Homoconjugation in Radical Cations of 7-Substituted Quadricyclanes and Norbornadienes

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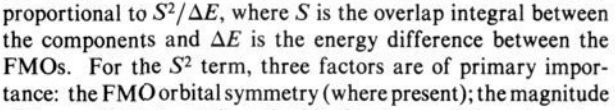
Abstract: Radical cations derived from norbornadiene (N) and quadricyclane (Q) systems bearing an *exo*-methylene function (M) or a spirocyclopropane group (Sp) in the 7-position have been generated by photoinduced electron transfer to tetrachlorobenzoquinone. CIDNP effects observed during these reactions illuminate the spin density distributions in these intermediates. Significant positive spin density is indicated for the *exo*-methylene carbon (C_8) of MN$^{\bullet+}$; this can be ascribed to a homoconjugative interaction between the N SOMO and the M FMO because of their compatible symmetries. The strong negative spin density indicated for the *exo*-methylene carbon (C_8) of MQ$^{\bullet+}$ is tentatively ascribed to an exchange interaction between the Q SOMO and the M FMO, which are aligned orthogonal to each other. These assignments are born out by ab initio molecular orbital calculations on the radical cations MN$^{\bullet+}$ and MQ$^{\bullet+}$ (at the MP2/6-31G* level). The effects for the spirocyclopropane signals of SpN and SpQ are weaker than those for MN and MQ; the homoconjugative and exchange interactions between the N or Q SOMOs, respectively, and the Sp FMO must be relatively weak.

Introduction

The interaction of strained ring moieties with olefinic fragments in organic radical cations has been of great interest in recent years.[1-3] A substantial number of substrates have been probed to delineate the changes in molecular geometry upon one-electron oxidation, to assess the spin density distribution in the resulting radical cations and to elucidate the parameters affecting the structures and reactivities of these intermediates.[4-8] Radical cations derived from substrates containing strained rings as well as olefinic moieties in suitable orientations may be stabilized by cyclic homoconjugation. Typical examples include the radical cations derived from benzonorcaradiene[9] or bicyclo[6.1.0]-nonatriene,[10] in which the cyclopropane bonds are merely weakened, and semibullvalene[11] or barbaralane,[12] in which one or two cyclopropane bonds are broken with formation of more extended π-systems.

In order to further probe the potential role of homoconjugation, we have chosen the radical cations formed from norbornadiene (N) and quadricyclane (Q) systems bearing appropriate substituents in the 7-position. We consider the intramolecular interactions between N and Q moieties, on the one hand, and a 7-exo-methylene[13] (M) or 7-spirocyclopropane group[14] (Sp), in the corresponding radical cations. The extent of the interaction can be derived by considering the component frontier molecular orbitals (FMOs). According to perturbational (P) MO theory,[15] the magnitude of the fragment perturbation is approximately proportional to $S^2/\Delta E$, where S is the overlap integral between the components and ΔE is the energy difference between the FMOs. For the S^2 term, three factors are of primary importance: the FMO orbital symmetry (where present); the magnitude of the coefficients at the point(s) of union; and the orientation of the fragments relative to each other.[2]

Because of the nature of the substituents and the way they are linked to the N and Q moieties, their interactions will be either stabilizing or nonbonding. The FMO symmetries of the ethene and spirocyclopropane functions are compatible with the symmetry of the N FMO and incompatible with the FMO of Q. Accordingly, the highest occupied molecular orbital (HOMO) of N should interact strongly with the FMOs of the *exo*-methylene or spirocyclopropane functions, leading to delocalized singly occupied (SO) MOs for MN$^{\bullet+}$ and SpN$^{\bullet+}$. In contrast, the interaction of the Q HOMO with the *exo*-methylene orbital should be nonbonding; therefore, spin and charge in the radical cations, MQ$^{\bullet+}$ and SpQ$^{\bullet+}$, should not be delocalized into the *exo*-methylene moiety. On the other hand, a 7-phenyl substituent (as in PQ, for example) might favor Q$^{\bullet+}$, as indicated by the favorable fragment PMOs shown below.



We have probed these interactions by three methods. First, we determined the electron-transfer quenching efficiencies of the potentially homoconjugated systems, MN and MQ, and SpN and SpQ, and compared them with those of N and Q, respectively,

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to evaluate any evidence for increased quenching efficiencies in the 7-substituted substrates. Further, we scrutinized the photoinduced electron-transfer reactions of the four substrates by the CIDNP technique. This method has brought to light a wealth of unusual structures and interactions;[1] the CIDNP results serve to delineate the spin density distribution of the four radical cations and to probe the extent of delocalization. Finally, we carried out ab initio molecular orbital calculations for $MN^{\bullet+}$ and $MQ^{\bullet+}$; these types of calculations have been applied previously to several unusual radical cations and have provided significant insights and helped to rationalize the hyperfine coupling patterns suggested by CIDNP results.[16–21]

Radical Cations of Norbornadiene and Quadricyclane. In order to provide a basis for the following discussion, we review briefly some of the features that have made the valence isomers norbornadiene and quadricyclane the target of considerable attention for the past two decades. These molecules contain two identical groups, either ethene units or cyclopropane moieties, held rigidly in orientations allowing the study of through-space or through-bond interactions, respectively.[22–27] The corresponding radical cations also have long been a target of interest. Three methods have been instrumental in elucidating various facets of the structure of norbornadiene radical cation, $N^{\bullet+}$: the polarization pattern of the CIDNP spectrum;[28] ab initio molecular orbital calculations;[16] and the hyperfine coupling pattern from ESR and ENDOR data.[29,30] In contrast, many attempts to observe the quadricyclane radical cation, $Q^{\bullet+}$, directly have failed; some of these resulted in rearranged radical cations.[27,31,32] Only CIDNP results[28] and ab initio molecular orbital calculations[16] are available, so far, for this elusive species. The good agreement between the spin density distributions obtained by the three different methods for $N^{\bullet+}$ not only reinforces the confidence in the structural details derived for $N^{\bullet+}$ but also gives us confidence that the $Q^{\bullet+}$ structure is adequately described by CIDNP data and ab initio calculations.

