycloadducts.^{28,40} Although this adduct is built up during the reaction and is sufficiently stable to be characterized in the reaction medium, it has so far eluded isolation.



The CIDNP effects observed during the electron-transfer reaction of 9-methylenebarbaralane (**1e**) with photoexcited chloranil at room temperature bear little resemblance with those of **1b-d**. This reaction results in enhanced absorption for all four types of

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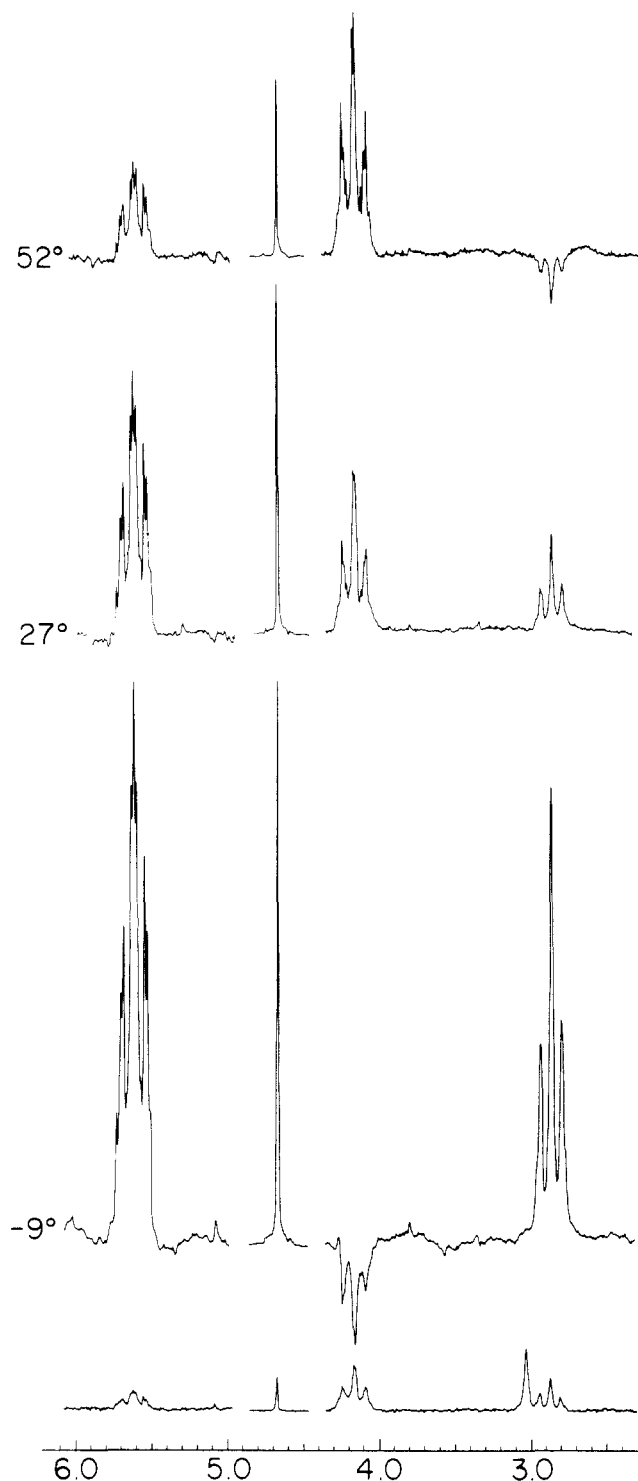


Figure 4. ^1H NMR spectra of acetone- d_6 solutions containing 0.02 M each of chloranil and 9-methylenebarbaralane in the dark and during UV irradiation at -9 , 27, and 52 $^\circ\text{C}$. The *exo*-methylene resonance at 4.7 ppm has been reduced by a factor of 4 in all spectra.

protons (Figure 4). By far the strongest effects are observed for the protons in positions 3 and 7 and for the *exo*-methylene protons; yet, the protons in positions 2, 4, 6, and 8 as well as 1 and 5 still show sizable enhancements.

