

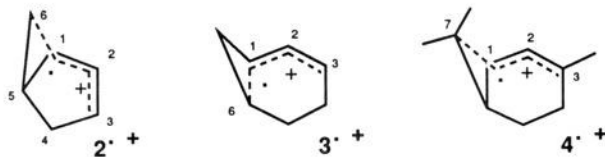
## The Structure of Simple Vinylcyclopropane Radical Cations: Evidence for Conjugation between Alkene and Cyclopropane Groups†

Heinz D. Roth\* and Torsten Herbertz

Rutgers University, Department of Chemistry  
Wright-Rieman Laboratories  
New Brunswick, New Jersey 08855-0939

Received July 6, 1993

The structures and reactions of organic radical cations have been the focus of much interest for the past decade.<sup>1</sup> In particular, the homoconjugative interactions of strained-ring moieties with olefinic fragments have been probed to delineate changes in the molecular geometry upon oxidation and to assess the spin density distribution in the resulting radical cations.<sup>2</sup> The simplest radical cation containing an olefinic moiety as well as a cyclopropane ring, the vinylcyclopropane system, has not been adequately characterized by either experiment or calculation.<sup>3-6</sup> In order to probe the structure of the corresponding radical cation ( $1^+$ ), we have studied the electron-transfer-induced CIDNP effects of three simple derivatives, in which the two functionalities are locked in a syn configuration, viz., bicyclo[3.1.0]hex-2-ene (2), bicyclo[4.1.0]hept-2-ene (norcarene; 3), and 3,7,7-trimethylbicyclo[4.1.0]hept-2-ene (carene; 4). The CIDNP results suggest two significantly different structure types, in which either the internal cyclopropane bond (as in  $3^+$ ) or a lateral one (e.g.,  $2^+$  or  $4^+$ ) is involved in delocalizing spin and charge. These findings elucidate the electronic and stereochemical requirements for conjugation between the two functionalities.

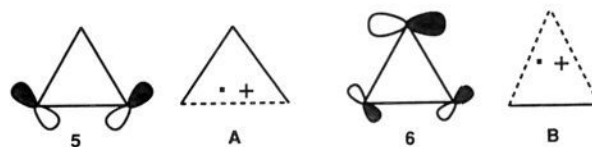


The frontier molecular orbital (FMO) of the cyclopropane unit plays a crucial role in the interaction between the two moieties. MO calculations suggest that the vertical ionization of cyclopropane occurs from a degenerate pair of in-plane  $e'$  orbitals (5, 6);<sup>7</sup> first order Jahn-Teller (JT) distortion of the resulting doubly degenerate  $2E'$  state leads to two nondegenerate electronic states,  $2A_1$  and  $2B_2$  ( $C_{2v}$  symmetry).<sup>7</sup> The  $2A_1$  component (orbital 5 singly occupied) relaxes to a "trimethylene" structure (type A) with one lengthened (but not broken) C-C bond. This structure type has been assigned to many cyclopropane radical cations, based on

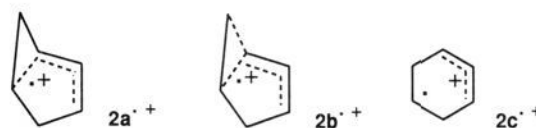
† Support of this work by the National Science Foundation through Grant NSF CHE-9110487 is gratefully acknowledged.

