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Photoinduced Electron-Transfer Reactions. The Radical Cations of Methano-Bridged Paracyclophanes

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Abstract: The radical cations **4** and **6** of 1,2:9,10-bismethano[2.2]paracyclophane (**3**) and of 10,11-methano[3.2]paracyclophane (**5**) have been generated by electron transfer to photoexcited (triplet) chloranil. ^{1}H and ^{13}C CIDNP effects observed during these reactions allow an insight into the structure of these species. The polarization patterns indicate that charge and spin are delocalized into the benzylic cyclopropane positions, i.e., that the tertiary–tertiary cyclopropane bonds are broken or weakened. The different enhancement of the secondary cyclopropane protons is ascribed to different dihedral angles with the singly occupied orbital at the benzylic carbon. The findings that only the benzylic cyclopropane carbons show ^{13}C polarization and that the ^{1}H polarization in this position is relatively weak are interpreted as evidence that these carbon atoms are pyramidal in the radical ion.

In a recent publication we reported evidence for the structure of the radical cations (**2**) derived from *cis*- and *trans*-diphenylcyclopropane (**1**).[1] This assignment was based on the pattern of nuclear spin polarization observed during the photoreaction of electron acceptors with **1** and provided yet another example of the successful application of the CIDNP technique.[2] This NMR method has been instrumental in gaining insights into the structures of short-lived radical ions and into mechanistic details of radical ion pair reactions in polar solvents. Other successful applications of the CIDNP technique include the identification of aminium radical ions and of aminoalkyl radicals in the photoreductions of keto compounds by tertiary amines,[3] the elucidation of several mechanisms underlying the electron-transfer-induced isomerization of different classes of olefins,[4] and the recognition that two discrete radical cations and not a single, common intermediate are derived from norbornadiene and quadricyclane.[5]

In continuing our studies of radical ions that can be generated by photoinitiated electron transfer, we investigated the photoreaction of chloranil with several arylcyclopropanes in which the cyclopropane ring is locked into a well-defined position relative to the aromatic moiety. In principle, the architecture of a molecule can lock the tertiary–tertiary cyclopropane bond into a position nearly parallel to the normal axis of the aromatic π system or into a position nearly orthogonal to it. Molecules such as benzonorcaradiene or 9,10-methanoacenaphthene are examples for the orthogonal orientation whereas a nearly parallel orientation is found in *syn*- and *anti*- 1,2:9,10-bismethanol[2.2]paracyclophane (**3**)[6] and in 10,11-methano[3.2]paracyclophane (**5**).[7] In this paper we present results that elucidate structural details of the radical cations **4** and **6**, respectively derived from these cyclophanes, and discuss them in the light of our conclusions concerning the diphenylcyclopropane radical cations. For the purpose of comparison we have also studied the reaction of chloranil with [2.2]paracyclophane (**7**), which provides an insight into the structure of the corresponding radical cation (**8**).

Experimental Section

Samples containing 2 × 10^{-2} M of an electron acceptor and typically the same concentration of *syn*- or *anti*-cyclophane (**3**) in acetone-d_6 (99%, Aldrich Gold Label) were deoxygenated by purging with argon for 3 min. They were irradiated with the collimated beam of a 100-W Hanovia high-pressure mercury lamp in the probe of a Bruker WH90 Fourier transform NMR spectrometer. A pulse angle of 90° was employed to minimize the total acquisition time when it could be shown that the polarization patterns and relative intensities were the same as those obtained with pulse angles as low as 30°.[8] This was the case for photoreactions with chloranil. On the other hand, the reactions with 9-cyanophenanthrene resulted in multiplet effects. Accordingly, these experiments required lower pulse angles; they were monitored with pulse angles of 30°.

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[2] (a) "Chemically Induced Magnetic Polarization"; Lepley, A. R., Closs, G. L., Eds.; Wiley: New York, 1973. (b) Roth, H. D. *Mol. Photochem.* **1973**, *5*, 91. (c) Buchachenko, A. L. "Chemical Polarization of Electrons and Nuclei"; Nauka: Moscow, 1974. (d) Kaptein, R. *Adv. Free-Radical Chem.* **1975**, *5*, 319. (e) "Chemically Induced Magnetic Polarization"; Muus, L. T., Atkins, P. W., McLauchlan, K. A. Pedersen, J. B., Eds.; Reidel: Dordrecht, The Netherlands, 1977.