The CIDNP effects observed for 9-methylenebarbaralane exhibit a pronounced temperature dependence in the range of $+52$ to -9 $^\circ\text{C}$ (Figure 4), even though the degenerate interconversion of the valence isomers is sufficiently fast to maintain an averaged NMR spectrum throughout this range. The overall polarization intensity increases with decreasing temperature, whereas the relative intensities of the four signals change substantially (Table I). Most strikingly two signals change direction in this tem-

Table I. Relative Enhancement of 9-Methylenebarbaralane Signals during Photoreaction with Chloranil as a Function of Temperature

	δ 5.6 $\text{H}_{3,7}$	δ 4.7 $=\text{CH}_2$	δ 4.2 $\text{H}_{2,4,6,8}$	δ 2.8 $\text{H}_{1,5}$
52 $^\circ\text{C}$	4	4	5	-3
27 $^\circ\text{C}$	16	9	3	2
-9 $^\circ\text{C}$	23	17	-4	15

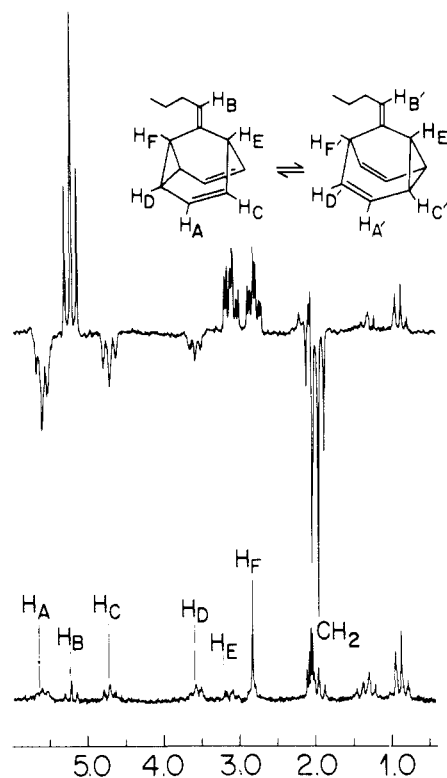


Figure 5. ^1H NMR spectra of acetone- d_6 solutions containing 0.02 M each of chloranil and 9-butylidenebarbaralane in the dark (bottom) and during UV irradiation (top).

perature range. The averaged triplet of the four "corner" protons appears in strongly enhanced absorption at $+52$ $^\circ\text{C}$ but is changed to an emission feature at -9 $^\circ\text{C}$. On the other hand, the triplet representing H_1 and H_5 appears in weak emission at $+52$ $^\circ\text{C}$ but changes to strongly enhanced absorption at -9 $^\circ\text{C}$.

A set of double resonance experiments were carried out to determine whether the lesser polarizations might arise as a result of nuclear Overhauser effects (cross relaxation).⁴¹ During the ultraviolet irradiation the strongly polarized transitions of $\text{H}_{3,7}$ and of the methylene group were saturated with a strong secondary field. These experiments did not affect the polarization of the adjacent protons, $\text{H}_{2,4,6,8}$ and $\text{H}_{1,5}$, respectively.

Finally, 9-methylenebarbaralane derivatives with substituents in the *exo*-methylene position, i.e., 9-ethylidenebarbaralane (**1f**), 9-butylidenebarbaralane (**1g**), 9-(chloromethylene)barbaralane (**1h**), and 9-(cyanomethylene)barbaralane (**1i**), showed strong absorption for the *exo*-methylene proton and somewhat weaker absorption for H_1 and H_5 (e.g., Figure 5). Interestingly, the triplet representing the internal olefinic protons, H_3 and H_7 , shows less strongly enhanced absorption for **1h** and **1i** than for **1e** and it appears in emission for **1f** and **1g** (Figure 5).