Scheme 1

$$A \longrightarrow {}^{1}A^{*} \longrightarrow {}^{3}A^{*} \qquad (1)$$

$${}^{3}A^{*} + D \longrightarrow {}^{3}\overline{A^{\cdot -}\ D^{\cdot +}} \qquad (2)$$

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

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

$${}^{3}\overline{A^{\cdot -}\ D^{\cdot +}} \longrightarrow {}^{2}A^{\cdot -} + {}^{2}D^{\cdot +} \qquad (5)$$

Fluorescence Quenching Experiments

The ability of an electron donor to suppress the fluorescence of a photoexcited electron acceptor is a measure for the electron donor ability. A characteristic constant can be determined from the quencher concentration dependence of the acceptor fluorescence intensity. The Stern–Volmer constant, K_{SV}, is the product of the acceptor fluorescence lifetime and the bimolecular rate constant of quenching by the donor, $K_{SV} = \tau_f k_q$. All four substrates discussed here, MN and MQ as well as SpN and SpQ, quench the fluorescence of excited-state acceptor molecules (viz., 9,10-dicyanoanthracene) efficiently. All Stern–Volmer plots (including those of N and Q) are nonlinear, presumably because of complex formation between the donors and the acceptor in the ground state. Accordingly, the data points have to be chosen at relatively low quencher concentrations, lower than 10^{-1} mol L^{-1} for N and its derivatives, lower than 10^{-2} mol L^{-1} for Q and its derivatives. Under these conditions, the Stern–Volmer intercepts were 1.00 ± 0.01 and the correlation coefficients of the plots were >0.9995.

In general, Q and its derivatives are significantly better quenchers than N and its derivatives. Within the two families, however, the differences are smaller. For example, the Stern–Volmer constant for the reaction of MN ($K_{SV} = 51$) is insignificantly lower than that of N ($K_{SV} = 65$), whereas the Stern–Volmer constant for quenching by SpN ($K_{SV} = 122$) is noticeably increased. On the other hand, the Stern–Volmer constant for the reaction of MQ ($K_{SV} = 173$) is marginally lower than that of Q ($K_{SV} = 210$), and that of SpQ ($K_{SV} = 195$) is also slightly lower. Interestingly, the introduction of the spirocyclopropane function improves the electron donor ability of N, but weakens the ability of Q. However, these differences are small and fall short of allowing major conclusions other than that all the substrates considered here are very efficient quenchers.

Nuclear Spin Polarization Results

A mild and versatile method for the generation of radical ion pairs in solution is based on the fact that the oxidative power of an acceptor and the reductive power of a donor are substantially enhanced by photoexcitation. Thus, electronic excitation of one of the reactants may result in (photoinduced) electron transfer (Scheme 1).[33–35] In order to prevent rapid electron return, it is advantageous to use triplet acceptors, most commonly ketones or quinones (eq 2), which generate triplet radical ion pairs. Even so, the resulting radical ion pairs readily undergo intersystem crossing (eq 3), followed by recombination of the singlet pairs (eq 4) or separation by diffusion (eq 5) to generate "free" radical ions.

When a photoinduced electron-transfer reaction is carried out in the probe of an NMR spectrometer, the competing processes (eqs 3–5) delineated in Scheme 1 may induce (chemically induced) nuclear spin polarization (CIDNP) effects, giving rise to a pattern of enhanced absorption or emission lines in the NMR spectrum. The polarization patterns observed for the reaction products are determined by four parameters, including the sign

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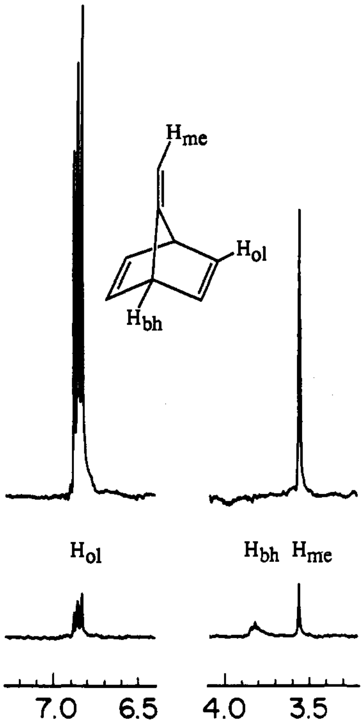

Figure 1. ^{1}H CIDNP spectra (90 MHz) observed during the photoreaction of chloranil with 7-methylenenorbornadiene (top). The individual resonances of the olefinic, bridgehead, and *exo*-methylene protons are denoted $H_{\cdot ol \cdot}$, H_{bh}, and H_{me}, respectively. The bottom trace is a dark spectrum.

and the magnitude of the hyperfine coupling constants for the paramagnetic intermediate and the spin multiplicity of the precursor as well as the mode of product formation.[36-39]

Representative results for such experiments are those obtained during the photoreactions of 2,3,5,6-tetrachloro-1,4-benzoquinone with N and Q, respectively. For these systems, as well as the ones to be discussed below, the polarization-determining parameters can be assigned readily. The *g* factor of the hydrocarbon radical cations ($g \sim 2.0026$) is significantly lower than the *g* factor of the semiquinone anion ($g = 2.0055$; $\Delta g < 0$); the radical ion pair is formed from the quinone triplet state ($\mu > 0$) and regenerates the starting materials by recombination ($\epsilon > 0$).[28] Given these parameters, enhanced absorption signals signify ^{1}H nuclei with negative hyperfine couplings (hfcs), i.e., nuclei directly attached to carbons bearing positive electron spin density.

CIDNP Effects of 7-Methylenenorbornadiene and -quadricyclane

Irradiation of chloranil in the presence of either 7-MN or 7-MQ gives rise to characteristic CIDNP effects, which support the existence of two independent radical cations, $MN^{\bullet+}$ and $MQ^{\bullet+}$ and give insight into their structural features.

Radical Cation of 7-Methylenenorbornadiene. The spectrum observed during the reaction of MN (Figure 1) shows strongly enhanced absorption for the two olefinic signals (6.85 ppm, H_{ol}; 3.55 ppm, H_{me}) and essentially no polarization for the bridgehead signals (3.8 ppm, H_{bh}). This pattern indicates negative hfcs for both types of olefinic protons, H_{ol} and H_{me}. Hyperfine interactions of this sign are determined by the well-established π,σ spin polarization mechanism,[40] typically observed for ^{1}H nuclei attached to sp^2-hybridized carbon atoms. The polarization of the *exo*-methylene protons (H_{me}) of MN is of particular interest, because the observed enhanced absorption indicates the delocalization of spin (and charge) onto the *exo*-methylene position of $MN^{\bullet+}$. These results provide a strong argument for the homoconjugative interaction between the two types of olefinic bonds, confirming the conclusion reached by qualitative examination of the FMOs.

