

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

### Conclusion

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

Registry No. 1, 287-13-8; 2, 35618-58-7; 3, 96482-23-4; 4, 287-12-7; 5, 659-85-8; 6, 34305-47-0; 7, 40480-63-5; chloranil, 118-75-2.

(34) Miller, D. L.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 4239-4243.

(35) Bischof, P.; Gleiter, R.; Taylor, R. T.; Browne, A. R.; Paquette, L. A. *J. Org. Chem.* **1978**, *43*, 2391-2396.

## Molecular Orbital Effects on the Structure of Cyclopropane Radical Cations

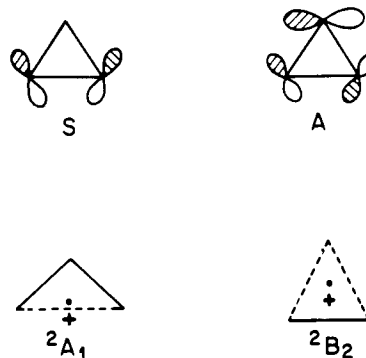
Heinz D. Roth,\* Marcia L. M. Schilling, and Frederic C. Schilling

Contribution from AT&T Bell Laboratories, Murray Hill, New Jersey 07974.  
Received January 4, 1985

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

In the framework of the continuing general interest in radical cations,<sup>1-4</sup> those derived from strained ring hydrocarbons are attractive targets because they can assume a variety of interesting structure types.<sup>5-8</sup> The relative energies of their accessible states are subject to substituent effects, and in selected cases, appropriately chosen substituents can alter the ordering of states. For example, cyclopropane radical cations can assume either a "trimethylene" structure in which one C-C bond is weakened (type A) or a structure resembling a  $\pi$  complex, i.e., with two weakened C-C bonds (type B).<sup>5</sup> A recent ab initio calculation of the cy-

clopropane radical cation<sup>9</sup> suggests that the lowest energy surface has low-lying saddle points corresponding to the general structure types  $^2A_1$  and  $^2B_2$ . The minima are of lower symmetry and have



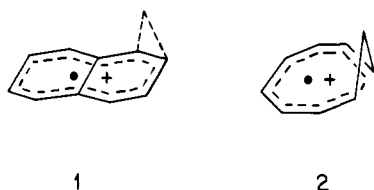
geometries intermediate between  $^2A_1$  and  $^2B_2$ . The structures of substituted cyclopropane radical cations are logically derived from the two degenerate highest occupied molecular orbitals (HOMOs)

- (1) Miller, T. A.; Bondybey, V. *Appl. Spectrosc. Rev.* **1982**, *18*, 105-169.
- (2) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1983**, 202-204. Toriyama, K.; Nunome, K.; Iwasaki, M. *Ibid.* **1983**, 1346-1347.
- (3) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180-186.
- (4) Knight, L. B., Jr.; Stedman, J.; Teller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1984**, *106*, 3700-3701.
- (5) Roth, H. D.; Schilling, M. L. M. *Can. J. Chem.* **1983**, *61*, 1027-1035.
- (6) Takahashi, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6511-6513.
- (7) Roth, H. D.; Schilling, M. L. M.; Mukai, T.; Miyashi, T. *Tetrahedron Lett.* **1983**, 5815-5818.
- (8) Roth, H. D.; Schilling, M. L. M.; Raghavachari, K. *J. Am. Chem. Soc.* **1984**, *106*, 253-255.

(9) Collins, J. R.; Gallup, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 1530-1533.

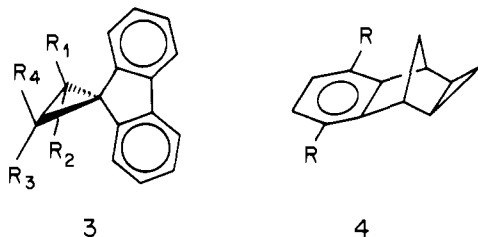
of cyclopropane; the predominant structure type can be rationalized in each case on the basis of the frontier MO/perturbation MO theory of homoconjugation.<sup>10</sup>

For example, the cyclopropane fragment of the radical cation of benzenorcaradiene<sup>5</sup> is a derivative of type B. This structure is determined by the nature of the primary donor fragment joined with the cyclopropane ring. Since the styrene HOMO has coefficients of opposite sign in the positions of union, it will interact preferentially with the antisymmetrical HOMO of cyclopropane. On the other hand, the cyclopropane fragment of the bicyclo-[6.1.0]nonatriene radical cation<sup>11</sup> is a derivative of structure type A. Again this is rationalized in terms of orbital control. The

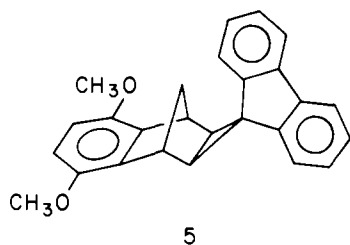


primary donor fragment of this molecule is the hexatriene moiety whose HOMO is symmetrical and therefore is compatible with the symmetrical HOMO of cyclopropane, hence the observation of structure type A.

After having reported predictions concerning the radical cation structures in a variety of cyclopropane systems,<sup>10</sup> we present in this contribution experimental evidence for the structures assumed by the radical cations of two of these, spiro[cyclopropane-1,9'-fluorene] (3) and benzocyclopropanorbornene (4). In these



systems the balance between the principal structure types appeared to be subtle and we suspected that it might be affected by minor changes in the substitution pattern. These systems were also of interest, because they comprise the principal fragments of a larger bichromophoric system (5) originally designed by DeMember and



Filipescu to study intramolecular energy transfer<sup>12</sup> and used recently as a potentially bifunctional electron donor.<sup>5</sup>

### Experimental Section

Spiro[cyclopropane-1,9'-fluorene] (3a) was prepared by the procedure of Mechoulham and Sondheimer.<sup>13</sup> The derivatives 3b-f are accessible via addition of fluorenylidene to appropriate olefins.<sup>14</sup> 2,3-Benzo-5,6-cyclopropanorbornene (4) was prepared from benzenorbornadiene by the

(10) Haddon, R. C.; Roth, H. D. *Croat. Chim. Acta* **1984**, *57*, 1165-1176.