Discussion

The principal structures to be considered for the radical cations of the fluxional molecules discussed here are derived directly from the extreme structures on the potential energy surface of the parent molecules. One potential structure involves a pair of rapidly interconverting degenerate divinylcyclopropane radical cations, derived from the highest occupied molecular orbital (S_4) and

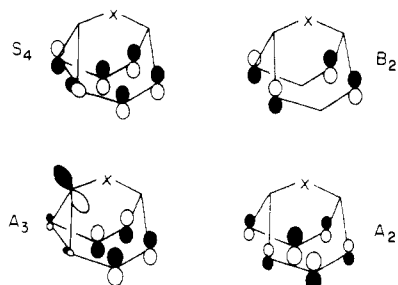
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Table II. Hyperfine Coupling Patterns of Radical Cation Types Derived from Bridged Bicyclo[5.1.0]octa-3,6-dienes and Projected CIDNP Effects

	divinyl-cyclopropane radical cation		bis-homoaromatic radical cations			
			B_2 SOMO		A_2 SOMO	
1	+	E	+	E	+ ^a	E
5	+		+		+ ^a	
2	-	A	-	A	-	A
4	-		-		-	
3	-	A	+ ^a	E	-	A ^b

^aSmall hfc. ^bPredominant effect.

analogous to the minima on the parent potential energy surface. The involvement of the second highest MO (A_3) of this structure is also considered. Alternatively, a bis-homoaromatic species with 5π electrons is considered, which corresponds to a maximum on the parent energy surface namely the transition state of the degenerate Cope rearrangement. The latter structure type may allow for additional structural variants because of the possibility of varying degrees of overlap between the two allyl fragments comprising this system. Further, the singly occupied molecular orbital (SOMO) of a potentially bis-homoaromatic radical cation may have B_2 or A_2 symmetry. The molecular orbitals shown below are assigned in analogy to those derived for semibullvalene.¹⁰



The distribution of electron spin density in the principal structure types and, hence, their hyperfine coupling patterns (Table II) can be expected to be sufficiently different to allow an unambiguous assignment of the radical cation structures. However, the comparison of these patterns with the experimental results is complicated by the degenerate rearrangement of the parent molecules. Although a radical cation may have a singularly defined structure during its lifetime (typically 1–30 ns), the rearrangement of the parent molecule may cause the superposition and possibly cancellation of effects induced in magnetically distinct protons. These considerations would apply specifically to the hyperfine pattern predicted if the second highest divinylcyclopropane MO (A_3) were involved.

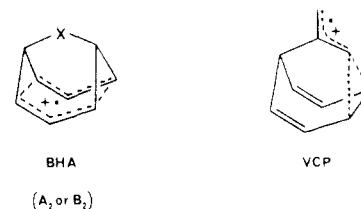
The CIDNP effects observed during the photoreactions of chloranil with barbaralane (**1b**), barbaralone (**1c**), and the ethylene ketal (**1d**) allow an unambiguous assignment of the radical cation structures. The strongly enhanced absorption signals for the protons in the "corner" positions, H_2 , H_4 , H_6 , and H_8 , suggest negative hfc's, whereas the strong emission multiplets for $H_{1,5}$ reveal positive hfc's in these positions. Both observations indicate that the principal electron spin density is localized on the four "corner" carbons.

Although the emission multiplets of H_3 and H_7 are the weakest effects observed in these reactions, they provide the decisive argument for the actual structure type of the intermediates. The weak positive hfc's indicated by these signals are compatible only with the bis-homoaromatic radical cations derived from the B_2 SOMO. These results rule out both a pure diolefin radical cation and the bis-homoaromatic radical cation derived from the A_2 SOMO, which have significant spin densities at C_3 and C_7 and,

hence, negative hfc's for H_3 and H_7 .

The identification of the bicyclo[5.1.0]octa-3,6-diene radical cations as bis-homoaromatic is significant because they constitute the first examples of homoaromaticity in radical cations and only the second case of homoaromaticity in open-shell systems. The apparent B_2 symmetry of these species is not surprising in view of their (inherent) substitution pattern. It is well-known that electron-donating substituents in adjacent positions raise the B_2 HOMO of a cyclic conjugated 6π -electron system relative to the A_2 HOMO and, thus, favor the B_2 SOMO of the corresponding radical cation. Accordingly the bicyclooctadiene is inherently designed to give rise to bis-homoaromatic radical cations of B_2 symmetry.

