11350 *J. Phys. Chem. A* **1999,** *103,* 11350−11354

Oxidation of Arylcyclopropanes in Solution and in a Zeolite: Structure and Rearrangement of the Phenylcyclopropane Radical Cation

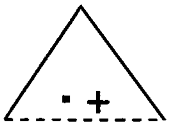
Heinz D. Roth,*,† Torsten Herbertz,† Prasad S. Lakkaraju,*,‡ Gregory Sluggett,§ and Nicholas J. Turro*,§

Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08855-0939,
Department of Chemistry, Georgian Court College, Lakewood, New Jersey 08701,
and Department of Chemistry, Columbia University, New York, New York 10027

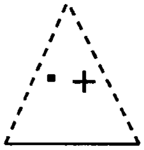
Received: May 19, 1999; In Final Form: October 4, 1999

The structure of phenylcyclopropane radical cation ($\mathbf{1}^{\bullet+}$, R = H) is derived from CIDNP effects observed during the electron transfer reaction of **1** with chloranil. This species is an example of an elusive structure type. The secondary cyclopropane protons show significantly divergent hyperfine coupling constants due to an unprecedented stereoelectronic effect. Incorporation into a redox-active pentasil zeolite (Na−ZSM-5) converts **1** or its *p*-methoxy derivative (**1**, R = OCH_3) to *trans*-propenylarene radical cations ($\mathbf{2}^{\bullet+}$, R = H, OCH_3).

The structure and reactivity of cyclopropane radical cations have attracted much attention;[1,2] the spin density distributions of many derivatives have been delineated, and many intra- and intermolecular reactions have been studied in gas phase,[3] solution,[1e,2] or solid matrices. Vertical ionization of cyclopropane from a degenerate pair of in-plane e′ orbitals (**s** and **a**) generates a doubly degenerate $^2\mathbf{E}'$ state, which undergoes first-order Jahn−Teller distortion to two nondegenerate electronic states, $^2\mathbf{A_1}$ and $^2\mathbf{B_2}$ (C_{2v} symmetry).[4] These components relax to structures with one ("trimethylene"; type **A**) or two lengthened C−C bonds ("π-complex"; type **B**).[1e,5] The majority of cyclopropane radical cations have structures of type **A**,[1e,5,6] whereas structure type **B** has been realized in only very few cases.[5c,7]



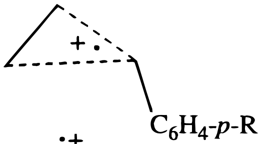
A



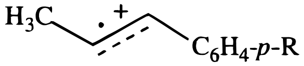
B

The stabilization of structure type **B** can be envisioned via three different mechanisms involving conjugative, hyperconjugative, or homoconjugative interactions. The homoconjugative approach first led to a structure of type **B**, as exemplified by the norcaradiene radical cation.[5c,7] On the other hand, hyperconjugation failed to stabilize the type **B** structure; thus, ab initio calculations on radical cations of 1-methyl- and 1,1-dimethylcyclopropane showed that their type **B** structures undergo second-order Jahn−Teller type distortions, resulting in scalene structures.[4i] Finally, conjugation with a delocalized π-system also stabilizes structure type **B**, as indicated by calculations on vinylcyclopropane[8] and phenylcyclopropane radical cations.[9]

The research described in this paper was undertaken to provide experimental evidence for the prevailing structure type of phenylcyclopropane radical cation ($\mathbf{1}^{\bullet+}$). This species has not been characterized by either ESR or CIDNP spectrum as of this date. We have studied electron transfer reactions of **1** in polar solvents and upon incorporation into a redox-active pentasil zeolite (Na−ZSM-5). In solution, we observed CIDNP effects delineating the spin densities and hyperfine coupling pattern of $\mathbf{1}^{\bullet+}$ (R = H). In the zeolite, on the other hand, the EPR results indicated rearrangement of **1** (R = H, OCH_3) to *trans*-propenylarene radical cations ($\mathbf{2}^{\bullet+}$, R = H, OCH_3).