(11) Roth, H. D.; Schilling, M. L. M., unpublished results.

(12) (a) DeMember, J. R.; Filipescu, N. *J. Am. Chem. Soc.* **1968**, *90*, 6425-6428. (b) Filipescu, N.; DeMember, J. R. *Tetrahedron* **1968**, *24*, 5181-5191. (c) Lamola, A. A. *J. Am. Chem. Soc.* **1969**, *91*, 4786-4790.

(13) Mechoulham, A. R.; Sondheimer, F. *J. Am. Chem. Soc.* **1958**, *80*, 4386-4388.

(14) Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833-6845.

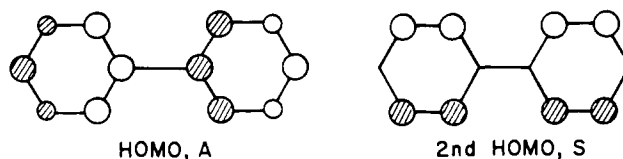
procedure of LeGoff<sup>15</sup> and purified by gas chromatography on a 10 ft  $\times$   $\frac{3}{8}$  in. column of 10% Carbowax on Fluoropak at 100 °C.

Typical samples used for the CIDNP experiments were acetone-*d*<sub>6</sub> (Aldrich, Gold Label, 99%) solutions containing 0.02 M each of an electron-acceptor (chloranil, Eastman Organics) and an electron-donor hydrocarbon. These samples were purged with argon for 2 min and irradiated with the collimated beam of an Osram 200-W 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 acquisition time for the spectra (typically 100 s for 25 pulses). All chemical shifts are given in parts per million (ppm) vs. tetramethylsilane.

The 500-MHz <sup>1</sup>H NMR spectrum was recorded at 23 °C on a JEOL GX-500 spectrometer with use of a 0.05 M solution in acetone-*d*<sub>6</sub> with tetramethylsilane as the internal reference. Fifty scans were accumulated with use of a pulse interval of 30 s. The 2D COSY experiment<sup>16</sup> was run on a Varian XL-200 spectrometer with Advanced Data System employing a recycle time of 6.0 s and collecting 16 transients for each  $t_1$  value. A total of 512 spectra, each consisting of 1024 points, were accumulated. The data matrix was zero-filled to 1024 by 1024 points with a frequency of 2000 Hz in both dimensions. A four-step phase cycling routine was included in the pulse sequence, and quadrature detection was used in both dimensions. The data were multiplied by a pseudo-echo window function in both dimensions prior to Fourier transformation. The absolute value spectrum was calculated in both dimensions and symmetrized to eliminate "t<sub>1</sub> noise" which results from instrumental instabilities over the length of the accumulation time.

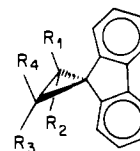
### Spiro[cyclopropane-1,9'-fluorene] and Derivatives

The application of FMO/PMO principles to substituted cyclopropanes leads to the prediction that aryl substitution at a single carbon will most effectively stabilize the A orbital whereas substitution at two carbons will favor involvement of the S orbital.<sup>10</sup> Geminal incorporation of the biphenyl moiety, as in 3, has the interesting consequence that its HOMO, because of unfavorable symmetry, cannot interact with either of the cyclopropane orbitals. However, a second MO lies within 0.7 eV of the HOMO, and it should interact most effectively with the A orbital.<sup>17</sup> We chose



this system to probe whether the preference of a second HOMO could be sufficiently strong to determine the structure of the cyclopropane radical cation. Furthermore, it was of interest to study the influence of additional ring substituents on the radical cation structure.

Accordingly, we have investigated the parent system, 3a, and several simple derivatives, 3b-e. The irradiation of strong electron acceptors, such as chloranil or fluoranil, in the presence of these hydrocarbons, when carried out in the probe of an NMR spectrometer, resulted in CIDNP effects which fall into three distinct categories.

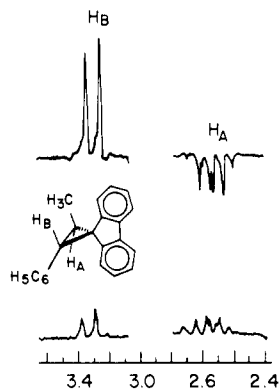


|   | R <sub>1</sub> | R <sub>2</sub>                      | R <sub>3</sub>  | R <sub>4</sub>  |         |
|---|----------------|-------------------------------------|-----------------|-----------------|---------|
| a | H              | H                                   | H               | H               |         |
| b | H              | C <sub>2</sub> H <sub>5</sub>       | CH <sub>3</sub> | H               |         |
| c | H              | C <sub>6</sub> H <sub>5</sub>       | H               | CH <sub>3</sub> | (trans) |
| d | H              | C <sub>6</sub> H <sub>5</sub>       | CH <sub>3</sub> | H               | (cis)   |
| e | H              | CH=C(CH <sub>3</sub> ) <sub>2</sub> | CH <sub>3</sub> | CH <sub>3</sub> |         |
| f | H              | CH <sub>3</sub>                     | CH <sub>3</sub> | CH <sub>3</sub> |         |

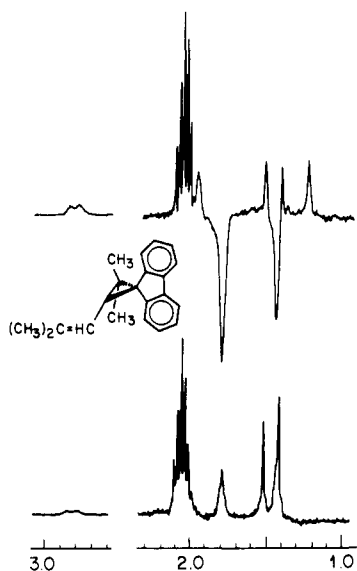
(15) LeGoff, E. *J. Org. Chem.* **1964**, *29*, 2048-2050.