Although it might not appear trivial to override the design features favoring the B_2 radical cation, the bridged bicyclooctadienes nevertheless allow structural modifications which ultimately destabilize the A_2 MO and, thus, favor a radical cation of A_2 symmetry. For example, introduction of a 1,1-ethylene moiety as a bridging unit, i.e., in the 9-methylenebarbaralane system, might bring about such a change in structure. However, the interaction with the ethylene HOMO must be expected to affect two high lying orbitals: it should raise the A_2 orbital of the potential cyclic conjugated 6π -electron system and, therefore, compensate or override the influence of the electron donating substituents; it should also affect the A_3 MO of the divinylcyclopropane system and, thereby, stabilize a vinylcyclopropane radical cation (VCP), in which spin and charge are delocalized throughout the *exo*-methylene and cyclopropane moieties. The actual results observed in this system suggest a rather delicate balance between at least two stabilizing forces, which manifests itself in the pronounced and unprecedented temperature dependence of the CIDNP effects.



The observed temperature dependence shows two components: a general increase of polarization intensity with decreasing temperature and a dramatic redistribution of the relative intensities of the four signals (Table I). The general effect should have no bearing on the intermediate's structure. CIDNP intensities are a complex function of rates, such as those of diffusion, exchange processes, or reaction, and of other factors, such as viscosity and acidity. All of these are affected by temperature changes. The increased polarization intensity at lower temperatures reflects an increased efficiency of spin sorting but cannot be viewed as a general trend. In cases where the spin sorting is optimized, lowering the temperature should cause the polarization intensity to decrease.

The redistribution of CIDNP intensities is relevant for the assignment of the radical cation structure; it is viewed as an indication of structure changes. The assignment is based on a comparison of the polarization patterns (Figure 4) with those predicted for several prototype radical cations (Table III). Although none of the spectra is compatible with any single structure, the effects observed at any temperature can be explained as a composite of contributions due to (at least) two prototype structures. The CIDNP spectrum observed at 52 °C suggests contributions from bis-homoaromatic structures of A_2 and B_2 symmetry. The enhanced absorption signals for H_3 and H_7 and for the methylene protons are expected for the radical cation with A_2 symmetry; the strongly enhanced absorption of the corner protons and the emission of H_1 and H_5 are compatible with a 2B_2 radical cation.

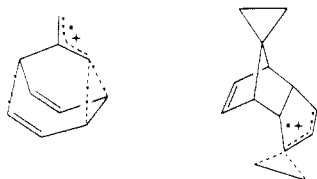
The effects observed at -9 °C suggest an increased contribution from the 2A_2 structure, but instead of the 2B_2 structure another structure type appears to be involved, which has not been en-

Table III. Hyperfine Coupling Patterns of Radical Cation Types Derived from Methylenebarbaralane and Projected CIDNP Effects

	A ₃ SOMO		B ₂ SOMO		A ₂ SOMO		π- complex
1	-	A ^b	+	E	+	E	- A
5	c		+		+		-
2, 8	+	E	-	A	-	A	a
4, 6	c		-		-		a
3, 7	c		+ ^a	E	-	A ^b	a
CH ₂	-	A ^b	c		-	A ^b	- A

^aSmall hfc. ^bPredominant effect. ^cUndeterminate or negligible.

countered so far. The strong absorption observed for the multiplet of H₁ and H₅ indicates high spin density in at least one of the corresponding carbons. This finding is compatible either with the vinylcyclopropane radical cation or with an unusual structure resembling a bidentate π complex between a trimethylenemethane radical cation and a bis-homoaromatic base. Of the possibilities, the π complex is without precedent, whereas the VCP radical cation appears plausible. The ionization energies of the S₄ (8.4 eV) and A₃ MO's (8.8 eV) of barbaralane⁴² are reasonably close so that the interaction with the ethylene orbital may well raise the antisymmetric MO above the symmetric one. The resulting radical cation structure resembles that assigned to the di(spiroheptadiene) radical cation.⁴³ Finally, the polarization at "ambient" temperatures (+27 °C) has the least specific information content. Since all four signals show enhanced absorption, positive spin density is indicated for every hydrogen bearing carbon atom. The actual structure of the radical cation at this temperature may have contributions from all three structure types, with only a minor contribution due to the VCP structure.