- (1) Roth, H. D. *Top. Curr. Chem.* **1992**, *163*, 131-250.
- (2) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343-350.
- (3) The reactivity of  $1^+$  has been studied in the gas phase.<sup>4</sup> Changes in the mass spectrum of the resulting ion(s) as a function of varying modes of ionization were interpreted as evidence that  $1^+$  suffers ring opening to penta-1,3-diene radical cation. This type of chemistry is not expected in solution.
- (4) Dass, C.; Peake, D. A.; Gross, M. L. *Org. Mass. Spectrom.* **1986**, *21*, 741-746.
- (5) An STO-3G calculation for  $1^+$  was carried out as a model for tricyclo[5.3.1.0<sup>1,7</sup>]undeca-2,4,9-triene with the vinyl group and two cyclopropane carbons held coplanar.<sup>6</sup>
- (6) Scott, L. T.; Erden, I.; Brunsvold, W. R.; Schultz, T. H.; Houk, K. N.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1982**, *104*, 3659-3664.
- (7) (a) Haselbach, E. *Chem. Phys. Lett.* **1970**, *7*, 428. (b) Rowland, C. G. *Chem. Phys. Lett.* **1971**, *9*, 169. (c) Collins, J. R.; Gallup, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 1530. (d) Bouma, W. J.; Poppinger, D.; Radom, L. *Isr. J. Chem.* **1983**, *23*, 21. (e) Wayner, D. D. M.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 3283; **1983**, *61*, 2310. (f) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 3405. (g) Krogh-Jespersen, K.; Roth, H. D. *J. Am. Chem. Soc.* **1992**, *114*, 8388-8394.

either CIDNP<sup>8</sup> or low-temperature ESR spectra,<sup>9,10</sup> as well as various electron-transfer-induced ring-opening reactions.<sup>11</sup>



Substitution at a single carbon may preferentially stabilize the  $2B_2$  component (orbital 6 singly occupied), generating a structure in which two C-C bonds are lengthened (type B). Since several species of type B have been invoked on the basis of CIDNP effects,<sup>12</sup> structures  $2-4b^+$  are considered for the radical cations of 2-4. In addition, we consider structures of type A, viz.,  $2-4a^+$ , and ring-opened bifunctional structures, i.e.,  $2-4c^+$  (type C), which have minimized strain energies, albeit at the expense of diminished delocalization. Ring-opened structures of type C have been invoked for 1-aryl-2-vinylcyclopropane radical cations.<sup>13</sup>



The irradiation of chloranil in the presence of 2-4 gave rise to CIDNP effects which, in each case, allow the unambiguous assignment of the radical cation structure. The photoreactions underlying these effects involve electron transfer from 2-4 to triplet chloranil; the resulting radical pairs undergo hyperfine-induced intersystem crossing; singlet pairs then recombine to regenerate the reactants with polarization patterns reflecting the hyperfine coupling (A) patterns of the radical cations. Since three of the polarization determining parameters are known ( $\mu$ ,  $\epsilon > 0$ ;  $\Delta g < 0$ ), the hyperfine coupling pattern can be derived from the CIDNP effects, revealing the spin density distribution and, hence, the structure of the radical cationic intermediates.<sup>2</sup>

CIDNP effects induced in the norcarene radical cation<sup>14</sup> and the EPR spectrum of this species have been mentioned previously;<sup>15</sup> a prominent hyperfine coupling ( $A \sim 50$  G) was assigned "to a single axial  $\beta$  proton in the 4-position". However, the delocalization of spin and charge onto the cyclopropane ring was not discussed. The CIDNP spectrum features strong emission for