(16) "Two-Dimensional Nuclear Magnetic Resonance in Liquids"; Bax, A., Ed.; D. Reidel: New York, 1982.

(17) Klasinc, L. *Pure Appl. Chem.* **1980**, *52*, 1509-1524.

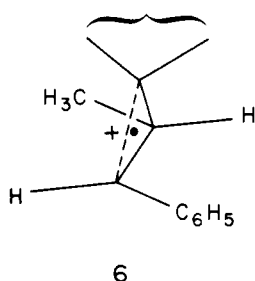


**Figure 1.** PMR spectra (90 MHz) observed during the UV irradiation of an acetone- $d_6$  solution containing 0.02 M each of chloranil and hydrocarbon **3c** (top) and of the same solution in the dark (bottom).



**Figure 2.** PMR spectra (90 MHz) of an acetone- $d_6$  solution containing 0.02 M each of chloranil and hydrocarbon **3e** in the dark (bottom) and during UV irradiation (top).

The first case is that of a pair of isomers, **3c** and **3d**, which are substituted with a phenyl group and a methyl group on different cyclopropane carbon atoms. The results observed during the reactions of these hydrocarbons support the predominant involvement of a single trimethylene radical cation (type A). The benzylic cyclopropane proton and the aromatic signals appear in enhanced absorption, indicating that the aromatic moieties and the benzylic carbon bear positive spin density. This suggests an intermediate in which the bond between the benzylic carbons is broken or weakened (**6**) in analogy to the diphenylcyclopropane radical cation.<sup>18</sup> This assignment is further supported by the



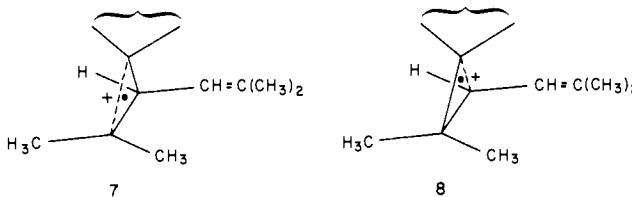
emission observed for the nonbenzylic proton and by the absence of any significant polarization in the methyl group (Figure 1).

**Table I.** Hyperfine Coupling Patterns of Radical Cations Derived from Spiro[cyclopropane-1,9'-fluorene] **3b** and CIDNP Results

|                 | <b>9a</b> | <b>9b</b> | <b>10</b> | <b>11</b> | CIDNP    |
|-----------------|-----------|-----------|-----------|-----------|----------|
| H <sub>A</sub>  | -         | +         | +         | -         | <i>a</i> |
| H <sub>B</sub>  | +         | -         | +         | -         | <i>a</i> |
| CH <sub>3</sub> | +         | <i>a</i>  | <i>a</i>  | +         | +        |
| CH <sub>2</sub> | <i>a</i>  | +         | <i>a</i>  | +         | +        |

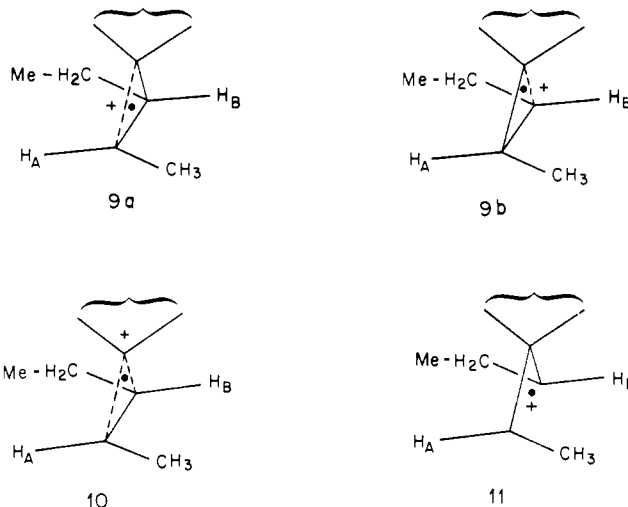
<sup>a</sup>Small or negligible.

A similar intermediate is derived from **3e**. Of the two possible stabilized structures, that involving participation of the allylic cyclopropane carbon ( $\rightarrow$ **8**) is favored over the participation of the tetrasubstituted bond ( $\rightarrow$ **7**). This assignment rests on the en-



hanced absorption signal observed for the only cyclopropane proton and on the emission observed for the allylic methyl groups. These results indicate that the cyclopropane proton and the allylic methyl groups are attached to positions of positive spin density. The preference for the allylic species, **8**, reflects the greater stabilization imparted to the system by allylic delocalization compared to the resonance electron donation by two methyl groups (Figure 2).

Distinctly different results are observed for the derivative **3b**, which is substituted with two alkyl groups on two different cyclopropane carbons. These groups may stabilize the radical cations **9a** and **9b**, respectively, to a similar degree. During the reaction



of **3b**, the methyl doublet (1.4 ppm) and the doublet of quartets (2.1 ppm) representing the methylene group appear in emission. This signal direction indicates that the methyl and the ethyl group are attached to cyclopropane carbons bearing positive spin density. However, the cyclopropane protons do not exhibit the enhanced absorption one would expect for protons directly attached to such carbons. This rules out radical cation **11**, which appears to be the least stable one, since it does not benefit from stabilization by the fluorene moiety.