[3] (a) Roth, H. D.; Lamola, A. A. *J. Am. Chem. Soc.* **1974**, *96*, 6270. (b) Roth, H. D.; Manion, M. L. *Ibid.*, **1975**, *97*, 6886.

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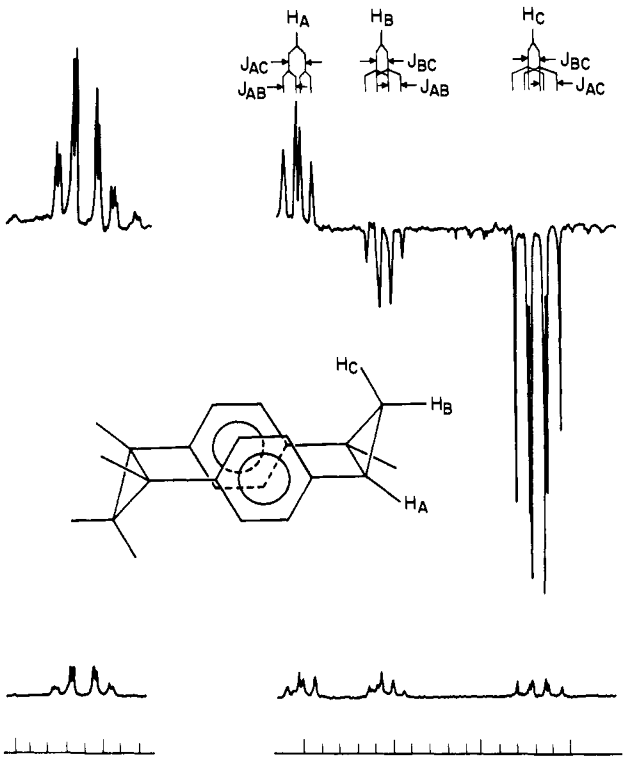

Figure 1. ^{1}H NMR spectrum (90 MHz) observed during the irradiation of chloranil (0.02 M) in acetone-d_6 solutions containing 0.01 M *anti*-1,2:9,10-bismethano[2.2]paracyclophane. A dark spectrum of the hydrocarbon is shown as the lower trace.

Results

The irradiation of chloranil in the presence of *syn*- and *anti*-**3** results in strong nuclear spin polarization effects for all protons of the reactant cyclophane (Figure 1); the aromatic and the benzylic (tertiary) cyclopropane protons appear in enhanced absorption (A) whereas both secondary cyclpropane protons appear in emission (E). No polarization was observed for the products of geometric isomerization or for other reaction products.

The photoreaction of chloranil with **3** also gave rise to ^{13}C polarization. The benzylic cyclopropane carbons (24.9 ppm) appeared in emission. However, the remaining resonances, the tertiary aromatic carbons (129.3, 135.3 ppm), the quaternary aromatic carbons (140.2 ppm), and the secondary cyclopropane carbons (4.9 ppm), showed negligible polarization or no polarization at all. Two signals showing enhanced absorption (120.8 and 145.4 ppm) and one signal showing emission (129.3 ppm) are not associated with **3**.

The irradiation of 1,4-dicyanonaphthalene in the presence of *syn*- or *anti*-**3** produced only weak ^{1}H polarization in the cyclophanes but resulted in substantial line broadening for the sensitizer.

The photoreaction of 9-cyanophenanthrene with the isomeric bismethanoparacyclophanes resulted in weak line broadening in the spectrum of the sensitizer/acceptor and in nuclear spin polarization for the nuclei of the cyclophane. The aromatic signals appear in enhanced absorption whereas the benzylic protons show a weak E/A multiplet effect superimposed on absorption; the secondary cyclopropane proton at lower field shows an E/A multiplet effect whereas the higher field cyclopropane proton is dominated by emission.