The substantial change in spin density distribution indicated for the 9-methylenebarbaralane radical cation over a relatively narrow temperature range is without precedent. We emphasize that we are not dealing with a rearrangement but with a change in a radical cation which remains closely related to the parent molecule and regenerates it upon electron return. In this context, it may be useful to consider how changes of this type may manifest themselves spectroscopically. In addition to changing CIDNP patterns there may be variations of EPR hyperfine splittings or shifts in optical spectra. We are not aware of any substantial temperature dependence in either CIDNP or optical spectroscopy. On the other hand, the EPR literature provides extensive documentation of temperature-dependent splittings, including changes in sign and negative temperature coefficients. The variations have been ascribed to dynamic or static equilibria or to changes in vibrational, rotational, or torsional motions. However, all observed changes are minor and in no case is a dramatic change in the structure of the paramagnetic intermediate indicated.

Considering the subtle balance between several canonical forms contributing to the overall structure of the 9-methylenebarbaralane radical cation, it appeared feasible to shift the apparent equilibrium by substituents in the *exo*-methylene position. Accordingly, the derivatives **1f-i** were synthesized and investigated. The NMR spectra of these derivatives are different from that of **1e**, because

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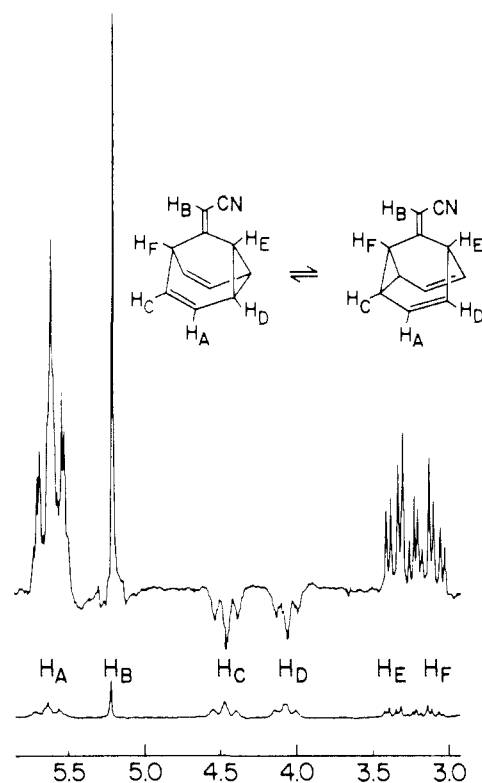


Figure 6. ¹H NMR spectra of acetone-*d*₆ solutions containing 0.02 M each of chloranil and 9-(cyanomethylene)barbaralane in the dark (bottom) and during UV irradiation (top).

the introduction of the substituents removes one element of degeneracy. Therefore, the positions C_{2,8} and C_{4,6} and C₁ and C₅ are no longer equivalent. However, in addition to these obvious changes, the CIDNP spectra observed for the derivatives with electron-donating (**1f,g**) and electron-withdrawing substituents (**1h,i**) are substantially different.

Derivatives of **1e** with electron-withdrawing substituents in the *exo*-methylene position, for example, the chloro and cyano derivatives (**1h,i**), give rise to CIDNP spectra (cf. Figure 6), which show an interesting relationship to those of **1e**. The polarization of **1h,i** at room temperature corresponds to that of **1e** at low temperature (-9 °C), and the effects observed for **1h,i** at 75 °C correspond to those observed for **1e** at ambient temperature. These spectra, once again, are compatible with contributions from the canonical structure with A₂ symmetry and from the vinylcyclopropane or the bidentate trimethylenemethane canonical forms. At elevated temperatures an additional contribution due to a BHA structure of B₂ symmetry manifests itself. Apparently, the electron-withdrawing substituents do not affect the principal structure type of these radical cations; rather, they raise the energy barrier for the involvement of the higher lying canonical forms.