The results observed for **3b** are also incompatible with a radical cation, **10**, derived from structure type B, since this structure would lead to emission for H<sub>A</sub> and H<sub>B</sub> and negligible polarization for the CH<sub>2</sub> and CH<sub>3</sub> groups. The results are compatible with the simultaneous involvement of **9a** and **9b**, since this would result in a cancellation of the polarization induced for the two cyclopropane protons, H<sub>A</sub> and H<sub>B</sub>, respectively, in the two intermediates. Each of these nuclei is expected to have negative hfc in one of the intermediates (Table I) and a positive hfc of comparable magnitude in the other. The cancellation can be explained by

(18) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7956-7958.

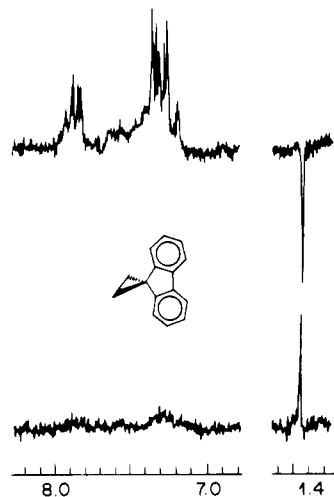
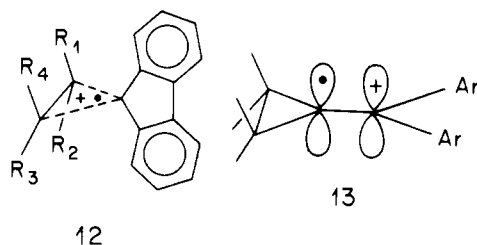


Figure 3. PMR spectra (90 MHz) of an acetone- $d_6$  solution containing 0.02 M each of chloranil and hydrocarbon **3a** (bottom) and CIDNP effects observed during UV irradiation (top).

two different mechanistic settings. It requires either a rapid equilibration of **9a** and **9b** or their simultaneous generation as two discrete species separated by a significant barrier. In either case, the cancellation is possible only if the energies of the two radical cations are closely matched. Although the experimental results do not allow us to differentiate between the two possibilities, we favor the latter one, since there does not appear to be any precedent for the equilibration of two radical cations on the nanosecond time scale.

The third type of polarization observed in the spiro[cyclopropane-fluorene] system is that of the parent, **3a**. For this hydrocarbon, the aromatic multiplets show enhanced absorption whereas the cyclopropane singlet (1.7 ppm) appears in emission (Figure 3). This pattern supports a radical cation structure with spin density in the fluorene moiety, including the quaternary carbon, but not on the secondary cyclopropane carbons. This structure is best understood as a derivative of structure type B (**12**).

We note that structure **12** is principally different from that of the radical cation **13** derived from 1-(diphenylmethylene)cyclopropane.<sup>19</sup> In the latter species, spin and charge occupy a pure  $\pi$  orbital which extends to one cyclopropane carbon but is orthogonal to the cyclopropane Walsh orbitals. In contrast, the



Walsh orbitals of **12** are aligned parallel to the fluorene  $\pi$  orbitals. In this system, the quaternary carbon can acquire spin density only through electron donation from the cyclopropane to the fluorene moiety.

In summary, the diverse polarization patterns observed for **3a** and its various derivatives (**3b-e**) illustrate that the structure type B is favored only for the parent. It appears that a single alkyl substituent on the cyclopropane ring is sufficient to revert the radical cation to structure type A. The preference for structure B is tenuous, indeed.

### 2,3-Benzo-5,6-cyclopropanorbornene

This system (**4**) contains two potential electron donors, a benzene and a cyclopropane functionality, which are separated

Table II. Hyperfine Coupling Pattern of the Cyclopropane Protons of Radical Cations Derived from 2,3-Benzo-5,6-cyclopropanorbornene (**4**) and CIDNP Results

|                     | 16 | 17 | 18    | CIDNP |
|---------------------|----|----|-------|-------|
| H <sub>B</sub> (3°) | -  | +  | +     | A     |
| H <sub>A</sub> (2°) | +  | -  | negl. | E     |
| H <sub>D</sub> (2°) | +  | -  | negl. | E     |

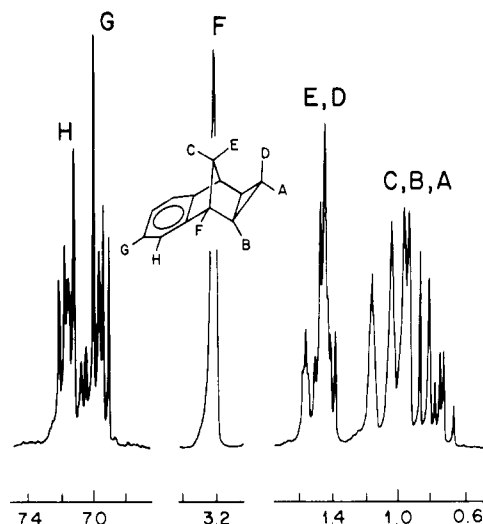
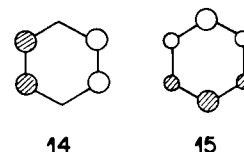


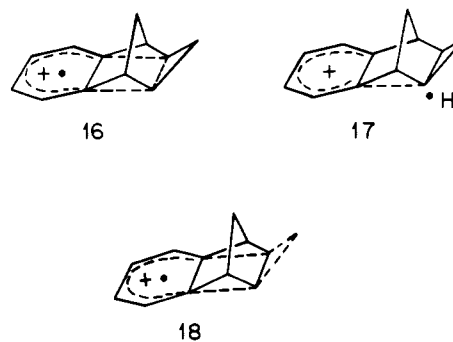
Figure 4. PMR spectrum (90 MHz) of an acetone- $d_6$  solution containing 0.3 M benzocyclopropanorbornene (**4**).

and held rigidly by a three-carbon spacer. Since both moieties have degenerate HOMOs, their potential interaction should provide a particularly interesting test for the FMO/PMO principles mentioned above.