The irradiation of chloranil in the presence of methano[3.2]-paracyclophane resulted in ^{1}H polarization for all but one multiplet of the hydrocarbon. The aromatic and the tertiary benzylic multiplets appeared in enhanced absorption whereas the secondary cyclopropyl protons and the secondary benzylic protons appeared in emission. No polarization was observed for the quintet representing the central methylene group of the trimethylene bridge. In addition to the signals representing the polarized reactant, several multiplets are observed in the olefinic region, indicating the formation of a reaction product.

The reaction of **5** also produced ^{13}C polarization. The benzylic cyclopropane signal (22 ppm) appeared in emission. In addition, the signals first noticed in the reaction of **3**, two enhanced absorption signals (120 and 145 ppm) and an emission signal (129 ppm), were observed again.

The reaction of [2.2]paracyclophane with either of the sensitizers failed to result in polarization at cyclophane concentrations $>10^{-3}$ M, but at lower concentrations enhanced absorption was observed for the aromatic protons whereas the benzylic protons appeared in emission.

Discussion

The directions and intensities of nuclear spin polarization effects observed during photochemical reactions are determined by several parameters characteristic for the (paramagnetic) reaction intermediates, for the precursor generating them, for the type of reaction by which the polarized product is formed, and for the physical mechanism by which the polarization is induced.[9,10] The observed effects can be used to gain an insight into details of the chemical reaction mechanism or the structure of an intermediate if the following prerequisites are fulfilled: (1) a reasonable chemical reaction sequence can be formulated; (2) the polarization mechanism can be established; (3) the observed signal intensities are not distorted as a result of spin lattice relaxation[11] or cross relaxation.[12] For the reactions discussed in this paper, the polarization mechanism is readily identified, a simple general reaction scheme is readily formulated, and potential distortions of the polarization pattern due to secondary effects have been eliminated.

The following simple scheme is common to many light-induced electron-transfer reactions and invoked here for reactions of sensitizer/acceptors with cyclophanes. Electron transfer from

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

$${}^{1}\mathrm{A}^{*} \rightarrow {}^{3}\mathrm{A} \qquad (2)$$

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

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

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

$${}^{3}\overline{\mathrm{A}^{-\cdot}\mathrm{D}^{+\cdot}} \rightarrow {}^{2}\mathrm{A}^{-\cdot} + {}^{2}\mathrm{D}^{+\cdot} \qquad (6)$$

the cyclophane to an acceptor excited state (eq 3) generates a pair of radical ions that may recombine to generate the reactants (eq 5) or undergo separation by diffusion (eq 6). In the case of chloranil, the reactive state is likely to be the triplet whereas in the case of 9-cyanophenanthrene or 1,4-dicyanonaphthalene the reactive state is likely to be the excited singlet. All these reactions are strongly exothermic, i.e., the free energies of the radical ion pairs, which can be calculated from the redox potentials of donor and acceptor and from a Coulomb term,[13]

$$\Delta G = E_{(\mathrm{D/D^{+}})} - E_{(\mathrm{A^{-}/A})} - e^{2}/\epsilon a \qquad (7)$$

lie well below the energies of the acceptor excited states. The elegant studies of Weller and his colleagues have shown that

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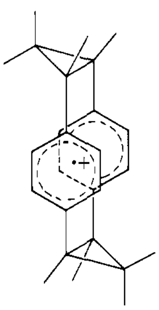
exothermic electron-transfer reactions can be very fast.

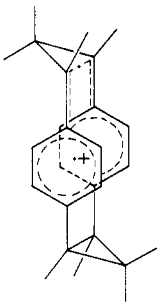
Potential Structures of Cyclophane Radical Cations. In the absence of secondary effects such as cross relaxation, the signal directions, and intensities of nuclear spin polarization effects reflect the signs and magnitudes of the hyperfine coupling constants of the individual nuclei. Therefore, the observed polarization patterns allow an insight into the structures of the paramagnetic intermediates. As in the case of the diphenylcyclopropane radical cation[1] we consider two different structure types for each of the radical cations, **4**, **6**, and **8**, derived from the bismethanoparacyclophane, the methanoparacyclophane, and [2.2]paracyclophane. One structure type has charge and spin "localized" in the aryl groups without affecting the doubly benzylic bonds. In such a structure, the aromatic protons would have negative hyperfine coupling constants ($a < 0$) whereas the benzylic protons would have positive hyperfine couplings ($a > 0$) because of a hyperconjugative interaction with the unpaired spin in the aromatic ring. One would expect opposite signal directions for these two types of protons. The remaining protons such as the secondary cyclopropane protons of **3** and **5** should have negligible hyperfine couplings and, thus, would show little or no polarization. CIDNP effects compatible with this type of structure were observed, for example, during the reaction of chloranil was [2.2]paracyclophane (vide infra).