$\mathbf{1}^{\bullet+}$



$\mathbf{2}^{\bullet+}$

Irradiation of chloranil in the presence of **1** (R = H)[10] generated strong polarization for the donor molecule: the aromatic multiplet near 7 ppm and the benzylic cyclopropane signals (t,t; δ = 1.9 ppm) showed enhanced absorption; the less shielded secondary cyclopropane resonances (δ = 0.95 ppm) showed strong emission whereas the more shielded ones (δ = 0.6 ppm) showed weakly enhanced absorption (Figure 1, top). These effects delineate the spin density distribution in the radical cation, $\mathbf{1}^{\bullet+}$ (R = H), and establish its structure; in addition, the signs and relative magnitudes of the hyperfine coupling constants derived for the secondary cyclopropane protons show an interesting stereoelectronic effect.

The enhanced absorption of the aromatic and the benzylic cyclopropane signals indicates negative hyperfine coupling (hfc) constants for these protons. Because the signals of the different aromatic protons are not resolved, the overall polarization is determined by the ortho and para protons, which outweigh the weaker effects of the meta nuclei. Negative hfcs typically arise

---

† Rutgers University.
‡ Georgian Court College.
§ Columbia University.

10.1021/jp991619u CCC: $18.00

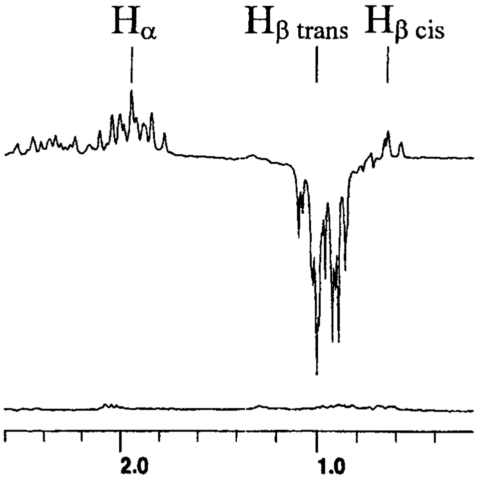


Figure 1. 60 MHz ^1H spectrum of an acetone-d_6 solution containing 10^{-2} M each of phenylcyclopropane (**1**, R = H) and chloranil (bottom) and CIDNP spectrum observed during UV irradiation (top). Of particular interest are the divergent effects of the secondary cyclopropane resonances ($\delta = 0.95, 0.6$ ppm).

via π,σ-polarization; accordingly, the CIDNP effects indicate spin density in the aromatic ring and on the benzylic carbon. The strongly polarized secondary protons confirm the presence of spin density on the benzylic carbon: the emission supports positive hfcs, which arise typically via π,σ-delocalization of spin density onto the ^1H nuclei (hyperconjugation). Overall, these results support a radical cation, $\mathbf{1}^{\bullet+}$, R = H, in which spin and charge are delocalized between the phenyl ring and the benzylic cyclopropane carbon and in which the two cyclopropane bonds are lengthened and weakened (type **B**). These conclusions are in full accord with the results of ab initio calculations (B3LYP/6-31G*), which documented the principal structural features and the charge density distribution in the radical cation, $\mathbf{1}^{\bullet+}$.[9]

The divergent signal directions for the two pairs of secondary cyclopropane protons document an interesting stereoelectronic effect. To understand the nature of this effect, it is crucial to assign the orientation of these protons relative to the phenyl group. The protons cis and trans to the phenyl group are readily differentiated by the magnitude of the vicinal spin−spin splitting constants ($^3J_{cis} > {}^3J_{trans}$). The nuclei cis to the phenyl group have one more trans ^1H neighbor whereas the trans nuclei have one more cis neighbor. Accordingly, the spectrum of the trans nuclei should be wider than that of the cis ^1H nuclei by ΔJ ($^3J_{cis} - {}^3J_{trans} = 8.4$ Hz − 5.1 Hz = 3.3 Hz). In the spectrum of **1** the downfield signal is wider by exactly 3.3 Hz. These considerations unambiguously identify the strongly polarized secondary protons as those trans to the phenyl group.