Of the two degenerate HOMOs of benzene, one has a nodal plane bisecting two carbon atoms (**14**); we call this HOMO symmetrical since it would interact favorably with the symmetrical HOMO of cyclopropane. Removal of an electron from this



HOMO would yield the radical cation **16**. The alternative benzene HOMO has a nodal plane between two pairs of carbon atoms (**15**); it would interact favorably with the antisymmetrical HOMO of cyclopropane. Removal of an electron from this HOMO would yield the radical cation **18**. In the system discussed here, the



presence of the ortho substituents should raise the symmetrical benzene HOMO and, therefore, favor the "symmetrical" structure (**16**) for the intermediate radical cation. However, an additional type of interaction, homohyperconjugation of the benzene radical cation with the tertiary cyclopropane protons, could not be ruled out for the larger system, **5**. Accordingly, we have considered a contribution from a structure such as **17** (cf. Table II).

(19) Miyashi, T.; Takahashi, Y.; Mukai, T.; Roth, H. D.; Schilling, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1079-1080.

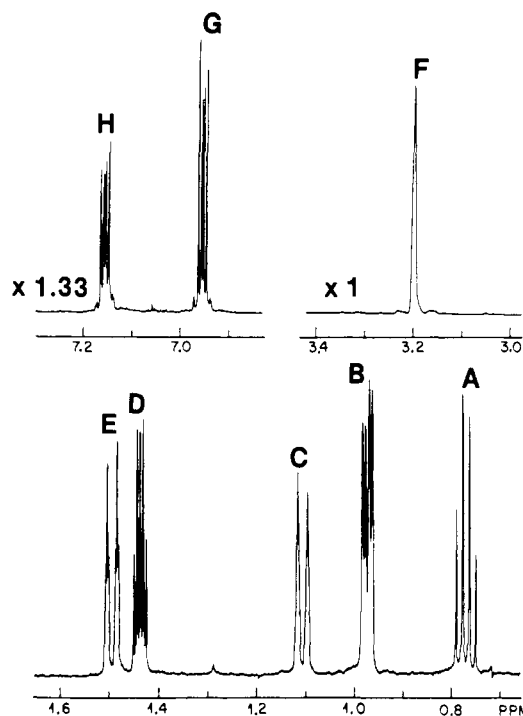


Figure 5. PMR spectrum (500 MHz) of a 0.05 M solution of **4** in acetone- $d_6$ .

As in all cases in which the structure of a paramagnetic intermediate is inferred from a CIDNP pattern, the correct identification of the intermediate stands or falls with the correct assignment of the parent NMR spectrum. The 90-MHz NMR spectrum of **4** is not unambiguous (Figure 4). Only 6 of the 12 protons are assigned readily. There is little doubt that the multiplets at 6.97 and 7.17 ppm each represent two aromatic protons and that the broad, featureless signal at 3.21 ppm is due to the allylic bridgehead protons. The remaining protons appear as two unresolved multiplets between 1.4 and 1.6 ppm (2 H) and between 0.7 and 1.2 ppm (4 H).

At 500 MHz (Figure 5), these multiplets are resolved into five well-defined features. One of these, the two-proton doublet of doublets at 0.97 ppm, obviously is the resonance of the tertiary cyclopropane protons (B). Corresponding coupling constants are found in the four-line feature at 0.77 ppm (A) and the five-line feature at 1.44 ppm (D). These resonances are best understood as doublets of triplets. In the case of A, the doublet (geminal, 6.3 Hz) and triplet (vicinal, 6.9 Hz) splittings are nearly identical, whereas in the case of D the triplet coupling (3.2 Hz) is half as large as the doublet coupling. The larger vicinal coupling identifies A as the resonance of the cis proton, leaving D as the resonance of the trans proton. The remaining doublets at 1.10 ppm (C) and 1.50 ppm (E) are assigned to the bridge protons. Both are further split by at least two protons (E) or at least four protons (C). The unusually high upfield shift of one of these protons (C) is due to the fact that it lies in the shielding cone of the aromatic ring. This assignment is further supported by the existence of a four-bond coupling constant ( ${}^4J = 0.8$  Hz) between this bridge proton and the tertiary cyclopropane protons. The magnitude of this coupling can be ascribed to the favorable (W) arrangement of these protons.<sup>20</sup>

Because of the crucial importance of these assignments for the identification of the intermediate, we sought to confirm them by two-dimensional  $J$ -correlated spectroscopy (COSY).<sup>16</sup> This technique is based on one of several two-dimensional NMR experiments which were conceived by Jeener<sup>21</sup> and reduced to experiment by Aue, Bartholdi, and Ernst.<sup>22</sup> It results in a two-

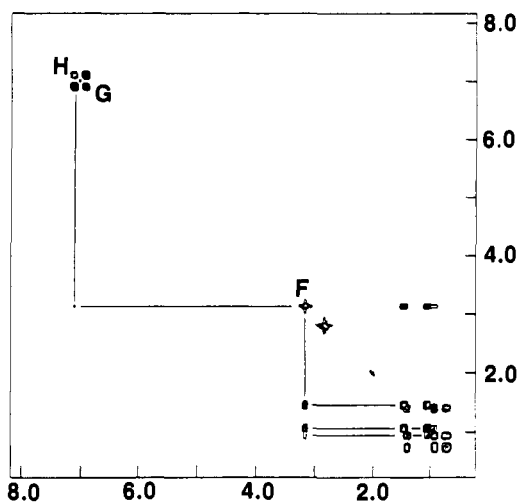


Figure 6.  ${}^1\text{H}$  2D COSY spectrum (200 MHz) of benzocyclopropanornbornene (**4**) recorded in acetone- $d_6$  at 23 °C.