In the alternative structure (e.g., **4b**), charge and spin are delocalized onto the benzylic carbon atoms so that the 3°–3° carbon–carbon bond is broken or weakened. The hyperfine pattern of this structure is substantially different from that of the "localized" structure. Because the electron spin density is extended to the benzylic carbon atoms, the protons at these centers are expected to have negative hyperfine coupling constants ($a < 0$) whereas the geminal cyclopropane protons have positive hyperfine coupling constants because of a hyperconjugative interaction with the benzylic centers. This polarization pattern was observed for the reaction of chloranil with diphenylcyclopropane.[1]

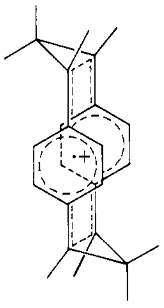
The radical cation of **3** poses an additional problem: if the unpaired spin is delocalized beyond the aromatic rings, either one or both of the 3°–3° cyclopropane bonds could be involved. Accordingly, the intermediate could be a 13-π-electron system in which charge and spin are delocalized over 14 carbon atoms (C_s symmetry, **4b**) or a 15-π-electron system in which charge and spin are delocalized over 16 carbon atoms (C_{2h} or C_{2v} symmetry, e.g., **4c**, for the anti or syn isomer, respectively). It is important to note that the 15-π-electron radical cation belongs to the same symmetry group as the parent hydrocarbon whereas the 13-π-electron radical cation belongs to a different symmetry group. The hyperfine coupling patterns expected for the potential intermediates are compared in Table I.


C_{2h}

4a


C_s

4b


C_{2h}

4c

The Radical Cation of [2.2]Paracyclophane. The reaction of [2.2]paracyclophane with electron acceptors was studied as a model for the methano compound **3** and **5**. The CIDNP effects observed during the reaction of chloranil with **7**, enhance absorption for the aromatic signal and emission for the benzylic one, portray the cation as a model of a "localized" cation. The observed effects are compatible with the simple mechanism delineated above and with polarization-determining parameters as described below. Electron transfer from **7** to triplet chloranil generates a radical ion pair in the triplet state ($\mu > 0$). Like many typical radical ions of aromatic hydrocarbons,[14] we assume that the radical cation **8** has a g factor near 2.0026, a value that is substantially lower than that of the tetrachlorosemiquinone ion (2.0056; $\Delta g < 0$).[14] The reactants are most likely regenerated by recombination of the radical ions. Since the triplet energies of both reactants, 62 kcal/mol for chloranil,[15] 72 kcal/mol for [2.2]paracyclophane,[16] lie well above the pair energy, ~31 kcal/mol,[17] only singlet recombination ($\epsilon > 0$) appears feasible energetically. The assignment of a "localized" structure, **8a**, to the radical cation derived from **7** is in keeping with the notion that an "open" structure, **8b**, would not undergo closure exclusively but suffer cleavage to form p-xylylene and its radical cation.

Table I. Nuclear Spin Polarization Observed for 1,2-Diphenylcyclopropane and Methano- and Bismethanoparacyclophane and Hyperfine Coupling Patterns of Related Radical Ions

proton	localized	open	CIDNP
Diphenylcyclopropane (1)			
aromatic	–	–	A
benzylic	+	–	A
2° cyclopropane	a	+	E
Bismethano[2.2]paracyclophane (3)			
aromatic	–	–	A
benzylic	+	–	A (m)
2° cyclopropane (exo)	a	+	E (m)
2° cyclopropane (endo)	a	+	E (s)
Methano[3.2]paracyclophane (5)			
aromatic	–	–	A
3° cyclopropane	+	–	A
2° cyclopropane	a	+	E
2° benzylic	+	+	E
2° aliphatic	a	a	b

[a] Small or negligible hyperfine coupling. [b] Negligible spin polarization observed.