The divergent hfcs of the cis and trans ^1H nuclei cannot be explained by a different orientation of the C−H bonds relative to the spin-bearing benzylic cyclopropane orbital. This orbital lies in the plane of the three-membered ring and has the same relative orientation to the cis and trans protons. Accordingly, we considered the overall spin density distribution in the radical cation. The previous authors did not comment on spin densities or hfcs; thus, we repeated their ab initio calculations[9] (B3LYP/6-31G*), focusing on spin densities and hfcs.

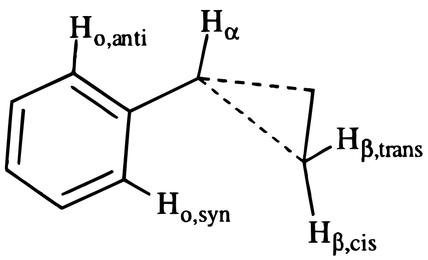
Not surprisingly, our calculations duplicated the published structural parameters exactly. For example, the cyclopropane bond lengths of $\mathbf{1}^{\bullet+}$ were calculated as $C_\alpha - C_\beta = C_\alpha - C_{\beta'} = 159.1$ pm, $C_\beta - C_{\beta'} = 145.0$ pm, and $C_{ipso} - C_\alpha = 143.1$ pm. More importantly, our calculations also reproduced the hyperfine coupling pattern derived from the CIDNP spectrum exactly, including the stereoelectronic effect on the hfcs revealed in this spectrum.

TABLE 1: Calculated Atomic-Atomic Spin Densities and Hyperfine Coupling Constants of Phenylcyclopropane Radical Cation

carbon	spin density, ρ	proton	spin density, ρ	hyperfine coupling
C-ipso	0.179			
C-o, syn	0.140	H-o,syn	−0.0076	−3.99
C-m, syn	−0.068	H-m,syn	0.0013	0.87
C-para	0.368	H-para	−0.0157	−9.04
C-m, anti	−0.076	H-m, anti	0.0015	1.04
C-o, anti	0.147	H-o, anti	−0.0077	−4.22
C-benzyl	0.136	H-benzyl	−0.0078	−4.34
C-2°	0.121	H-cis	0.0002	−0.70
		H-trans	0.0103	7.80
C-2°	0.120	H-cis	0.0002	−0.67
		H-trans	0.0104	7.84

The hfc constants of the (formal) benzyl moiety are unexceptional. The ortho, para, and benzylic ^1H nuclei all have large negative hfcs; the two ortho^1H nuclei show slightly different hfcs ($A_{o,syn} = -4.0$ G vs $A_{o,anti} = -4.2$ G), essentially identical to the benzylic proton ($A_\alpha = -4.2$ G); the para ^1H nucleus is most strongly coupled ($A_p = -9.05$ G). These couplings directly reflect the spin densities on the corresponding carbons ($\rho_{o,syn} = 0.14$; $\rho_{o,anti} = 0.149$; $\rho_\alpha = 0.147$; ρ_p 0.368). The negative hfcs support π,σ polarization as the mechanism by which the ^1H nuclei interact with the unpaired electron spin.[11] The ipso carbon also carries significant spin density ($\rho_{ipso} = 0.179$; Table 1).

While the hfc coupling pattern of the aryl moiety is unexceptional, the spin density distribution in the cyclopropane moiety has little, if any precedence. Both the benzylic and secondary cyclopropane carbons have positive spin density; the difference between ρ_α (0.147) and ρ_β (0.121), $\Delta\rho = 0.026$ (~20%), is larger than that between the ortho carbons ($\Delta\rho = 0.009$, 5%). However, this difference in quantity explains neither the diametrical difference between β-cis and β-trans hfcs nor the principal difference between the β-trans-hfcs and the benzylic, ortho and para hfcs. Clearly, the classical hyperfine mechanisms, π,σ-polarization or π,σ-delocalization,[11] which typically give rise to negative and positive hfcs, respectively, do not apply to the β-^1H nuclei of $\mathbf{1}^{\bullet+}$.