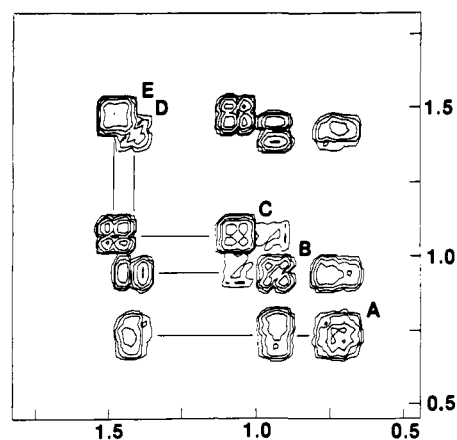


Figure 7. Expansion of the upfield resonances shown in Figure 6.

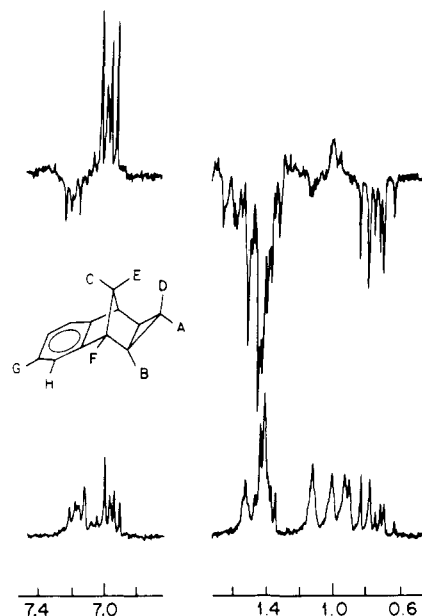


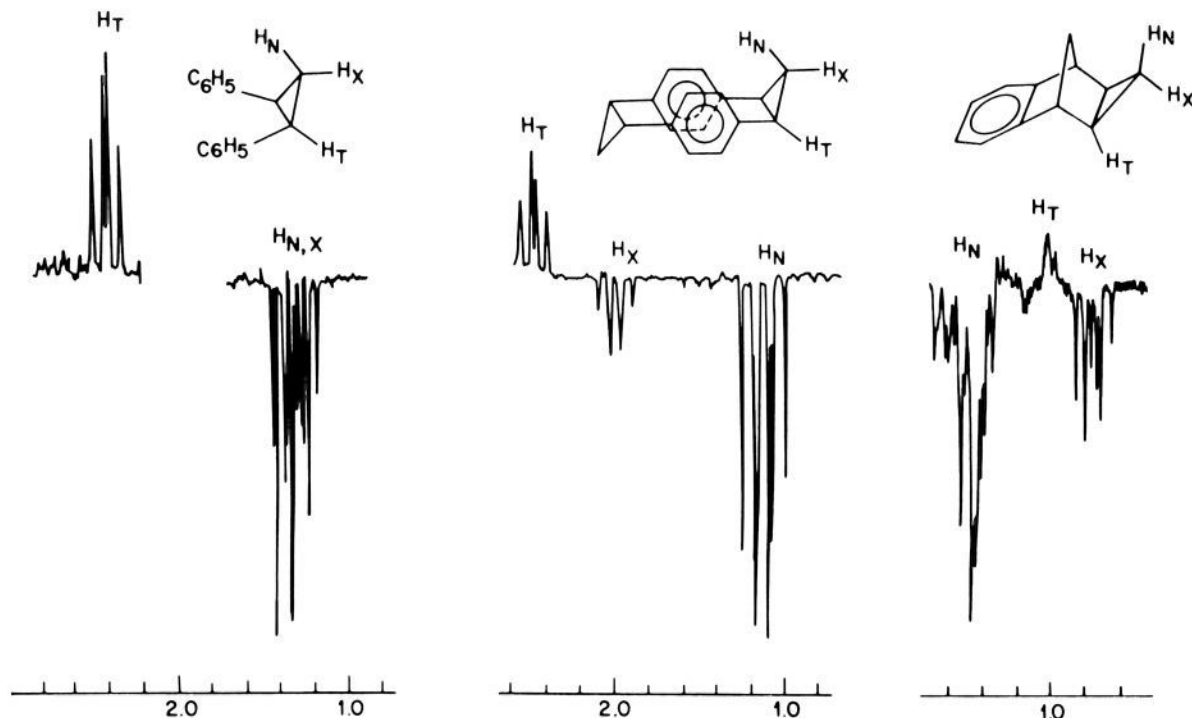
Figure 8. PMR spectra (90 MHz) of an acetone- $d_6$  solution containing 0.02 M each of chloranil and benzocyclopropanornbornene (**4**) in the dark (bottom) and during UV irradiation (top).

dimensional display of the entire network of homonuclear spin-spin interactions in a given molecule.

(20) Barfield, M.; Dean, A. M.; Fallick, C. J.; Spear, R. J.; Sternhell, S.; Westerman, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1482-1492.

(21) Jeener, J., Ampère International Summer School, Basko Polje, Yugoslavia, 1971.

(22) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229-2246.



**Figure 9.** Comparison of the CIDNP effects observed for the cyclopropane protons of *cis*-diphenylcyclopropane (left), 1,2:9,10-bis(methano[2.2]-paracyclophane) (center), and 2,3-benzo-5,6-cyclopropanobornene, **4** (right).

