

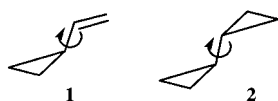
Radical Cations of Ethano-Bridged Dicyclopropyl Systems: Remarkable Stereoelectronic Effects

Torsten Herbertz and Heinz D. Roth*

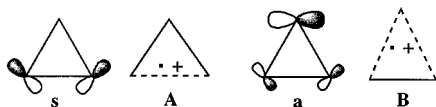
Department of Chemistry, Rutgers University
New Brunswick, New Jersey 08854-8087

Received February 25, 1997

Structures and reactions of organic radical cations have been studied for over two decades.^{1,2} The spin density distribution in radical cations containing two functional groups has attracted particular attention. Thus, several vinylcyclopropane systems (**1**) have been probed by experiment and calculation.^{3–7} For simple derivatives, in which the functionalities are locked in either the syn or the anti configuration, electron transfer induced CIDNP effects suggest different structure types.^{3,7} Either the internal cyclopropane bond, or a lateral one, or possibly two bonds are involved in delocalizing spin and charge. These findings elucidate the electronic and stereochemical requirements for conjugation between the two functionalities.



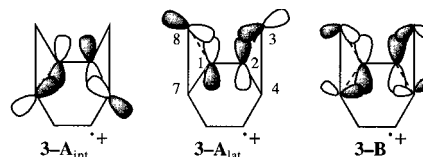
We have extended these studies to interactions between two cyclopropane functions, e.g., in radical cations of bridged dicyclopropyl systems (**3**). Cyclopropane radical cations may assume structures with either one or two weakened C–C bonds. Vertical ionization of cyclopropane (from a degenerate pair of in-plane e' orbitals; **s**, **a**) forms a doubly degenerate ²E' state.⁸ First-order Jahn–Teller distortion leads to two nondegenerate electronic states, ²A₁ and ²B₂ (C_{2v} symmetry).⁸



The ²A₁ component (orbital **s** singly occupied) relaxes to a “one-electron-bonded trimethylene” structure (type **A**; one weakened C–C bond) whereas the ²B₂ component forms a structure type resembling a π complex (type **B**; two weakened C–C bonds). Structure type **A** is well documented,^{1,2,9,10} structure type **B** is less common.^{9c}

Radical cations of the tricyclo[5.1.0.0^{2,4}]octanes (**3**) will have two structure elements related to structure type **A** or **B**. The

framework of **3** allows two different structures of type **A**, involving either the internal (**3-A_{int}^{•+}**) or the lateral bonds (**3-A_{lat}^{•+}**). Both structures have four carbons with positive spin density, pairwise symmetrical around a node (in the center of the C₁–C₂ bond). The two “outside” carbons (C₄–C₇ for **3-A_{int}^{•+}**; C₃–C₈ for **3-A_{lat}^{•+}**) are expected to have larger orbital coefficients than the “internal” carbons flanking the node (C₁–C₂). Structure **3-B^{•+}** has significant spin density on only two carbons (C₁–C₂). Schematic structures are shown below without attention to stereochemistry.



The most thoroughly studied dicyclopropyl system is quadricyclane, in which the cyclopropane rings are linked by two direct bonds and a methylene bridge; the rigid orientation allows the study of their through-bond interactions.¹¹ The radical cation, **Q^{•+}**, relieves an optimum degree of strain;^{2,12} its structure rests firmly on CIDNP results,^{12a,b} a TR-ESR spectrum,^{12d,13} and *ab initio* molecular orbital calculations.^{12c} The SOMO of **Q^{•+}** consists of an anti-symmetrical combination of two ²A₁ orbitals (cf., **3-A_{int}^{•+}**) with large orbital coefficients on four equivalent carbons.

The dicyclopropyl isomers discussed here have lower symmetry; the six carbons of the cyclopropane entities are at most pairwise symmetrical. The hyperfine coupling (hfc) patterns of the three structures (and the expected CIDNP effects) are determined by the principal spin densities. For **3-A_{int}^{•+}**, the spin density at C_{4,7} (ρ_{4,7}) will induce negative hfc (enhanced absorption) for H_{4,7} and give rise to positive hfc (emission) for the adjacent H_{3,8} and H_{5,6}. For **3-A_{lat}^{•+}**, ρ_{3,8} will lead to negative hfc (absorption) for H_{3,8} and to positive hfc (emission) for H_{4,7} and H_{5,6}. Finally, for **3-B^{•+}**, ρ_{1,2} will induce negative hfc (absorption) for H_{1,2} and lead to positive hfc (emission) for H_{4,7} and H_{3,8}. The polarization patterns induced in the three species appear uniquely suited to distinguish them.