On the other hand, the calculated hfcs of the β-cis and trans ^1H nuclei ($A_{cis} = -0.70$ G; $A_{trans} = 7.81$ G) reproduce both the relative magnitude and the difference in sign suggested by the CIDNP results. In this context, it is of interest that related stereoelectronic effects and very similar hyperfine patterns were obtained by ab initio calculations for the syn and anti conformational isomers of vinylcyclopropane radical cation (*syn*- and *anti*-$\mathbf{3}^{\bullet+}$).[8] In this case, too, large hfcs were calculated for the trans nuclei, whereas small or negligible hfcs were found for

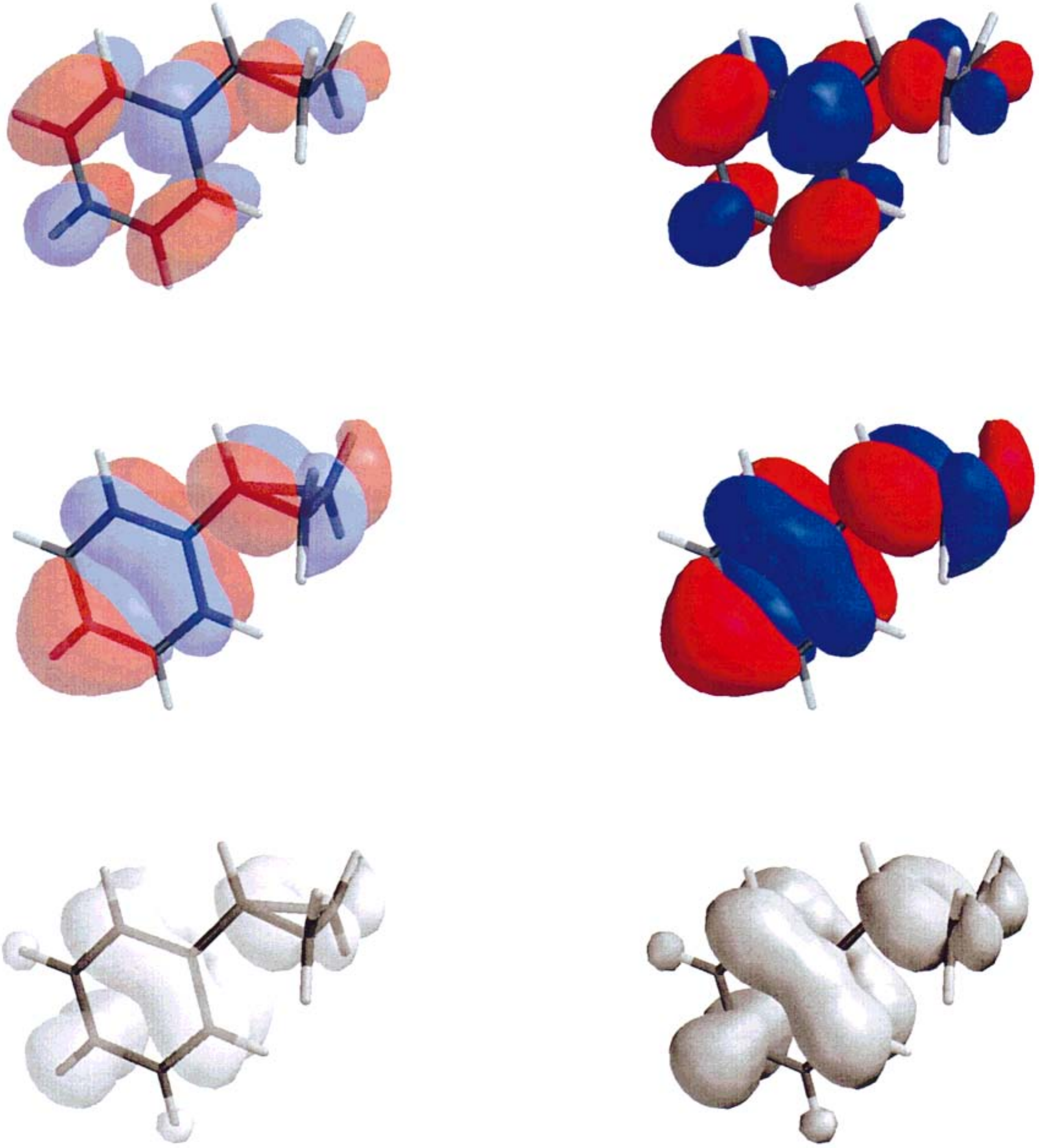
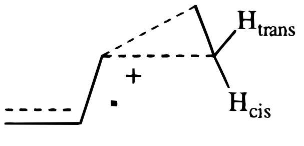
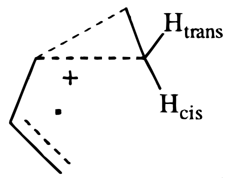