The bridgehead protons (H_{bh}) of MN, not unlike those of N, show negligible polarization. These nuclei are two bonds removed from a carbon of positive spin density. Given this relationship, one might expect positive hyperfine couplings due to π,σ spin delocalization (hyperconjugation).[40] However, the bridgehead protons of $N^{\bullet+}$ and $MN^{\bullet+}$ lie in the nodal planes of the corresponding SOMOs, causing the π,σ spin delocalization mechanism to be inefficient. While the β-proton of MN shows negligible polarization, a weak *negative* hfc was indicated for $N^{\bullet+}$. The sign of the bridgehead hfcs was ascribed to "residual" π,σ polarization,[30] an assignment born out by ESR/ENDOR results,[30] CIDNP effects,[28] and calculations[18,30] alike. This type of interaction is usually obscured by the much stronger π,σ spin delocalization mechanism and competes only in a few special cases.

The assignment of a homoconjugative interaction between the N fragment and the *exo*-methylene bond is fully compatible with the results of photoelectron spectroscopic (PES) studies of MN.[41-43] In the PES experiment, a substrate is ionized vertically and "instantly" (within one molecular vibration); the resulting species is a radical cation with the geometrical features and the orbital energies of the parent. The observed transitions, viewed in the light of Koopmans' theorem,[44] delineate the ordering of MOs for the neutral molecule, from which the electron is ejected, including the MO energies.[43] The CIDNP results reported here elucidate the singly occupied (SO) MO of the relaxed radical cationic species. The results suggest that the HOMO of the neutral molecule[41-43] becomes the SOMO of the relaxed radical cation and, thus, extend the interactions established for vertical transitions to the relaxed radical cationic species.

Radical Cation of 7-Methylenequadricyclane. The CIDNP effects observed during the electron-transfer reactions of photoexcited tetrachlorobenzoquinone with 7-MQ (Figure 2) are also in line with the FMO considerations discussed above. The four protons of the cyclobutane moiety (1.85 ppm, $H_{\cdot ol \cdot}$) appear in enhanced absorption, whereas the bridgehead (1.55 ppm, H_{bh}) and the olefinic protons (5.1 ppm, H_{me}) appear in emission. This pattern suggests the two cyclopropane moieties as the principal seat of spin and charge density, inducing the polarization of $H_{\cdot ol \cdot}$ via the π,σ spin polarization mechanism (negative hfc)[40] and of H_{bh} as protons coupled via a hyperconjugative interaction (positive hfc).

The strong emission of the *exo*-methylene protons (H_{me}) is of particular interest; the observed effect requires either a long-range (hyperfine) interaction between H_{me} and the electron spin (on $C_{2,3,5,6}$) or an appreciable cross relaxation between H_{me} and a second group of nuclei (H_{bh}), whose polarization arises because they are coupled with the unpaired electron spin.[45-47] We eliminate the second possibility, because the cross relaxation mechanism is known to depend critically on the scalar nuclear spin-spin coupling in the diamagnetic precursor[45-47] and the *exo*-methylene protons of MQ do not have appreciable J coupling. However, regardless of the coupling mechanism, there can be no

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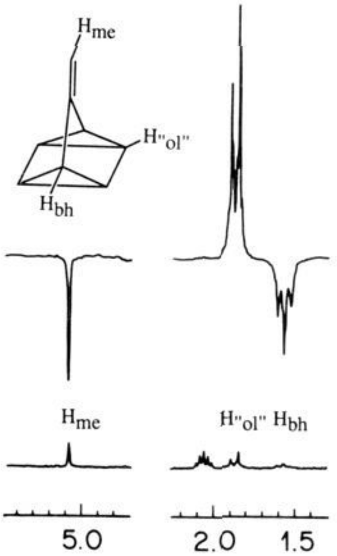
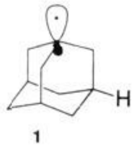


Figure 2. ^{1}H CIDNP spectra (90 MHz) observed during the photoreaction of chloranil with 7-methylenequadricyclane (top). The individual resonances of the cyclobutane, bridgehead, and *exo*-methylene protons are denoted H-$_{\text{ol}}$", H_{bh}, and H_{me}, respectively. The bottom trace is a dark spectrum.

doubt that the *exo*-methylene protons of $MQ^{\bullet+}$ have sizable hfcs. The ab initio calculations discussed below suggest one possible mechanism for this type of coupling; this will be discussed in detail below, in the light of PES results.

Long-Range Hyperfine Interactions in Bi- or Tricyclic Systems. The large hfcs indicated for the *exo*-methylene protons of $MN^{\bullet+}$ and $MQ^{\bullet+}$ suggest a comparison with the γ hfcs of other systems with comparably rigid structures. The γ hfcs of linear alkyl radicals (coupling through two or more C—C bonds) need not be considered in this context, because they are more than 1 order of magnitude smaller than the β hfcs (*n*-hexyl: $A_\beta = 30.0$ G; $A_\gamma = 0.7$ G).[48] However, free radicals derived from rigid bi- or tricyclic systems may have significant couplings for ^{1}H nuclei three or even four bonds removed from the center of nearest spin density. For example, the 1-adamantyl (**1**),[49] 7-norbornyl (**2**),[50] or benzonorbornen-7-yl radicals[51] have γ hfcs, A_γ, of 4.66, 3.53, and 1.93 G, respectively. Similarly, the benzvalene radical cation (**3**) contains a pair of strongly coupled bridgehead (γ) protons ($A = +27.9$ G), also interacting with a spin center two C—C bonds removed,[52,53] this assignment is supported by ab initio calculations.[21] Also, the radical cation (**4**) derived from 9-methylenebicyclo[4.2.1]nonatriene has sizable positive hfcs for the protons in the 7- and 8-positions, caused by the substantial spin densities in the *exo*-methylene position (C_{10}) and at C_3 and C_4.[54] Finally, the bridge protons of $N^{\bullet+}$ have sizable hfcs ($A \sim 3.0$ G), again formally through two C—C bonds;[28-30] the magnitude of the γ hfcs were, once again, reproduced by ab initio calculations.[16] These "*long-range*" hyperfine couplings provide appropriate analogies for the *positive* coupling of the *exo*-methylene protons of $MQ^{\bullet+}$.

In the context of homoconjugation, it is significant that the corresponding protons of $MN^{\bullet+}$ have *negative* hyperfine couplings, an observation that is most readily explained by delocalization



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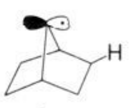

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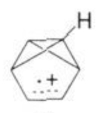

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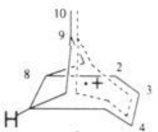

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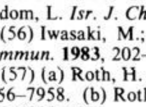
of the electron spin into the *exo*-methylene function. However, the bridge protons of $Q^{\bullet+}$ also have sizable negative hfcs,[16,28] and this system definitely requires a different mechanism, possibly σ,σ polarization of the γ-protons by those in the β-positions. The carbon skeleton of radical cation **4** is formally related to that of $MN^{\bullet+}$.[54] The substantial spin density in the *exo*-methylene position of **4** can be explained via cycloaddition of the diene system, C_2—C_5, to the monoene, C_7—C_8. The C_1—C_2 and C_5—C_6 (cyclopropane) bonds mediate the delocalization of spin and charge between C_3—C_4 and C_9—C_{10}. An analogous delocalization in $MN^{\bullet+}$ is unlikely, leaving homoconjugation as the primary mechanism. Additional support for this assignment will be derived from the ab initio calculations and will be discussed in detail below.