- (8) (a) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7956. (b) Roth, H. D.; Schilling, M. L. M. *Can. J. Chem.* **1983**, *61*, 1027. (c) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6805.
- (9) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1983**, 202.
- (10) (a) Qin, X. Z.; Snow, L. D.; Williams, F. *J. Am. Chem. Soc.* **1984**, *106*, 7640. (b) Qin, X. Z.; Williams, F. *Tetrahedron* **1986**, *42*, 6301.
- (11) (a) Arnold, D. R.; Humphreys, R. W. R. *J. Am. Chem. Soc.* **1979**, *101*, 2743. (b) Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 6458. (c) Mizuno, K.; Ogawa, J.; Kagano, H.; Otsuji, Y. *Chem. Lett.* **1981**, 437. (d) Mizuno, K.; Ogawa, J.; Otsuji, Y. *Chem. Lett.* **1981**, 741. (e) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. (f) Gassman, P. G.; Olson, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 3740. (g) Mazzocchi, P. H.; Somich, C.; Edwards, M.; Morgan, T.; Ammon, H. P. *J. Am. Chem. Soc.* **1986**, *108*, 6828. (h) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462. (i) Hixson, S. S.; Xing, Y. *Tetrahedron Lett.* **1991**, *32*, 173.
- (12) (a) Roth, H. D.; Schilling, M. L. M. *Can. J. Chem.* **1983**, *61*, 1027-1035. (b) Roth, H. D.; Schilling, M. L. M.; Schilling, F. C. *J. Am. Chem. Soc.* **1985**, *107*, 4152-4158. (c) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *Tetrahedron* **1986**, *42*, 6157-6166. (d) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 6098-6099.
- (13) (a) Dinnocenzo, J. P.; Schmittl, M. *J. Am. Chem. Soc.* **1987**, *109*, 1561. (b) Dinnocenzo, J. P.; Conlon, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 2324.
- (14) (a) Roth, H. D.; Schilling, M. L. M.; Gassman, P. G.; Smith, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2711-2712. (b) Abelt, C. J.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4148-4152.
- (15) Arnold, A.; Burger, U.; Gerson, F.; Kloster-Jensen, E.; Schmidlin, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 4271-4281.

the multiplet near 1.80 ppm (H-4<sub>syn,anti</sub>; H-5<sub>syn,anti</sub>);<sup>16</sup> enhanced absorption for the multiplets at 5.42 ppm (H-3) and 1.23 ppm (H-1, H-6); and emission for the multiplet at 0.68 ppm (H-7<sub>syn,anti</sub>). Enhanced absorption signals indicate negative values of  $A_H$  for the corresponding  $^1H$  nuclei, caused by positive electron spin densities at carbons C-1, C-3, and C-6 via  $\pi, \sigma$  polarization; the emission signals are characteristic for positive values of  $A_H$  caused by  $\pi, \sigma$  delocalization (hyperconjugation) of spin density at an adjacent carbon. Overall, the effects support a radical cation,  $3^{+\cdot}$ , with spin and charge delocalized between the olefinic group and the Walsh orbital of the (more highly substituted) internal cyclopropane bond.

The CIDNP effects observed for carene suggest a different structure. The three methyl groups show strong emission, indicating positive spin density for carbons C-3 and C-7, to which they are attached; weakly enhanced absorption for signals at 5.55 (H-2) and 0.9 ppm (H-1) indicate weak positive spin density at C-1 and C-2; the signal of H-6 (0.7 ppm) shows emission, due to  $\pi, \sigma$  delocalization of the positive spin density at C-7 (and C-1). These results suggest a radical cation,  $4^{+\cdot}$ , in which spin and charge are delocalized between the olefinic group and the Walsh orbital of the (more highly substituted) lateral cyclopropane bond. The change in structure ( $4^{+\cdot}$  to  $3^{+\cdot}$ ) caused by the introduction of the geminal methyl groups at C-7 reflects a more stable radical cation due to the hyperconjugative interaction with the methyl groups.

Surprisingly, the CIDNP effects observed for **2** also indicate conjugation of the (less substituted) lateral, and not the (more highly substituted) internal, cyclopropane bond with the olefinic moiety. The effects observed for **2** are particularly clear-cut, since all protons are fully resolved (Figure 1).<sup>17</sup> The key to the structure of  $2^{+\cdot}$  lies in the prominent enhanced absorption signals of H-3 (5.2 ppm) and H-6<sub>syn</sub> (0.2 ppm) and the strong emission of H-4<sub>anti</sub> (2.4 ppm), H-4<sub>syn</sub> (2.2 ppm), and H-5 (1.5 ppm). This polarization pattern supports a species with spin density on C-3 and C-6, indicating the delocalization of spin and charge into the lateral cyclopropane bond. Weakly enhanced absorption observed for H-2 (5.8 ppm), H-6<sub>anti</sub> (0.8 ppm), and H-1 (1.75 ppm) and weak emission for H-5 further support this structure type.