Figure 2. Pictorial representation of the spin density distribution (bottom) of SOMO (center) and LUMO (top) of phenylcyclopropane radical cation ($\mathbf{1}^{\bullet+}$) calculated by Spartan.

the cis protons, although no experimental data are available for comparison.[8]



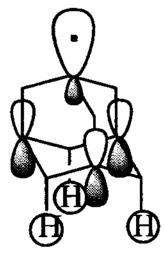
anti-$\mathbf{3}^{\bullet+}$



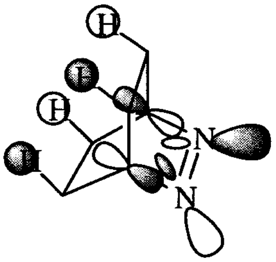
syn-$\mathbf{3}^{\bullet+}$

Accordingly, we examined the nature of the singly occupied molecular orbital (SOMO) and the spin density distribution in the cyclopropane moieties in more detail; the results are illuminating (cf., Figure 2). Adjacent to a nodal surface between the ipso and benzylic carbons, nearly 40% of the spin density of $\mathbf{1}^{\bullet+}$ is contained in a pair of Walsh lobes which encompass the benzylic (C_α) and extend along the 3°−2° cyclopropane bonds to secondary cyclopropane carbons (C_β). The back lobes of these orbitals are distorted toward the trans-β protons, actually enveloping them and placing positive spin density on them (Figure 2). In contrast, the cis-β protons have only very minor spin density, very likely because they lie in or near the nodal plane bisecting the $C_{ipso}-C_\alpha$ bond (Figure 2). The negative sign of the $H_{\beta,cis}$ coupling implies π,σ-polarization from the modest spin density at C_β ($\rho_\beta = 0.121$).

The sizable positive β-trans hfcs (+7.8 G) must be induced by a delocalization mechanism, albeit not directly analogous to the typical hyperconjugation mechanism. Similar direct coupling was invoked for several free radicals derived from rigid bi- or tricyclic systems, for example, to explain the significant γ hfcs of 1-adamantyl radical, $\mathbf{4}^\bullet$, $A_\gamma = 4.66$ G,[12] or the sizable hfcs for the anti ^{1}H nuclei at $C_{5,6,7,8}$ of 2,3-diazabicyclo[2.2.2]oct-2-ene radical cation, $\mathbf{5}^{\bullet+}$.[13] In both cases, the coupling was ascribed to σ-delocalization. Similarly, the significant difference between the *E*- and *Z*- azomethine ^{1}H hfcs of iminoxyl radicals ($\mathbf{6}^\bullet$; $A_E \sim 25$ G; $A_Z \sim 6$ G) reflects preferential σ delocalization due to back lobe overlap in the trans geometry.[14]



$4^{\bullet}$



$5^{\bullet+}$

However, the coupling mechanism in the phenyl-($1^{\bullet+}$) and vinylcyclopropane radical cations ($3^{\bullet+}$) cannot be completely analogous to those operating in species $4^{\bullet+}$, $5^{\bullet+}$, and $6^{\bullet}$. Although the $C_{\beta}-H_{trans}$ bonds are aligned in the general direction of the $C_{ipso}-C_{\alpha}$ bond, their dihedral angles ($\Theta_{trans} = \sim 140°$) allow less than perfect back lobe overlap. As a possible rationale for the divergent hfcs we note that the nodal surface through the β-carbons appears to be aligned in such a fashion as to avoid bisecting the nodal plane between C_{ipso} and C_{α}. Whatever the detailed mechanism, the ab initio calculations reproduce the remarkable stereoelectronic effects deduced from the CIDNP spectrum. The spin density distribution of $1^{\bullet+}$ (Figure 2) illustrates the observed differentiation between cis and trans ^{1}H nuclei.