Indeed, the CIDNP pattern observed during electron transfer from *anti*-**3** to photoexcited chloranil (Figure 1) unambiguously defines the radical cation structure.¹⁴ The strong absorption of the geminal cyclopropane protons (H_{3,8s,ab}, δ = 0.2 ppm) requires significant spin density at C₃ and C₈; this assignment is born out by the strong emission of the tertiary protons (H_{4,7}, δ = 0.7 ppm). The third cyclopropane resonance (H_{1,2}, δ = 1.0 ppm) and the signal of the tether (H_{5,6}, δ = 1.7 ppm) show minor effects. The polarization pattern uniquely fits a structure (*anti*-**3-A_{lat}^{•+}**) in which spin and charge are delocalized through the lateral bonds (C₁–C₈, C₂–C₃) causing them to be lengthened and weakened. This structure type has precedent in the radical

- (1) Roth, H. D. *Top. Curr. Chem.* **1992**, *163*, 131–250.
 (2) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343–350.
 (3) Roth, H. D.; Herbertz, T. *J. Am. Chem. Soc.* **1993**, *115*, 9804–9805.
 (4) (a) Weng, H.; Sethuraman, V.; Roth, H. D. *J. Am. Chem. Soc.* **1994**, *116*, 7021. (b) Weng, H.; Sheik, Q.; Roth, H. D. *J. Am. Chem. Soc.* **1995**, *117*, 10655–10661.
 (5) Arnold, D. R.; Du, X.; de Lijsler, H. J. P. *Can. J. Chem.* **1995**, *73*, 522.
 (6) Herbertz, T.; Roth, H. D. *J. Am. Chem. Soc.* **1996**, *118*, 10954–10962.
 (7) (a) Roth, H. D.; Weng, H.; Herbertz, T. *Tetrahedron*. In press. (b) Herbertz, T.; Roth, H. D. *J. Am. Chem. Soc.* Submitted for publication.
 (8) (a) Haselbach, E. *Chem. Phys. Lett.* **1970**, *7*, 428. (b) Collins, J. R.; Gallup, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 1530. (c) Bouma, W. J.; Poppinger, D.; Radom, L. *Isr. J. Chem.* **1983**, *23*, 21. (d) Wayner, D. D. M.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 3283; **1983**, *61*, 2310. (e) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 3405. (f) Krogh-Jespersen, K.; Roth, H. D. *J. Am. Chem. Soc.* **1992**, *114*, 8388–8394.
 (9) (a) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7956–7958. (b) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1981**, *103*, 7210. (c) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6805. (d) Roth, H. D.; Schilling, M. L. M. *Can. J. Chem.* **1983**, *61*, 1027. (e) Haddon, R. C.; Roth, H. D. *Croat. Chem. Acta* **1984**, *57*, 1165.
 (10) (a) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1983**, 202. (b) Qin, X. Z.; Snow, L. D.; Williams, F. *J. Am. Chem. Soc.* **1984**, *106*, 7640–7641. (c) Qin, X. Z.; Williams, F. *Tetrahedron* **1986**, *42*, 6301–6313.

- (11) (a) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 1745–1749. (b) Hoffmann, R.; Heilbronner, E.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 706–707. (c) Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3506–3508. (d) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1–9. (e) Heilbronner, E.; Martin, H. D. *Helv. Chim. Acta* **1972**, *55*, 1490–1502. (f) Heilbronner, E. *Isr. J. Chem.* **1972**, *10*, 143–156. (g) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936–967. (h) Haselbach, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Helv. Chim. Acta* **1979**, *62*, 583–592.
 (12) (a) Roth, H. D.; Schilling, M. L. M.; Jones, G., II *J. Am. Chem. Soc.* **1981**, *103*, 1246–1248. (b) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1981**, *103*, 7210–7217. (c) Raghavachari, K.; Haddon, R. C.; Roth, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 3110–3114. (d) Ishiguro, K.; Khudyakov, I. V.; McGarry, P. F.; Turro, N. J.; Roth, H. D. *J. Am. Chem. Soc.* **1994**, *116*, 6933.
 (13) Cromack, K. R.; Werst, D. W.; Barnabas, M. V.; Trifunac, A. D. *Chem. Phys. Lett.* **1994**, *218*, 485.
 (14) For an assignment of the ¹H NMR spectra of *anti*- and *syn*-**3**, see: Braun, S.; Lüttke, W. *Chem. Ber.* **1997**, *130*, 320–328.