The failure to observe any polarization at higher cyclophane concentrations is an interesting result that deserves comment. We ascribe this result to the fortuitous cancellation of the two polarization components induced in a radical (ion) pair by a spin-sorting process. Such cancellation has been invoked repeatedly in photoreactions proceeding via radical ions and involving a fast, degenerate electron exchange between radical ions and their diamagnetic precursors.[3a,20] At sufficiently high reactant concentrations, [D], the "lifetime", τ_e, of a free radical ion escaping from its geminate counter ion may be substantially shorter than its relaxation time, T_1.

$$\tau_e = (k_e[D])^{-1} \ll T_1 \tag{8}$$

Accordingly, the polarization associated with diffusive separation of pairs ($\epsilon < 0$) would be transferred without loss to the same reactant/product (D) that carries the polarization associated with recombination ($\epsilon > 0$).

For the radical cation **8** relaxation apparently becomes a factor at substrate (**7**) concentrations near 10^{-3} mol L^{-1}. This observation would place the relaxation time of **8** in the generally accepted range 10^{-5}–10^{-6} s if the rate constant of exchange lies between 10^8 and 10^9 L mol^{-1} s^{-1}, typical for the exchange reactions of ketones with ketyl anions[21] and of aromatic hydrocarbons with their ions.[22]

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(17) Calculated from the redox potentials of the acceptor, $E_{A^-/A} = -0.02$ V,[18] and of the donor, $E_{D/D^+} = 1.47$ V,[19] according to eq 7.[13]

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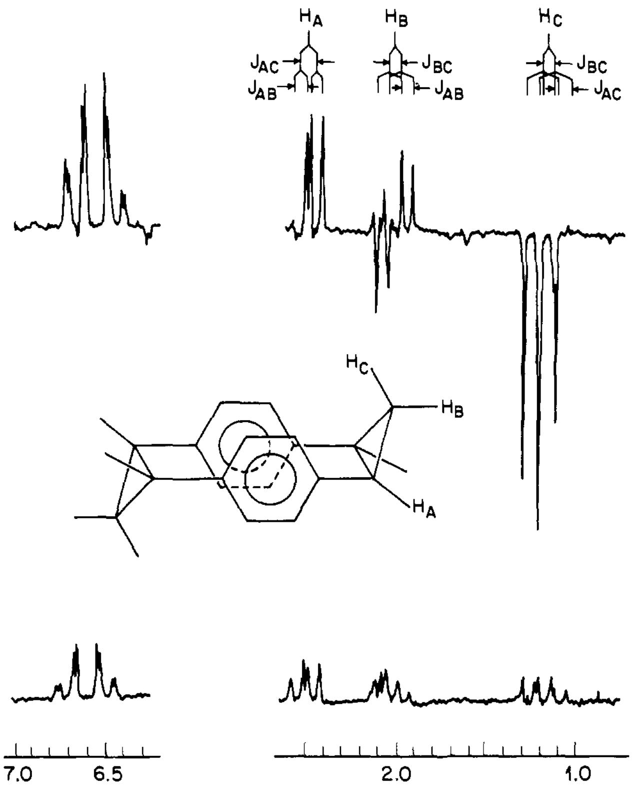

Figure 2. ^{1}H NMR spectrum (90 MHz) observed during the irradiation of 9-cyanophenanthrene (0.04 M) in acetone-d_6 solutions containing 0.01 M *anti*-1,2:9,10-bismethano[2.2]paracyclophane. A dark spectrum of the hydrocarbon is shown as the lower trace.