Finally, derivatives of **1e** with alkyl groups in the *exo*-methylene position (**1f,g**) give rise to CIDNP effects with yet another polarization pattern. They show enhanced absorption for H₁, H₅, and H₁₀ and emission for H_{3,7} as well as for H_{2,8} and H_{4,6}. According to the CIDNP results, these species have spin density only in the *exo*-methylene and the bridgehead positions (C₁, C₅). Therefore, the canonical forms with A₂ and B₂ symmetry must be eliminated, and the vinylcyclopropane structure or the bidentate structure remain as plausible contributors to the radical cation structure of these derivatives.

Two facets of this assignment need further comment. First, it is not quite clear how the protons H₃ and H₇ acquire the relatively high positive hyperfine coupling constants indicated by the CIDNP results. One might envisage a through-space interaction with spin density at C₉, but we are not aware of any precedent for such an assignment. Second, we emphasize that the polarization of H₁ and H₅ for all four derivatives requires the intermediacy of two VCP radical cations for each derivative. This

follows from the fact that the Cope rearrangement of these fluxional molecules no longer interchanges C₁ and C₅ (or C_{2,8} and C_{4,6}). Of course, the pairs of valence isomers of **1f–i** should have nearly identical oxidation potentials so that their rates of quenching are essentially determined by their equilibrium concentrations.

Conclusion

The radical cations of the bridged bicyclooctadienes **1b–e, h–j** have been recognized as bis-homoaromatic structures, the first class of homoaromatic radical cations, and only the second class of open-shell homoaromatic systems. The influence of the substituted *exo*-methylene groups in **1e–i** on the radical cation structure is an unusual and unprecedented manifestation of mo-

lecular orbital effects in radical cation chemistry.

The intermediates **1b–e, h–j** are also of interest because their structure type is different, in principle, from that of the parent molecules. The latter have two-well potential energy surfaces, whereas the radical cations have a single minimum corresponding to the transition state for the degenerate rearrangement of the parent molecules. This qualifies the radical cations as further examples of the family of nonvertical radical cations, to which we have previously assigned the one-electron oxidation products of *endo*-dicyclopentadiene,²⁷ 1,1-diphenyl-2-methylenecyclopropane,²⁸ and a pentamethyl-substituted 5-methylenebicyclo[2.2.0]hex-2-ene.²⁶ We are actively pursuing further examples of this interesting class of radical cations.

Isomerization of 1-Butene Catalyzed by (η^6 -Arene)NiR₂. A Very Active Homogeneous Catalyst System

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Abstract: (η^6 -Arene)NiR₂ (R = SiCl₃, SiF₃, C₆F₅) complexes exhibit very high catalytic activity for the isomerization of 1-butene, especially in bromobenzene solution. The isomerization is generally first order in both 1-butene and Ni complex. The catalytic activity decreases in the order SiCl₃ > SiF₃ > C₆F₅. The reaction rate in toluene solution increases with increasing 1-butene concentration below a ratio of 1-C₄H₈/Ni = 100 but decreases at higher ratios apparently due to induced decomposition of the Ni complex. However, the rate is not adversely affected by high 1-C₄H₈ concentration in bromobenzene solution. The ratio of *cis*-2-butene to the *trans* isomer is also dependent on solvent, suggesting that an important step in the mechanism is the involvement of solvent in the catalytic cycle. The reaction of ethylene with (η^6 -arene)Ni(SiCl₃)₂ gives vinyltrichlorosilane and ethyltrichlorosilane. A mechanism is proposed which involves the intermediacy of nickel hydride species generated by the insertion of 1-butene into the Ni–R bond followed by β -hydride elimination.