CIDNP Effects in 7-Spirocyclopropane–Norbornadiene and –Quadricyclane

Having established evidence for the existence of homoconjugation in the radical cation $MN^{\bullet+}$, the corresponding radical cation derived from SpN offered itself as a natural extension of our studies. In this system, the polarization of the cyclopropane protons provides the logical criterion for the extent of homoconjugation. The nature of the cyclopropane frontier molecular orbital (FMO) will play a major role in determining the magnitude of its interaction with the fragment FMOs of N and Q, respectively.

Cyclopropane FMOs and Its Interaction with the N and Q SOMOs. MO calculations suggest that the vertical ionization of cyclopropane occurs from a degenerate pair of in-plane e′-orbitals (**5**, **6**);[55] first-order Jahn–Teller (JT) distortion of the resulting doubly degenerate $^2E'$ state leads to two nondegenerate electronic states, $^2A_1$ and $^2B_2$ (C_{2v} symmetry).[55] Radical cations derived from cyclopropane systems may resemble a "trimethylene" species (type A; derived from the $^2A_1$ component; orbital 5 singly occupied) with one lengthened (but not broken) C—C bond. Low-temperature EPR studies of the parent,[56] and extensive CIDNP studies,[1,2,9,57] in part confirmed by EPR results,[58] support radical cations of the $^2A_1$ prototype; ab initio calculations also show this species to be of lowest energy.[19,59] Alternatively, radical cations derived from cyclopropane systems may resemble a "π-complex" (type B; derived from the $^2B_2$ component; orbital 6 singly occupied; C_{2v} symmetry). This structure type has been invoked for few radical cations, viz., those derived from benzonorcaradiene[9] or spiro[cyclopropane-1,9′-fluorene].[60] The radical cation of the spiroheptadiene dimer may also fall into this category.[7b,c]



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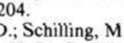
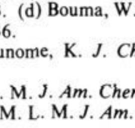


A



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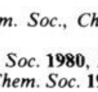

B

A qualitative examination of the cyclopropane orbitals indicates that the antisymmetrical orbital (6) is more likely to interact

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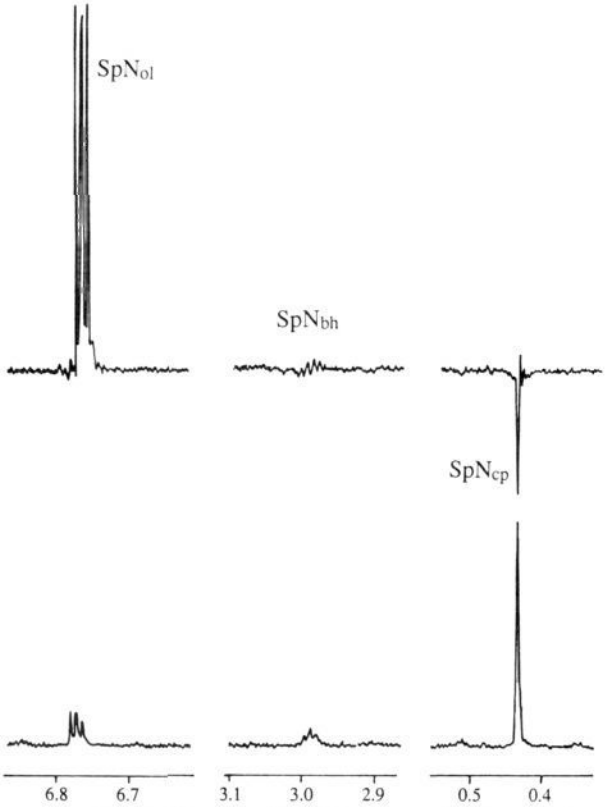
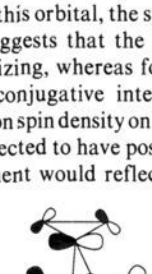
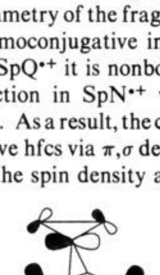


Figure 3. ^{1}H CIDNP spectra (250 MHz) observed during the photoreaction of chloranil with 7-spiro[cyclopropanenorbornadiene]. The resonances of the olefinic, bridgehead, and cyclopropane protons are denoted $H_{\text{-ol-}}$, H_{bh}, and H_{cp}, respectively. The bottom trace is a dark spectrum.

with the adjoining chromophores of N or Q, respectively, since it has a considerably larger orbital coefficient at the point of union (C_7) than does the symmetrical orbital (5). Given the involvement of this orbital, the symmetry of the fragment FMOs of N and Q suggests that the homoconjugative interaction in SpN$^{\bullet+}$ is stabilizing, whereas for SpQ$^{\bullet+}$ it is nonbonding. The putative homoconjugative interaction in SpN$^{\bullet+}$ would place unpaired electron spin density on C_7. As a result, the cyclopropane protons are expected to have positive hfcs via π,σ delocalization; their enhancement would reflect the spin density at C_7.



SpN



SpQ

Radical Cation of 7-Spiro[cyclopropanenorbornadiene]. The spectrum observed during the reaction of SpN with photoexcited chloranil (Figure 3) shows strongly enhanced absorption for the olefinic multiplet (6.78 ppm, H_{ol}), essentially no polarization for the bridgehead signals (3.0 ppm, H_{bh}), and weak emission for the cyclopropane protons (0.42 ppm, H_{cp}). This pattern indicates negative hfcs for the olefinic protons, H_{ol}, typical for the π,σ spin polarization mechanism.[40] The minimal polarization of the bridgehead (β) protons once again is ascribed to the fact that these protons lie in the nodal plane of the SpN$^{\bullet+}$ SOMO, rendering the coupling mechanism due to π,σ spin delocalization inefficient.