While the signal directions by themselves may be sufficient to identify the structure type of the intermediate radical cation, the relative signal intensities reveal additional insights. In the case of [2.2]paracyclophane, the intensity of the benzylic emission signal appears to be considerably higher than that of the aromatic absorption signal. Since both types of protons have comparable spin–lattice relaxation times ($T_{1,\mathrm{arom}}$ = 4.4 s; $T_{1,\mathrm{benz}}$ = 3.6 s), this observation suggests that the benzylic hyperfine couplings are considerably larger than the aromatic ones. The hyperfine coupling pattern suggested by these results for the radical cation of **7** is substantially different from the pattern of the radical anion, which is derived from EPR results.[23] The difference in hyperfine patterns reflects the difference in symmetry of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals of [2.2]paracyclophane.[24]

The Radical Cations of Bismethano[2.2]paracyclophane. The photoreactions of chloranil or 9-cyanophenanthrene with the bismethanol[2.2]paracyclophanes resulted in CIDNP effects (Figures 1 and 2) that are, in principle, quite similar to those observed for the diphenylcyclopropane isomers. In the specific case of the chloranil reaction, the aromatic and benzylic signals show polarization of like direction (enhanced absorption) and the signals of the secondary cyclopropane protons show polarization of the opposite direction. These results indicate an intermediate with an open, delocalized structure not unlike that assigned to the diphenylcyclopropane radical cations. However, the relative signal intensities are noticeably different. The secondary cyclopropane multiplet centered at 1.20 ppm, which is assigned to the endo proton, shows a considerably stronger enhancement than does the multiplet of the exo proton, which is centered at 1.96 ppm. In addition, the benzylic multiplet is comparably weaker than in the case of **1**. The different enhancement factors observed for the two secondary protons are ascribed to nonidentical hyperfine coupling constants. This implies that the dihedral angles, θ_B and θ_C, between the single occupied orbital and the two adjacent C–H bonds are different.

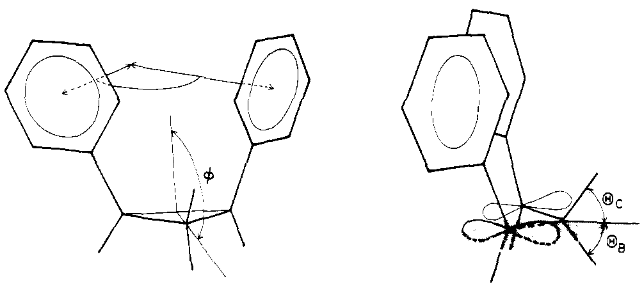

Figure 3. Two schematic views of the *cis*-diphenylcyclopropane radical cation.

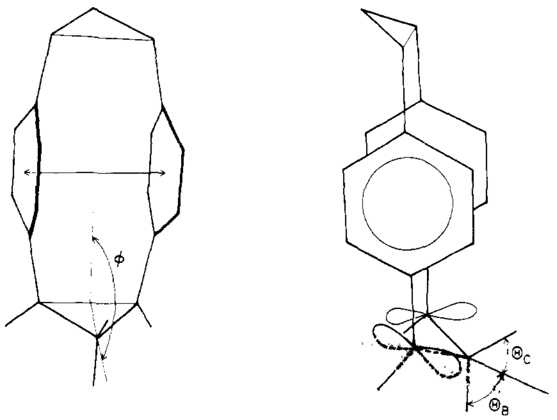

Figure 4. Two schematic views of the *anti*-bismethano[2.2]paracyclophane radical cation.

A comparison of the radical cation **4** with an unstrained model, the radical cation of *cis*-diphenylcyclopropane (**2**), illuminates why the two secondary protons may become nonequivalent. For the unstrained model, we have derived a structure in which each pair of benzylic substituents lies in a different plane perpendicular to the cyclopropane ring and in which the benzylic π orbitals overlap in the plane of this ring. Figure 3 shows two views of this structure that illustrate several important features. Most importantly, the dihedral angles θ_B and θ_C, are identical and the two benzene rings are arranged in a fashion that combines optimum overlap with a minimum of steric repulsion. The π orbitals of each ring overlap fully with one of the benzylic π orbitals and the two para positions are located much farther apart than the two quaternary carbons. It is obvious that this structure cannot accommodate, without modification, a three-carbon unit bridging the para positions as in **4**.