The synthesis, structure, and reactivity of π -arene complexes of late transition metals have been of great interest.^{1–3} The π -arene ligand bound to groups 8–10 metals is often quite labile in solution allowing for unique reactivity at the metal center.^{1–5} Three coordination sites are opened by the loss of an η^6 -arene, and the interconversion from $\eta^6 \rightarrow \eta^4 \rightarrow \eta^2 \rightarrow \eta^0$ facilitates catalytic cycles for H–D exchange and hydrogenation of arenes.⁵

In previous papers we have reported on the synthesis and reactivity of π -arene nickel(II) and cobalt(II) systems.^{4,6} Complexed arenes in (η^6 -arene)MR₂ (M = Ni, Co; R = SiCl₃, C₆F₅) are easily displaced by ligands such as CO, R₃P, dienes, and THF. In addition, (η^6 -toluene)Ni(C₆F₅)₂ catalyzes the oligomerization of 1,3-butadiene, the polymerization of norbornadiene, and the hydrogenation of toluene.^{4a} We now report a detailed study of 1-butene isomerization by these interesting homogeneous catalysts.

Experimental Section

Materials. 2-Methylallyl chloride, *n*-heptane, bromobenzene, iodobenzene, anisole, 2-chlorotoluene, and a mixture of 3- and 4-bromotoluene (1:3) were purchased from Fisher and Aldrich Chemicals and used without further purification. Nickel metal, cobalt metal, and nickel bromide were purchased from J. T. Baker, Matheson, and Aldrich

Chemicals. Diethyl ether and tetrahydrofuran (THF) were refluxed over sodium benzophenone ketyl and distilled before use. Methylene chloride and toluene were refluxed over calcium hydride and distilled. Chlorobenzene and fluorobenzene were refluxed over phosphorus pentoxide and distilled. 3-Chlorotoluene was distilled just before use. All solvents were stored in a nitrogen atmosphere. 1-Butene was purchased from Matheson Co. and ethylene-*d*₄ (99%) was obtained from Merck and Co.

Preparation of (η^6 -Arene)NiR₂ (Arene = Benzene, Toluene, Mesitylene; R = SiCl₃, SiF₃, C₆F₅). Bis(2-methylallyl)nickel was prepared from nickel bromide and 2-methylallylmagnesium chloride in ether.⁷ (η^6 -Toluene)Ni(SiCl₃)₂ and (η^6 -toluene)Ni(SiF₃)₂ were prepared from bis(2-methylallyl)nickel and SiHCl₃ (SiHF₃) as described earlier.⁸ (η^6 -Toluene)Ni(C₆F₅)₂ was prepared from nickel vapor, C₆F₅Br, and toluene as described earlier.^{4a,9} (η^6 -Benzene)- and (η^6 -mesitylene)Ni(SiCl₃)₂ were prepared by displacement of toluene from the η^6 -toluene complex with excess benzene and mesitylene, respectively.

Isomerization of 1-Butene with (η^6 -Toluene)NiR₂. (η^6 -Toluene)NiR₂ (0.1 mmol) was placed in a 100-mL three-necked flask. A solvent (15 mL) was added and the solution was frozen in liquid nitrogen. 1-Butene (10 mmol) was added. The flask was immersed in an ice-water bath and the mixture was stirred magnetically. The start of the reaction was taken to be the time the frozen mixture was completely thawed. At intervals, 0.3–0.5-mL aliquots were withdrawn and analyzed on a Varian 940 gas chromatograph with a 24-ft 25% bis(2-methoxyethyl) adipate on Chromosorb-P column operating at room temperature.

Reaction of Ethylene with (η^6 -Toluene)Ni(SiCl₃)₂ or (η^6 -Toluene)Ni(C₆F₅)₂. (η^6 -Toluene)Ni(SiCl₃)₂ or (η^6 -toluene)Ni(C₆F₅)₂ (0.2 mmol) was placed in a 100-mL three-necked flask. Nitrogen head gas was removed under vacuum and then the complex was exposed to ethylene gas (2.0 mmol) and the system allowed to stand for 42 h at room tem-

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