The cyclopropane protons (H_{cp}) for SpN have an unusually low chemical shift (0.42 ppm), even compared to the analogous protons of SpQ (0.79 ppm). We ascribe the low chemical shift to shielding by the two endocyclic double bonds. The emissive polarization observed for H_{cp} has the correct direction for a homoconjugated species, SpN$^{\bullet+}$. However, the very weak polarization intensity fails to support any significant delocalization of spin (and charge) onto the cyclopropane function of SpN$^{\bullet+}$. In fact, the various γ-couplings discussed for assorted bi- and tricyclic systems in the previous section also have positive hfcs; some of these are significantly larger than suggested by the CIDNP results for the cyclopropane protons of SpN$^{\bullet+}$. As a result, it is hard to discern whether the weak coupling observed should be ascribed to a coupling through four intervening bonds (δ-coupling) or to a homoconjugative interaction. The lack of significant delocalization of electron spin density into the spiroannelated moiety can be ascribed to the less than perfect match in orbital energies (the HOMO of N lies at 8.7 eV,[61] compared to a HOMO of 10.1 eV for dimethylcyclopropane)[62] and the less than perfect overlap between the cyclopropane Walsh orbitals and the olefinic p-orbitals. Accordingly, the SOMO of SpN$^{\bullet+}$ resembles essentially that of N$^{\bullet+}$; any spin delocalization onto C_7 is too weak to be clearly distinguishable from a long-distance polarization through four intervening bonds.

Radical Cation of 7-Spiro[cyclopropanequadricyclane]. The final radical cation to be discussed is that generated upon photoinduced electron transfer from SpQ to chloranil. The CIDNP spectrum observed during this reaction (Figure 4) shows strongly enhanced absorption for the cyclobutane multiplet (1.61 ppm, $H_{\text{-ol-}}$), strong emission for the bridgehead signals (0.87 ppm, H_{bh}), and noticeable emission for the cyclopropane protons (0.79 ppm, H_{cp}). This pattern indicates negative hfcs for the protons of the twin cyclopropane rings, $H_{\text{-ol-}}$, the same as for Q$^{\bullet+}$ and MQ$^{\bullet+}$, once again ascribed to π,σ spin polarization.[40] The significant polarization of the bridgehead (β) protons of SpQ also was expected in view of related effects observed for Q and MQ; the π,σ spin delocalization mechanism applies to these protons in SpQ$^{\bullet+}$ as well. The emission for H_{cp}, noticeably stronger than the effects induced in SpN$^{\bullet+}$, further weakens the case for homoconjugation in SpN$^{\bullet+}$.

The photoinduced electron-transfer reaction of SpQ also gives rise to significant CIDNP effects for SpN (Figure 4). The polarization of SpN clearly shows a pattern with the relative intensities compatible with SpQ$^{\bullet+}$. However, each signal is inverted relative to that of SpQ, suggesting that SpN is an escape product ($\epsilon < 0$). These results provide evidence for the relative energies of the two radicals and for the height of the barrier separating them. While SpQ$^{\bullet+}$ rearranges to SpN$^{\bullet+}$, there is no evidence for the reverse rearrangement of SpN$^{\bullet+}$. The signal directions indicate that the conversion of SpQ$^{\bullet+}$ to SpN$^{\bullet+}$ occurs after diffusive separation of the geminate radical ion pair. The signal intensities, on the other hand, indicate that the free radicals live through approximately two relaxation half-lives, suggesting a radical cation lifetime $\tau \geq {}^2T_1$. Given a typical free radical relaxation time $^2T_1 \sim 10^{-6}$ s,[63] this would correspond to a barrier height $\Delta G^* \geq 10$ kcal mol^{-1}.

The [4 + 2] dimer of spiro[4.2]heptadiene (**7**) provides an interesting comparison between the degree of stabilization attained by conjugation vs that by homoconjugation. Each of the 1,1-disubstituted cyclopropane functions of **7** is held rigidly in a well-defined orientation relative to a 1,2-dialkyl-substituted olefin.

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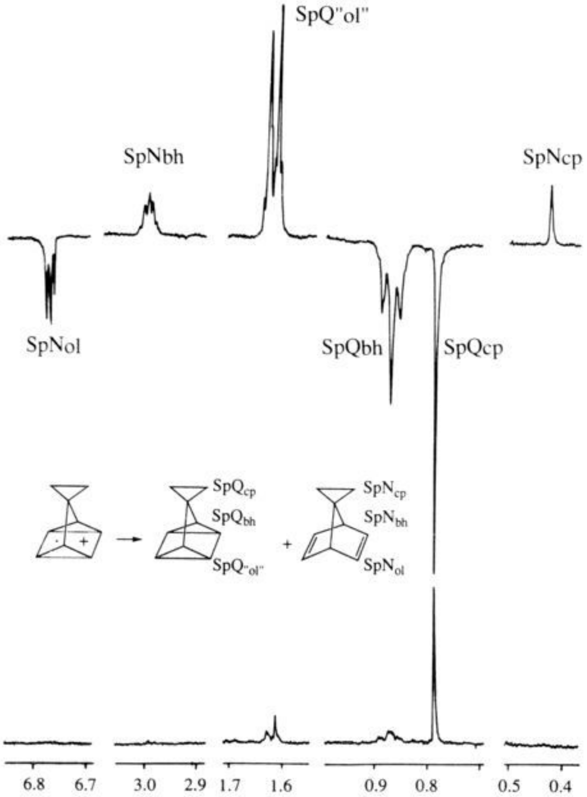
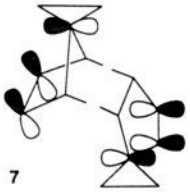


Figure 4. ^{1}H CIDNP spectra (250 MHz) observed during the photoreaction of chloranil with 7-spiro[cyclopropanequadricyclane]. The individual resonances of the cyclobutane, bridgehead, and cyclopropane protons are denoted H$_{\text{"ol"}}$, H$_{bh}$, and H$_{cp}$, respectively. The spectrum shows that SpN is generated with the polarization pattern characteristic for SpQ, but with opposite signal directions, apparently as an "escape" product ($\epsilon < 0$). The bottom trace is a dark spectrum.

We envision two possible "localized" radical cations derived from **7**, stabilized either by homoconjugative interaction with the π-orbital of the bicyclo[2.2.1]heptane fragment or by conjugation with the cyclopentene π-orbital. CIDNP results[7b,c] clearly identify the resulting radical cation as a "vinylcyclopropane" species. Thus, stabilization by conjugation outweighs the possible stabilization by homoconjugation. In the SpN$^{\bullet+}$ species considered here, the cyclopropane Walsh orbital interacts with two olefinic moieties and is, presumably, stabilized by twice the homoconjugation energy available for **7**.