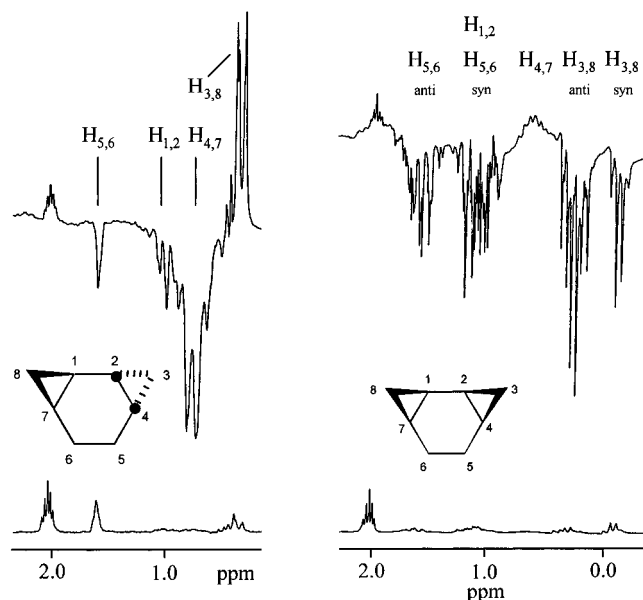
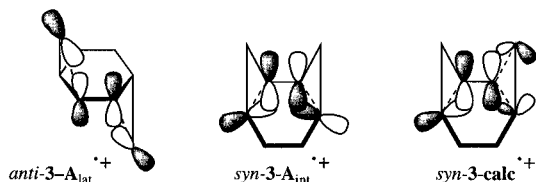


Figure 1. ^1H CIDNP spectra (90 MHz) observed during the photo-reaction of chloranil with *anti*-**3** (left) and *syn*-**3** (right), respectively, in acetone- d_6 . The bottom traces are dark spectra.

cation of bicyclo[3.1.0]hex-2-ene; the delocalization into the (less substituted) lateral bond was ascribed to stereoelectronic effects.³ An analogous explanation applies to the tricyclic radical cation, *anti*-**3**⁺, whose structure also permits favorable overlap between the Walsh orbitals of the two lateral cyclopropane bonds.



The assignment of the **3-A_{lat}**⁺ structure types to the *anti* isomer is borne out by *ab initio* molecular orbital calculations at the B3LYP/6-31G*//MP2/6-31G* level.^{7a,15–17} The two lateral bonds are lengthened to 165.2 pm (+9.5%), and the adjacent secondary (C_{3,8}) and tertiary (C_{1,2}) cyclopropane carbons bear most of the spin density ($\rho_{3,8} = 0.322$; $\rho_{1,2} = 0.192$). The tertiary cyclopropane protons (H_{4,7}) show large positive hfc ($A = 20.0$ G), whereas the pairs of geminal protons, H_{3,8a} and H_{3,8b} ($A_s = -7.2$ G; $A_a = -0.5$ G) and H_{5,6a} and H_{5,6b} ($A_s = 0.1$ G; $A_a = 2.2$ G), show significantly divergent hfc. Stereoelectronic effects on hfc have been recognized in various cyclopropane radical cations.^{3,7b,18,19}

Interestingly, the *syn* isomer shows an entirely different polarization pattern. The CIDNP spectrum (Figure 2) is almost entirely emissive, suggesting that most protons of *syn*-**3**⁺ have

positive hfc. Only the signal of H_{4,7} (0.5–0.8 ppm) shows weakly enhanced absorption, indicating (weak) positive spin density for C_{4,7}; in addition, C_{1,2} may have limited positive spin density. The signal of H_{1,2} (0.9–1.2 ppm) overlaps that of H_{5,6}; the overall multiplet shows emission; thus, the possible negative hfc of H_{1,2} and the spin density at C_{1,2} cannot be substantial. The overall polarization pattern is compatible with a structure having spin and charge localized in the internal bonds, i.e., **3-A_{int}**⁺, with the major exception that the enhancement of H_{4,7} is unusually weak for protons attached to centers of major spin density. Because of this potential discrepancy, we consider an alternative structure for *syn*-**3**⁺.