In the structure containing two three-carbon bridges (Figure 4) steric repulsion is minimized if the phenyl rings adopt a nearly parallel orientation, i.e., if their normal axes become nearly identical. Of course, the benzylic π orbitals cannot sustain an orientation fully parallel to the π system of the phenyl moieties. However, model considerations suggest that the strain can be partially relieved, yet a reasonable degree of overlap be maintained, if the angle, ϕ, between the plane of the three-membered ring and the plane defined by the benzylic and quaternary carbons is increased relative to **2**. In the resulting structure (Figure 4) the two secondary protons are nonequivalent. The proton that in the diamagnetic molecule lies in the shielding cone of the aromatic moieties has in the radical the smaller dihedral angle, θ_C, with the benzylic π orbital. This proton is expected to have the greater hyperfine coupling. Qualitatively, this assignment is in full agreement with the experimental results.

The postulated change in dihedral angle can account for the intensity difference between the two geminal cyclopropane protons but it fails to explain the comparably weak enhancement of the benzylic signals. This results could be interpreted as evidence for

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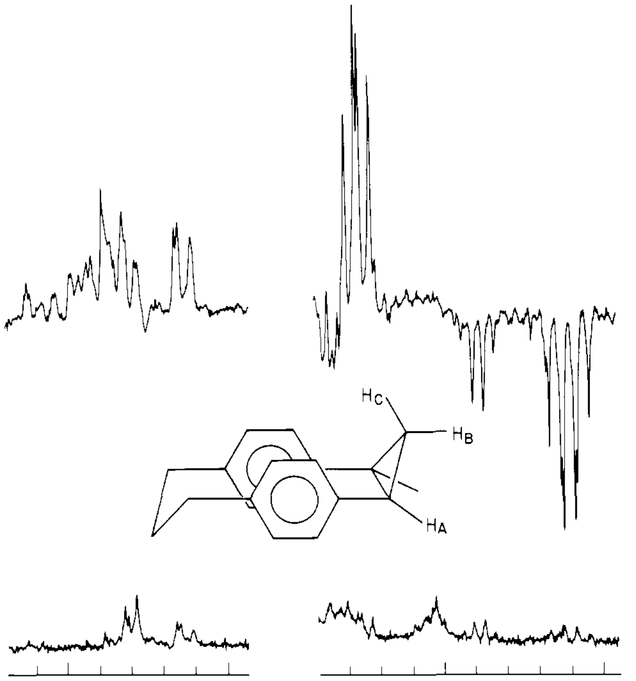

Figure 5. ^1H NMR spectrum (90 MHz) observed during the irradiation of chloranil (0.02 M) in acetone-d_6 containing 0.01 M 10,11-methano-[3.2]paracyclophane. A dark spectrum of the hydrocarbon is shown below the CIDNP spectrum.

an intermediate with a weak α splitting and with one strong β splitting. Hyperfine patterns of this type have been observed for species with a pyramidal carbon such as a series of cyclopropyl radicals.[25] The radical cation **4** might relieve some strain if the benzylic carbon atoms assume a pyramidal configuration. The presence of a pyramidal carbon in an intermediate can, in principle, be evaluated experimentally. It has been established that the ipso ^{13}C splittings of nonplanar carbon radicals increase with increasing deviation from planarity whereas the splittings of carbons attached to these centers decrease.[26] The magnitude of these splittings should be reflected in the ^{13}C polarization that may be generated in photoreactions involving **4** as an intermediate.

However, the ^{13}C polarization observed for **3** is weak and incomplete. During its photoreaction with chloranil only one of five types of carbon atoms shows any polarization; the benzylic cyclopropane carbon (24.9 ppm) appeared in emission. This observation is compatible with a positive ^{13}C hyperfine splitting and positive spin density in this position. The lack of polarization in all other positions is compatible with a structure possessing a pyramidal carbon in the benzylic position.