7

Ab Initio Calculations

Although the CIDNP results appear to describe unambiguously the structures of the radical cationic intermediates derived from MN and MQ, we have attempted to further probe and illuminate them by performing ab initio molecular orbital calculations. Of particular interest are the spin density distributions (which determine the hyperfine coupling patterns) and the changes in bond lengts and angles (which indicate the structural changes upon one-electron oxidation). We have previously performed calculations on various radical cations with unusual structures, including those derived from the following: norbornadiene and quadricyclane;[16] Dewar benzene[17] and prismane;[18] a series of methyl-substituted cyclopropanes;[19] semibullvalene;[20] and bicyclobutane and benzvalene.[21] These calculations appear to provide reasonable geometries as well as spin densities, although no experimental data are available to compare directly with these results. We have also demonstrated in several systems that ab initio calculations reproduce *positive* hfcs quite well. Positive splittings arise from hyperconjugative interactions between magnetic nuclei and the unpaired electron spin; they are proportional to the calculated Fermi contact terms (FCT). For example, the positive hfcs calculated for several methyl-substituted cyclopropane radical cations reproduce the experimental values, assigned on the basis of ESR data,[58] within ±15%.[19] The agreement is even better for rigid structures; thus, an hfc of 76.9 G is calculated for the endo protons of bicyclobutane radical cation,[21] compared with a measured value of 77.1 G.[64] These results lead us to expect a reliable calculation for the (positive) hfcs. On the other hand, negative hfcs, which result from π,σ polarization, are reproduced only poorly by these calculations; they are significantly overestimated, often by factors greater than 2.[16,19]

In some previous ab initio calculations, especially those on norbornadiene,[16] benzvalene,[21] and cyclopropane-derived radical cations,[19] the HF/6-31G* basis set was sufficient to predict the structure of the radical cation and provide positive hfcs in excellent agreement with experimental data. However, for a proper evaluation of radical cation structures with localized spin and charge, the inclusion of electron correlation at the MP2 level has been suggested.[65] Accordingly, we have optimized the geometries for MN$^{\bullet+}$ and MQ$^{\bullet+}$ at the MP2/6-31G* level.

Bond Lengths and Angles. The changes in bond lengths, bond angles, and flap angles, Φ, upon ionization of MN and MQ are very similar to those observed for the analogous conversion of N and Q (Table 1). The removal of one electron from the (bonding) HOMO brings MN and MQ structurally closer. At the HF/6-31G* level of theory, ionization of MN causes the C_2—C_3 bond to lengthen from 1.321 to 1.366 Å (+0.045 Å; +3%), whereas the nonbonding distance, C_2—C_6, is reduced from 2.484 to 2.270 Å (−0.214 Å; −7.5%). These changes reflect the reduced bonding forces between C_2 and C_3 and the diminished antibonding forces between C_2 and C_6. At the same time, the C_7—C_8 bond remains essentially unchanged (1.313 vs 1.314 Å; +0.1%). Upon ionization of MQ the C_2—C_6 bond increases from 1.494 to 1.666 Å (+0.172 Å; +11.5%), whereas the C_2—C_3 bond decreases from 1.546 to 1.469 Å (−0.077 Å; −5%); once again the *exo*-methylene bond, C_7—C_8, shows no significant change (1.318 vs 1.316 Å; −0.15%). The minimal changes for the C_7=C_8 bond length upon electron loss eliminate any appreciable conjugation for MN$^{\bullet+}$ and MQ$^{\bullet+}$, but do not address the question of homoconjugation.

The changes in bond and "flap" angles, Φ, reflect the above changes in C—C distances; they also illustrate that MN$^{\bullet+}$ and MQ$^{\bullet+}$ are structurally closer than are MN and MQ. The C_6—C_1—C_2 bond angle of MN$^{\bullet+}$ is decreased from 107.6° to 96.6°, whereas the flap angle is decreased from 115.5° to 102.9°; in the case of MQ$^{\bullet+}$ the C_6—C_1—C_2 angle and the flap angle increase from 59.2° to 67.7° and from 61.3° to 70.9°, respectively. The similarity of the C_2—C_3—C_5—C_6 framework within the pairs N and MN, N$^{\bullet+}$ and MN$^{\bullet+}$, Q$^{\bullet+}$ and MQ$^{\bullet+}$, and Q and MQ is graphically illustrated in Figure 5; which shows a correlation of the C_2—C_6 with the C_2—C_3 bond distances for the C_7 prototypes (■) and their *exo*-methylene derivatives (○).

Spin Densities and Hyperfine Coupling Constants. Although the changes in bond lengths and angles provide a convenient means to assess the changes in molecular geometry upon ionization, no experimental results are available for comparison with the

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Table 1. Bond Distances and Angles for 7-Methylenenorbornadiene (7-MN) and 7-Methylenequadricyclane (7-MQ) and Their Radical Cations, $7\text{-MN}^{\bullet+}$ and $7\text{-MQ}^{\bullet+}$

	methylenenorbornadiene			methylenequadricyclane		
		$7\text{-MN}^{\bullet+}$			$7\text{-MQ}^{\bullet+}$	
	7-MN HF/6-31G*	HF/6-31G*	MP2/6-31G*	7-MQ HF/6-31G*	HF/6-31G*	MP2/6-31G*
			Distance (Å)			
C_1—C_2	1.539	1.520	1.520	1.512	1.496	1.501
C_2—C_3	1.321	1.366	1.384	1.546	1.469	1.479
C_2—C_6	2.484	2.270	2.245	1.494	1.666	1.664
C_1—C_7	1.527	1.523	1.522	1.486	1.501	1.501
C_7—C_8	1.313	1.314	1.308	1.318	1.316	1.304
C_1—C_4	2.241	2.271	2.281	2.298	2.304	2.309
			Bond Angle (deg)			
C_6—C_1—C_2	107.6	96.6	95.2	59.2	67.7	67.3
C_1—C_7—C_4	94.4	96.4	97.1	101.3	100.3	100.6
			Flap Angle, Φ (deg)			
	115.5	102.9	101.2	61.3	70.9	70.4

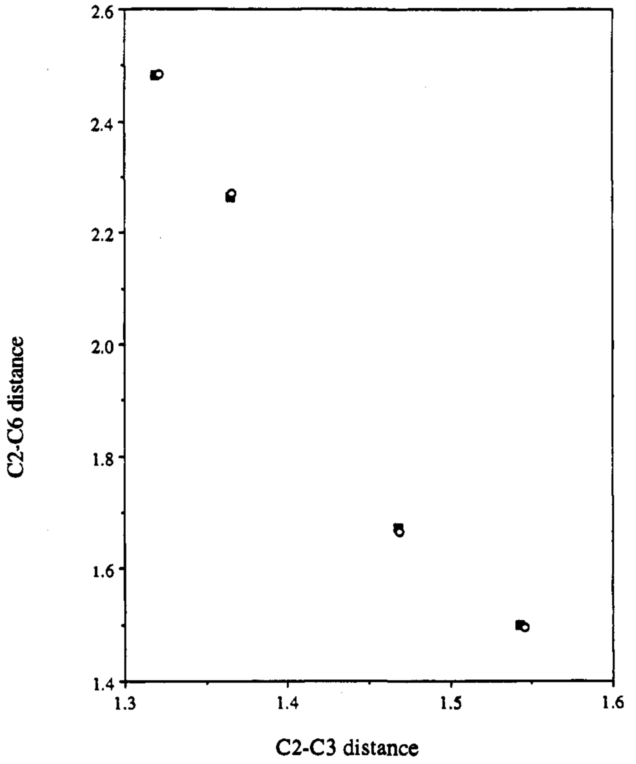
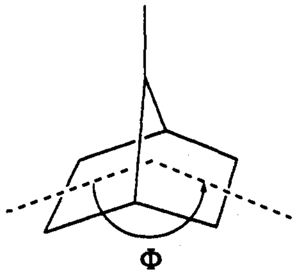