Ab initio calculations at the B3LYP/6-31G*//MP2/6-31G* level suggest an unusual unsymmetrical structure for *syn*-**3**⁺; three cyclopropane C–C bonds are lengthened, C₁–C₇ (165.1 pm; +9.1%), C₂–C₃ (158.9 pm; +5.6%), and C₂–C₄ (162.9 pm; +7.7%), and the five carbons of these bonds bear significant spin densities. The lengthened internal (C₁–C₇) bond and the spin densities at C₁ ($\rho_1 = 0.2$) and C₇ ($\rho_7 = 0.31$) support a contribution due to a structure of type **A**. However, the lengthened C₂–C₃ and C₂–C₄ bonds and the spin densities at C₂ ($\rho_2 = 0.24$), C₃ ($\rho_3 = 0.15$), and C₄ ($\rho_4 = 0.17$) support a contribution due to a structure of type **B**. Thus, the calculation supports a structure, *syn*-**3_{uns}**⁺, with two dissimilar cyclopropane fragments and 12 distinct ^1H nuclei, each with a unique hfc.

The ^1H NMR spectrum of *syn*-**3**, on the other hand, has six pairs of magnetically equivalent protons; thus, the CIDNP effects for each pair of protons is composed of two contributions. The overlapping signal of H_{1,2}/H_{5,6a} has four individual contributions. A comparison of each pair of calculated hfc with the observed CIDNP pattern shows, in general, excellent agreement, including for the overlapping signals of H_{1,2} and H_{5,6b}. The lone (minor) disagreement is found for the signal of H_{4,7}. The hfc calculated at the B3LYP/6-31G*//MP2/6-31G* level¹⁷ ($A_4 = 6.2$ G; $A_7 = -3.9$ G) predict net emission, instead of the observed weak absorption. Calculations at the MP2/6-31G*//MP2/6-31G* level ($A_4 = 3.0$ G; $A_7 = -9.9$ G) mirror the experimental result; however, it is well-known that this level of theory overestimates negative hfc.^{8f,12c,20} Thus, both structures considered for *syn*-**3**⁺ are slightly flawed. One reason why the unsymmetrical structure, *syn*-**3-A_{uns}**⁺, may be favored lies in the fact that it may reduce the repulsion between the *syn*-hydrogens, H_{3s} and H_{8s} at the bridge carbons, C₃ and C₈, respectively. As a result, the symmetrical structure, *syn*-**3-A_{int}**⁺, may be a low-lying transition state between two equivalent “distorted” structures.

However, regardless of the detailed structure of *syn*-**3**⁺, the CIDNP effects observed during photoinduced electron transfer reactions of *syn*- and *anti*-tricyclo[5.1.0.0^{2,4}]octane isomers (*syn*-, *anti*-**3**) clearly indicate significantly different structures for the two isomeric radical cations. The divergent structures are interpreted as evidence of different stereoelectronic effects governing the conjugative interaction between the pairs of cyclopropane rings and the delocalization of spin and charge in these radical cations. Other manifestations of stereoelectronic effects are under investigation.

Acknowledgment. Financial support of this work by the National Science Foundation through grant CHE-9414271 and equipment grants CHE-9107839 and CHE-9520633 is gratefully acknowledged. This paper is dedicated, on the occasion of his retirement, to Professor Fabian Gerson, for his many elegant studies contributing to the understanding of radical cation structure.

Supporting Information Available: Comparison of CIDNP effects with calculated hyperfine coupling constants (Table 1) and stereoviews of fully optimized (MP2/6-31G*) radical cations *anti*- and *syn*-**3**⁺ (2 pages). See any current masthead page for ordering and Internet access instructions.

JA9706209

(20) (a) Raghavachari, K.; Roth, H. D. *J. Am. Chem. Soc.* **1989**, *111*, 253. (b) Roth, H. D.; Schilling, M. L. M.; Raghavachari, K. *J. Am. Chem. Soc.* **1984**, *106*, 253.

(15) A detailed description of the theoretical methods used in this work is contained in: Hehre, W. J.; Radom, L.; Pople, J. A.; Schleyer, P. v. R. *Ab Initio Molecular Orbital Theory*; Wiley Interscience, New York, 1986.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J. P.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*; Gaussian, Inc.: Pittsburgh, PA.

(17) (a) Eriksson, L. A.; Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *J. Chem. Phys.* **1993**, *99*, 9756–9763. (b) Eriksson, L. A.; Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *Int. J. Quantum Chem.* **1994**, *52*, 879–901. (c) Batra, R.; Giese, B.; Spichty, M.; Gescheidt, G.; Houk, K. N. *J. Phys. Chem.* **1996**, *100*, 18371–18379.

(18) Gerson, F.; Qin, X.-Z.; Ess, C.; Kloster-Jensen, E. *J. Am. Chem. Soc.* **1989**, *111*, 6456.

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