A comparison of this polarization, however weak, with the ^{13}C polarization observed for the diphenylcyclopropanes lends support to this conclusion. For example, *trans*-**1** shows polarization not only for the ortho, para, and benzylic carbons (emission) but also for the quaternary and meta carbons of the aromatic rings and for the secondary cyclopropane carbon (enhanced absorption). These results and the fact that **1** shows comparable enhancements (though of opposite sign) for the benzylic and secondary cyclopropane protons are fully compatible with a planar π radical.

The fact that the ^1H and ^{13}C polarization patterns observed for **1** and **3** are different in important details supports the assignment of different structure types to the intermediates **2** and **4**, respectively, in which this polarization is generated. Nevertheless, we emphasize that the ^{13}C polarization of **3** is incomplete and weak so that our assignment cannot be completely unambiguous. The ^1H polarization observed for **3** rules out the "localized" structure **4a** (C_{2h} symmetry) for the intermediate but it provides no information that would differentiate between the two "open" structures, **4b** and **4c**, with C_s and C_{2h} symmetry, respectively. In contrast, the ^{13}C polarization provides indirect evidence in favor of the C_s structure or of an equilibrium of two C_s structures. The suggestion of a pyramidal carbon atom and, consequently, largely localized spin density appears to be incompatible with the fully delocalized structure, **4c**.

The Radical Cation of 10,11-Methano[3.2]paracyclophane. The recent synthesis of 10,11-methano[3.2]paracyclophane (**5**)[7] allows an interesting extension of the study reported here. The trimethylene bridge in **5** should impose less strain than does the second three-membered ring in **3**. Accordingly, the trimethylene-bridged radical cation (**6**) should have a geometry somewhat closer to that of *cis*-**2**. These considerations are born out by the CIDNP effects observed during the photoreaction of chloranil with **5** (Figure 5). The aromatic, the tertiary benzylic, and the secondary cyclopropane protons show the same signal directions as observed for **1** and **3**, suggesting an intermediate of the same general structure type as that of **2** and **4**.

The partial release of strain in **6** relative to **4** is indicated by the relative intensities of the two secondary cyclopropane multiplets (1.8 and 1.2 ppm). The enhancement ratio of the endo and exo protons is close to 2:1, intermediate between the ratios observed for the unbridged (**1**) and the "cyclopropane-bridged" diphenylcyclopropane (**3**). The relative enhancement of the benzylic cyclopropane multiplet is considerably greater than that observed for the analogous signals of **3** and similar to the relative enhancement of these signals in **1**.

However, the ^{13}C CIDNP spectrum once again shows polarization only for the benzylic cyclopropane carbons (emission), suggesting once again an intermediate with a pyramidal carbon in the corresponding positions. Obviously, the hydrocarbon **5** and the radical cation **6** are still substantially strained, and a pyramidal structure may alleviate some of this strain.

The enhancement of the benzylic cyclopropane protons of **5** relative to the benzylic methylene protons is of interest because it sheds light on one possible explanation for the weak benzylic polarization observed for **3**. If the intermediate **4** and C_s symmetry, one might argue that the benzylic ^1H polarization of the "opened" cyclopropane ring and of the unaffected cyclopropane ring might cancel each other. For the hydrocarbon **5**, the two types of benzylic protons are observed separately. The benzylic cyclopropane protons (2.5 ppm) show enhanced absorption whereas the benzylic methylene protons (2.7 ppm) shows much weaker emission.

To the extent that the cation **6** is a suitable model for the radical cation **4b** with C_s symmetry, these findings eliminate internal cancellation as an explanation for the weak benzylic polarization observed for **3**.

Conclusion

The observation of ^1H and ^{13}C nuclear spin polarization during the photoreaction of chloranil with three methano-bridged paracyclophanes has been interpreted in terms of electron-transfer quenching reactions involving radical cations with pyramidal benzylic carbons as intermediates. These findings provide an interesting contrast to the radical cations[2] of *cis*- and *trans*-diphenylcyclopropane, which are not subject to the severe steric restrictions of **4** and **6**, and to the radical cations of methanoacenaphthene or benzonorcaradiene, in which the 3°–3° cyclopropane bond is orthogonal to the π system.

Registry No. 3, 83944-24-5; **4**, 83944-25-6; **5**, 83876-63-5; **6**, 83876-64-6.

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