Figure 5. A correlation of the C_2—C_6 with the C_2—C_3 bond distances for the C_7 prototypes (■) N (top left), $N^{\bullet+}$, $Q^{\bullet+}$, and Q (bottom right), with their *exo*-methylene derivatives (○) MN (top left), $MN^{\bullet+}$, $MQ^{\bullet+}$, and MQ (bottom right).



calculated parameters. On the other hand, the electron spin densities calculated for the intermediates can be used as a basis for comparison; the spin density distribution causes the hyperfine coupling patterns of paramagnetic intermediates, which are observed experimentally as EPR splitting patterns or are reflected in the observed CIDNP patterns.

Table 2. Carbon Unpaired Spin Densities for the Radical Cations of 7-Methylenenorbornadiene and 7-Methylenequadricyclane

	unpaired spin density[a]	
carbon	$7\text{-MN}^{\bullet+}$	$7\text{-MQ}^{\bullet+}$
1	−0.005	−0.032
2	+0.328	+0.412
7	−0.246	+0.319
8	+0.211	−0.269

[a] Diagonal terms in the unpaired spin density matrix, calculated with an MP2/6-31G* basis set.

Table 3. Calculated ^1H Hyperfine Coupling Constants for the Radical Cations of 7-Methylenenorbornadiene and 7-Methylenequadricyclane

	$7\text{-MN}^{\bullet+}$ hfc (G)		$7\text{-MQ}^{\bullet+}$ hfc (G)	
nucleus	HF/6-31G*	MP2/6-31G*	HF/6-31G*	MP2/6-31G*
1	1.1	-1.1	+9.8	+9.9
2	-13.0	-13.4	-10.8	-10.6
8	-14.0	-8.3	+14.4	+12.6

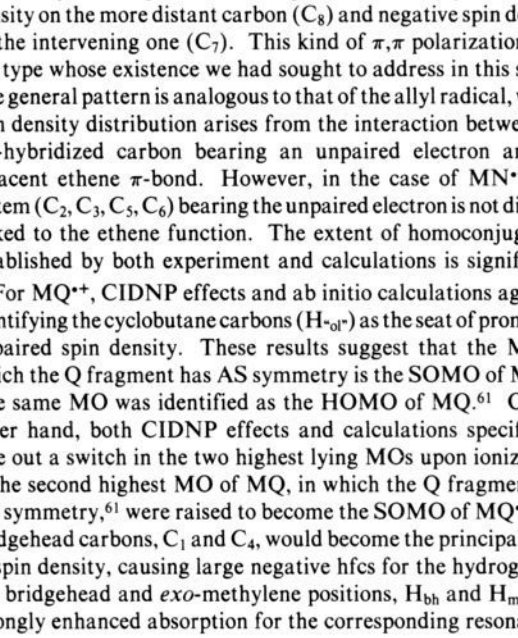
For the two species $MN^{\bullet+}$ and $MQ^{\bullet+}$, significant spin densities are expected in the four "base" carbons, C_2, C_3, C_5, and C_6. The calculated total atomic spin densities or the diagonal terms in the unpaired spin density matrix can be used for the comparison; both give similar results (the diagonal terms are listed in Table 2). Spin densities of 0.328 are calculated for these carbons in $MN^{\bullet+}$, whereas values of 0.412 are derived for $MQ^{\bullet+}$. These values suggest large negative hyperfine coupling constants (cf. Table 3), and this conclusion is compatible with the strongly absorptive CIDNP effects observed for both MN and MQ (cf. Figures 1, 2). The calculated spin densities at C_1 and C_4 are minimal for $MN^{\bullet+}$ and small for $MQ^{\bullet+}$. On the other hand, the hfcs for the protons in these positions are significantly different; the $H_{1,4}$ hfcs of $MN^{\bullet+}$ are small because they lie in the nodal plane of the SOMO. In contrast, the corresponding nuclei of $MQ^{\bullet+}$ have substantial positive hfcs ($A = 9.9$ G) in full agreement with the strong emissive polarization observed for MQ (Figure 2).

However, the key feature for the assessment of homoconjugation in these radical cations is the interaction between the "base" carbons sharing the unpaired electron density and the *exo*-methylene function, $>C_7{=}C_8<$. The calculations show only small *net* spin densities on these bonds; however, the exocyclic bonds of both $MN^{\bullet+}$ and $MQ^{\bullet+}$ are significantly spin polarized. Both $>C_7{=}C_8<$ bonds show substantial spin densities, although of opposite sign on C_7 and C_8. $MN^{\bullet+}$ has negative spin density at

C_7 ($\rho = -0.246$) and positive spin density at C_8. Both the spin density ($\rho_8 = 0.211$) and the hfc in this position ($A_{H8} = -8.3$ G) amount to ~2/3 of the corresponding values at $C_{2,3,5,6}$ ($\rho = 0.328$; $A_{H2,3,5,6} = -13.4$ G). In contrast, $MQ^{\bullet+}$ has positive spin density at C_7 ($\rho = +0.319$), but negative spin density at C_8 ($\rho = -0.269$). This gives rise to a strong positive hfc ($A_{H8} = 12.6$ G) for the protons at C_8. The calculated hfc is larger than that for $H_{1,4}$, a prediction that is born out by the strong emissive polarization observed for MQ (Figure 2).

Hyperfine Coupling Mechanisms. We explain the calculated spin densities and hyperfine coupling constants as manifestations of stereoelectronic interactions between the four-carbon-three-p-electron system (C_2, C_3, C_5, C_6) of the N or Q fragments, respectively, and the *exo*-methylene function. In the case of $MN^{\bullet+}$, the symmetries of the N SOMO and the FMO of the *exo*-methylene fragment are compatible, causing positive spin density on the more distant carbon (C_8) and negative spin density on the intervening one (C_7). This kind of π,π polarization is of the type whose existence we had sought to address in this study. The general pattern is analogous to that of the allyl radical, whose spin density distribution arises from the interaction between an sp^2-hybridized carbon bearing an unpaired electron and an adjacent ethene π-bond. However, in the case of $MN^{\bullet+}$, the system (C_2, C_3, C_5, C_6) bearing the unpaired electron is not directly linked to the ethene function. The extent of homoconjugation established by both experiment and calculations is significant.