We rationalize the involvement of the less substituted lateral bond of **2** instead of its more highly substituted internal bond as reflecting the need for orbital overlap. The bicycloheptene system is quite flexible, allowing either its internal ( $3^{+\cdot}$ ) or its lateral cyclopropane bond ( $4^{+\cdot}$ ) to align with the alkene p-orbitals. In contrast, the bicyclohexene system appears more rigid, allowing

(16) For an assignment of the  $^1H$  NMR spectrum of **3**, see: Paquette, L. A.; Wilson, S. E. *J. Org. Chem.* 1972, 37, 3849–3852.

(17) For an assignment of the  $^1H$  NMR spectrum of **2**, see: Schneider, M. P.; Crawford, R. J. *Can. J. Chem.* 1970, 48, 628–632. The assignment is borne out by a COSY 2D spectrum recorded at 200 MHz.

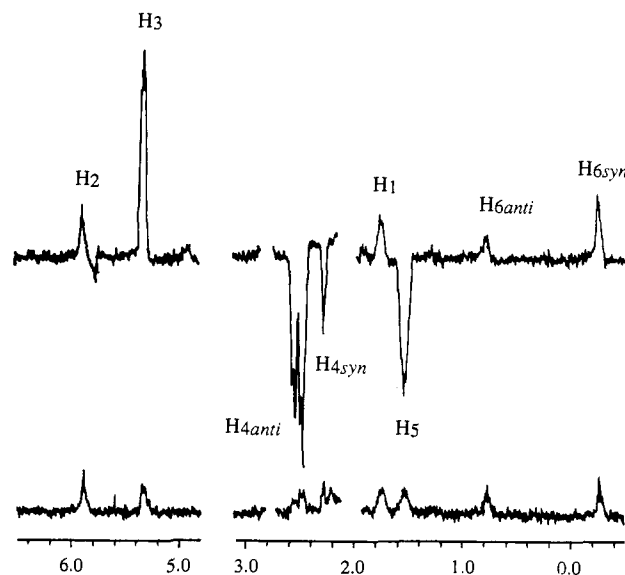


Figure 1.  $^1H$  NMR spectra (250 MHz) of acetone- $d_6$  solutions containing 20 mM each of bicyclo[3.1.0]hex-2-ene and chloranil in the dark (bottom) and during UV irradiation (top). The identity of the CIDNP signals is assigned in the figure; the signals of an impurity (2.8 ppm) and of the residual protons of the solvent (2.0 ppm) have been omitted in both traces for reasons of clarity.

only the lateral cyclopropane bond efficient overlap with the alkene p-orbitals ( $2^{+\cdot}$ ). The more flexible substrate, **3**, delocalizes spin and charge into the more highly substituted bond, whereas the more rigid substrate, **2**, involves the less highly substituted cyclopropane bond, because it allows more significant orbital overlap. The involvement of the lateral bicyclohexene bond in delocalizing spin and charge is also supported by ab-initio calculations, carried to the MP2/6-31G\* level of theory. The lateral cyclopropane bond is lengthened ( $C_1-C_6 = 1.748 \text{ \AA}$ ), and carbons C<sub>3</sub> and C<sub>6</sub> carry prominent spin density, with lesser spin density at C<sub>2</sub> and C<sub>1</sub>.<sup>18</sup>

In summary, CIDNP data observed during the photoinduced electron transfer reactions of **2**, **3**, and **4** support two different structure types for the respective radical cations, in which either the internal ( $3^{+\cdot}$ ) or a lateral cyclopropane bond ( $2^{+\cdot}$ ,  $4^{+\cdot}$ ) delocalizes spin and charge. These results raise interesting questions concerning the preferred site and the stereochemistry of nucleophilic capture. We are currently probing these aspects in a variety of chiral substrates.

(18) Details of the ab-initio calculation on  $2^{+\cdot}$  and  $1^{+\cdot}$  will be reported separately: Lakkaraju, P. S.; Herbertz, T.; Roth, H. D. To be submitted for publication.