The 200-MHz 2D COSY spectrum of **4** is shown in Figure 6 with an expansion of the upfield region presented in Figure 7. The one-dimensional resonances can be seen to lie on the diagonal running from upper left to lower right. Protons which are *J*-coupled show a correlating crosspeak on either side on this diagonal. These data confirm that A, B, and D interact strongly; they are likely to represent the cyclopropane protons. Similarly, C interacts prominently with E; these multiplets must represent the bridgehead protons. Finally, the bridgehead protons (F) interact with both bridge protons (C and E), with the tertiary cyclopropane protons (B), and with the downfield aromatic protons (H). This finding is of special interest since it establishes the identity of the aromatic protons. With this assignment, all proton resonances of **4** are uniquely defined. Accordingly, the CIDNP effects can be interpreted in terms of the electron spin density distribution in the intermediate.

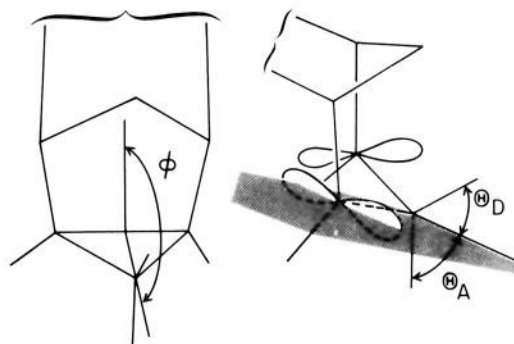
When the photoreaction of chloranil with **4** is carried out in the probe of a 90-MHz NMR spectrometer, nuclear spin-polarization effects are observed for the donor hydrocarbon and for at least one product (Figure 8). We will discuss principally the polarization of the regenerated donor. Of the aromatic signals, the upfield multiplet shows strongly enhanced absorption whereas the downfield multiplet shows only minor changes. The benzylic bridgehead protons are essentially unchanged. Furthermore, the upfield sections of the two-proton multiplet and of the four-proton multiplet appear in emission, and finally another section of the upfield multiplet appears in weakly enhanced absorption.

These effects can be interpreted in terms of an intermediate which is fully in line with the predictions of the FMO/PMO theory. The emission signals observed at high fields are ascribed to the geminal cyclopropane protons (A and D), whereas the enhanced absorption signals are ascribed to the tertiary cyclopropane protons. This polarization pattern suggests that the tertiary carbons carry positive spin density, a result expected for the involvement of the symmetrical cyclopropane HOMO. The aromatic polarization complements and confirms this interpretation. High spin density on two adjacent carbons, and essentially no spin density on the pair of carbons flanking them, suggests the involvement of the symmetrical HOMO and is compatible with the intermediacy of **16**. At the same time, the results are incompatible with the involvement of the unsymmetrical HOMOs

(and structure **18**) and eliminate any significant contribution due to homohyperconjugation.

The pattern of signal intensities observed for the three types of cyclopropane protons reveals further structural details. The secondary cyclopropane multiplet assigned to the endo proton (D) shows a considerably stronger enhancement than does the multiplet of the exo proton (A). In addition, the enhanced absorption observed for the tertiary multiplet (B) is comparably weak. This intensity pattern is quite different from that observed for diphenylcyclopropane<sup>23</sup> and resembles that of bismethanoparacyclophane (Figure 9).<sup>24</sup> As in the latter system, the different enhancements of the two secondary protons are ascribed to nonidentical hyperfine coupling constants. This implies that the dihedral angles,  $\theta_A$  and  $\theta_D$ , between the singly occupied orbital and the two adjacent C-H bonds are different.

Nonidentical dihedral angles for  $H_A$  and  $H_D$  can result if the angle,  $\phi$ , between the plane of the three-membered ring and the plane defined by the secondary cyclopropane carbons and the bridgehead carbons is *increased* in the radical cation relative to the parent hydrocarbon. In the resulting structure, the endo



proton has the smaller dihedral angle,  $\theta_D$ , with the partially occupied cyclopropane orbital. Accordingly, D is expected to have

(23) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7956-7958.

(24) Roth, H. D.; Schilling, M. L. M.; Hutton, R. S.; Truesdale, E. A. *J. Am. Chem. Soc.* **1983**, *105*, 153-157.

the larger hyperfine coupling constant.

The comparatively weak enhancement of the tertiary protons can be explained if the tertiary cyclopropane carbons adopt a pyramidal structure. Although pyramidal radicals are reasonably rare, they have been established for several strained ring systems.<sup>25</sup> For the radical cation **16**, the change in the angle,  $\phi$ , and the adoption of a pyramidal structure apparently relieve some of the strain in the system, yet maintain a reasonable degree of overlap between the tertiary carbon orbitals and the benzene ring.

### Conclusion

The results observed for the spiro[cyclopropane-1,9'-fluorene] and the benzocyclopropanorbornene systems demonstrate the importance of molecular orbital effects for the structures of strained ring radical cations and underscore the value of the FMO/PMO approach. The structure assumed by the radical

cation of **4** is dictated by the favorable interaction between the S orbital of benzene and the S orbital of cyclopropane. The radical cations of the spiro compounds **3** are derived in most cases from the S orbital. However, the radical cation **12** of the parent species is derived from the A orbital of cyclopropane and owes its relative stability to the interaction with the second HOMO of biphenyl. The degree of structural detail derived for these radical cations illustrates the fact that CIDNP patterns reflect subtle structural details. These results underscore the value of the CIDNP method in the study of electron transfer generated intermediates.

**Acknowledgment.** We are indebted to several colleagues for generous gifts of some of the donor molecules. G. B. Schuster provided samples of **3b-e** and M. Jones, Jr., contributed **3f**. We also thank M. D. Bruch for many helpful discussions concerning 2D NMR.