For $MQ^{\bullet+}$, CIDNP effects and ab initio calculations agree in identifying the cyclobutane carbons ($H_{\text{-ol-}}$) as the seat of prominent unpaired spin density. These results suggest that the MO in which the Q fragment has AS symmetry is the SOMO of $MQ^{\bullet+}$. The same MO was identified as the HOMO of MQ.[61] On the other hand, both CIDNP effects and calculations specifically rule out a switch in the two highest lying MOs upon ionization. If the second highest MO of MQ, in which the Q fragment has SA symmetry,[61] were raised to become the SOMO of $MQ^{\bullet+}$, the bridgehead carbons, C_1 and C_4, would become the principal seats of spin density, causing large negative hfcs for the hydrogens in the bridgehead and *exo*-methylene positions, H_{bh} and H_{me}, and strongly enhanced absorption for the corresponding resonances.



Concerning the mechanism by which the H_{me} hfcs of $MQ^{\bullet+}$ are induced, we note that the SOMO of the Q fragment and the *exo*-methylene FMO are orthogonal to each other. The incompatible symmetry between the FMOs eliminates the type of π,π interaction invoked for $MN^{\bullet+}$, but may allow, instead, an exchange interaction between the two moieties. Since an exchange interaction is favored between like spins, the *exo*-methylene π-system develops positive spin density at C_7 and negative spin density at C_8. Both CIDNP results and ab initio calculations suggest that this alternative mechanism of π,π polarization is even stronger than the homoconjugative interaction established for $MN^{\bullet+}$. If our past experience in predicting positive hyperfine coupling constants holds true, the hfcs induced by this mechanism are, indeed, sizable.

While the ab initio calculations on the $MN^{\bullet+}$ and $MQ^{\bullet+}$ systems provided significant insight into the hyperfine coupling mechanisms operative in these species, particularly the interaction of the unpaired electron spin density with the protons of the *exo*-methylene function, no calculations were performed on the 7-spirocyclopropane derivatives, $SpN^{\bullet+}$ and $SpQ^{\bullet+}$. The decision not to pursue such calculations was based, in part, on the substantial computer time required for the calculations of a C_9 system. More importantly, however, the CIDNP results for these compounds did not suggest sufficiently significant homoconjugative effects to warrant such calculations.

Conclusion

The radical cations $MN^{\bullet+}$ and $MQ^{\bullet+}$ and $SpN^{\bullet+}$ and $SpQ^{\bullet+}$ have been characterized by CIDNP effects observed during photoinduced electron-transfer reactions of their precursors to tetrachlorobenzoquinone. The significant *positive* spin density suggested by the results for the *exo*-methylene carbon (C_8) of $MN^{\bullet+}$ is ascribed to a homoconjugative interaction between the N and M fragments, since the N SOMO and the M FMO have compatible symmetries. In contrast, the significant *negative* spin density suggested for the *exo*-methylene carbon (C_8) of $MQ^{\bullet+}$ is ascribed to an exchange interaction between the Q SOMO and the M FMO, since these moieties are orthogonal to each other. These assignments are further illuminated by ab initio molecular orbital calculations, at the MP2/6-31G* level of theory, on the radical cations $MN^{\bullet+}$ and $MQ^{\bullet+}$. The corresponding interactions of the N and Q functions with the spirocyclopropane groups of SpN and SpQ are weaker than the interactions with the *exo*-methylene groups of MN and MQ, respectively.

Experimental Section

Materials and Solvents. Norbornadiene (Aldrich, 99%) was purified by fractional distillation; quadricyclane (Aldrich, 99%) was used as received. Methylenequadricyclane was synthesized from 7-quadricyclanone[66,67] by Wittig reaction according to literature procedures[68] with minor modifications. Methylenenorbornadiene was prepared by bis(norbornadiene)palladium(II) chloride catalyzed valence isomerization of methylenequadricyclane in refluxing toluene.[68] 7-Spiro[cyclopropanenorbornadiene] was synthesized by reductive desulfonylation[69] of the Diels–Alder adduct between spiro[2.4]hepta-4,6-diene[70] and *cis*-1,2-bis(phenylsulphonyl)ethylene. 7-Spiro[cyclopropanequadricyclane] was prepared by benzoquinone-photosensitized cyclization of 7-spiro[cyclopropanenorbornadiene].

9,10-Dicyanoanthracene (Eastman Kodak) was purified by recrystallization from acetonitrile; 2,3,5,6-tetrachloro-1,4-benzoquinone (Aldrich, 99%) was used as received. Methylene chloride (Fischer; Spectranalyzed) was distilled from calcium hydride and stored over 4-Å molecular sieves in brown bottles under an argon atmosphere. Acetonitrile-d_3 (Aldrich, 99% D) and acetone-d_6 (Aldrich, 99% D) were used as received.

Stern–Volmer Quenching Studies were carried out on a Perkin-Elmer spectrophotofluorimeter. DCA was excited with 380-nm light, and the relative fluorescence intensities were measured at 437 and 462 nm as a function of the quencher concentration. Methylene chloride solutions containing 5×10^{-5} M DCA and six different concentrations of the quenchers were prepared from solvent that had been purged with argon for 15 min at room temperature; after mixing under argon, the samples were deoxygenated for an additional 3 min and measured in 1-cm cuvettes.

CIDNP Experiments. Solutions of 10–20 mM donor and 10 mM chloranil in acetonitrile (Aldrich, 99% D) were purged with argon for 5–10 min and irradiated in an NMR probe, as described elsewhere.[6b,7]

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The CIDNP experiment at 21 kG was executed on a Bruker WH 90 FT NMR spectrometer with a 200-W Hanovia high-pressure mercury lamp as a light source. The experiments at 58.3 kG were performed on a Bruker 250-MHz AF FT NMR spectrometer. The collimated beam ofa Hanovia 1000-W high-pressure mercury lamp was filtered through an aqueous $CoSO_4$ solution and guided via a fused silica rod, with mirrors at both ends, into a modified NMR probe. In all experiments, a pulse angle of 15–25° was used to minimize distortion of the multiplet intensities. The number of scans was adjusted to obtain a satisfactory S/N ratio. All CIDNP spectra were obtained by subtraction of a dark spectrum, recorded either immediately before or after photolysis, from the spectrum recorded during irradiation.

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