**Registry No.** **3a**, 167-02-2; **3b**, 87319-62-8; **9b<sup>+</sup>**, 96612-27-0; **3c**, 87319-59-3; **3d**, 87319-58-2; **3e**, 87319-57-1; **3f**, 87319-61-7; **4**, 15577-76-1; **4<sup>+</sup>**, 96612-28-1; chloranil, 118-75-2.

(25) Kawamura, T.; Tsumura, M.; Yokomichi, Y.; Yonegawa, T. *J. Am. Chem. Soc.* **1977**, *99*, 8251-8257.

## Applications of the Reduced Isotope Shift to General Estimation of One-Bond Isotope Shifts in NMR

Cynthia J. Jameson<sup>\*1a</sup> and H.-Jörg Osten<sup>1b</sup>

Contribution from the Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680, and Academy of Sciences of the GDR, Central Institute of Physical Chemistry, 1199 Berlin, German Democratic Republic. Received November 21, 1984

**Abstract:** We discuss general magnitudes of isotope shifts in NMR in terms of an electronic and a dynamic factor. The electronic factor is shown to be related to other measures of shielding sensitivity such as ranges of chemical shifts and  $\langle a_0^3/r^3 \rangle$  values for free atom of the observed nucleus. The dynamic factors can essentially be separated out by defining a reduced isotope shift. A table of values of reduced isotope shifts for a major part of the periodic table is provided, from which it is possible to estimate the order of magnitude of a one-bond isotope shift for these nuclei in any bond. Estimates for specific <sup>2/1</sup>H- and <sup>18/16</sup>O-induced isotope shifts are also given for nuclei in groups 4-7 in the periodic table.

NMR isotope shifts are differences in nuclear magnetic shielding between isotopically related species which are observed in high-resolution NMR spectra. Comprehensive reviews by Batiz-Hernandez and Bernheim<sup>2</sup> and by Hansen<sup>3</sup> include most of the reported data. The general trends noted by Batiz-Hernandez and Bernheim have been explained in a series of papers.<sup>4,5</sup> The feasibility of observing a one-bond isotope shift, e.g., <sup>80/77</sup>Se-induced <sup>13</sup>C shift, depends on the mass factors and on the shielding sensitivity. In this paper we discuss the general magnitudes of observed isotope shifts and provide estimates of others. We also provide a periodic table of relative sensitivities of nuclei to isotopic substitution at a nearest neighbor. The feasibility of observing the isotope shift for a nucleus upon isotopic replacement of an atom bonded to it can be estimated from this table by simply multiplying by appropriate mass factors.

### The Dynamic Factor for End Atom Substitution

It has been shown that one-bond isotope shifts of nucleus A due to substitution of <sup>m</sup>X by <sup>m'</sup>X in a symmetrical AX<sub>n</sub> molecule in which the mean bond angle distortions do not contribute sig-

nificantly to the isotope shift can be interpreted by the following equation:<sup>5</sup>

$${}^1\Delta A(m'/mX) = \sigma_0 - \sigma_0' = (\partial\sigma^A/\partial\Delta r_{AX})_e \sum_n (\langle\Delta r\rangle - \langle\Delta r'\rangle) + \dots \quad (1)$$

We found that secondary isotope effects on  $\langle\Delta r\rangle$  and isotope effects on centrifugal stretching can be neglected so that the sum of isotope effects on the mean bond displacements  $\sum_n (\langle\Delta r\rangle - \langle\Delta r'\rangle)$  by a single substitution can be replaced by the isotope effect on the bond in question,  $\langle\Delta r_{Am}\rangle - \langle\Delta r_{Am'}\rangle$ , and the latter, the mass dependence of the vibrational contribution, can be quantitatively estimated by  $\langle\Delta r_{Am}\rangle \cdot (m' - m)/m \cdot (1/2)m_A/(m_A + m)$ .<sup>5</sup> Under these conditions, the one-bond isotope shift can be expressed as

$${}^1\Delta A(m'/mX) \simeq (\partial\sigma^A/\partial\Delta r_{AX})_e \langle\Delta r\rangle \frac{m' - m}{m} \frac{1}{2} \frac{m_A}{m_A + m} \quad (2)$$

where  $\langle\Delta r\rangle$  is the mean bond displacement in the unsubstituted molecule A<sup>m</sup>X<sub>n</sub>. The observed additivity of multiple isotopic substitutions of equivalent atoms has been interpreted quantitatively.<sup>5</sup> In this paper we will consider only single isotopic replacement.

Calculations of the mean bond displacement  $\langle\Delta r\rangle$  and mean bond angle deformations  $\langle\Delta\alpha\rangle$  in bent triatomic molecules using anharmonic force fields showed that the mass dependence of  $\langle\Delta r\rangle$  is 6 to 80 times as large as that of  $r\langle\Delta\alpha\rangle$ , so that in these molecules  $\langle\Delta\alpha\rangle$  does not contribute significantly to the isotope shift of the

(1) (a) University of Illinois. (b) Academy of Sciences of the GDR.  
 (2) Batiz-Hernandez, H.; Bernheim, R. A. *Prog. NMR Spectrosc.* **1967**, *3*, 63-85.  
 (3) Hansen, P. E. *Ann. Rep. NMR Spectrosc.* **1983**, *15*, 105-234.  
 (4) Jameson, C. J. *J. Chem. Phys.* **1977**, *66*, 4983-4988.  
 (5) Jameson, C. J.; Osten, H. J. *J. Chem. Phys.* **1984**, *81*, 4293-4299, 4300-4305.  
 (6) Osten, H. J.; Jameson, C. J. *J. Chem. Phys.*, to be published.