The results discussed above delineate the structure and spin density distribution of phenylcyclopropane radical cation, $1^{\bullet+}$, and establish it as a species with a unique coupling mechanism and as an example of a structure type for which only few examples are known.[5c,7] We found it surprising that this relatively simple species, which can be obtained from a readily accessible precursor, was not characterized earlier and, apparently, has not been studied by EPR. This method would allow direct observation and provide detailed structural information. These considerations led us to attempt generation of $1^{\bullet+}$ in a zeolite host and to characterize it by its EPR spectrum. We incorporated **1** into the channels of pentasil zeolite (Na−ZSM-5). This approach appeared promising since various radical cations are generated spontaneously upon incorporating appropriate precursors ($E_{ox} \leq 1.65$ V) into zeolites.[15] The restrictive environment of these hosts enhances the stability of the guest intermediates and increases their lifetimes by restricting their mobility and/or limiting the access of external reagents.

On the other hand, the zeolite active sites may promote additional reactions. In some cases, zeolites serve the dual function of one-electron oxidant and proton acceptor, converting oximes to iminoxyl radicals or phenols to phenoxyl radicals.[16] In others, more complex conversions occur, such as formation of *p*-propenylanisole radical cation from *p*-propylanisole (net loss of 3 e^{-} plus 2 H^{+}),[17] or the conversion of 2-phenyl-1,3-dithiane to 1,2-dithiolane radical cation, which requires ring contraction with extrusion of a benzyl function.[18] The available precedent left little doubt that **1** could be oxidized in the ZSM-5 channels, but the ultimate fate of $1^{\bullet+}$ could not be predicted.

Sequestering **1** (R = H, OCH_3) into ZSM-5[19] resulted in strong EPR quintets ($g = 2.0032 \pm 0.0002$; A = 11.2 G, 4H; e.g., Figure 3, R = OCH_3). These spectra were identified by analogy with the known spectra of anethol radical cation, $2^{\bullet+}$ (R = OCH_3), as those of 1-arylpropene radical cations, $2^{\bullet+}$ (R = H, OCH_3); the allylic methyl protons and the olefinic β-proton are the strongly coupled nuclei.[17] The conversion of **1** to $2^{\bullet+}$ within the zeolite is yet another example of the interesting, complex, and occasionally specific reactions of organic substrates in redox- and/or acid−base-active zeolites. The restrictive environment of zeolites often increases the stability of radical cations by protecting them from external reagents and/or restricting their mobility. These features fail to protect species such as $1^{\bullet+}$, which react with the zeolite active sites.[20] While this is an interesting observation, it hardly contributes to elucidating the structure of phenylcyclopropane radical cation. The EPR spectrum of this species remains elusive.

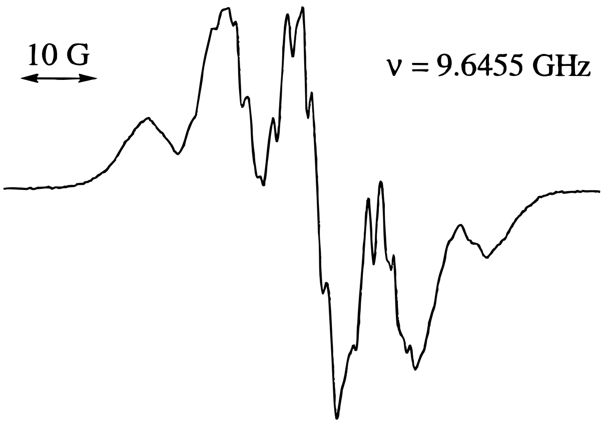


Figure 3. X-band EPR spectrum generated upon incorporation of phenylcyclopropane (**1**, R = OCH_3) into pentasil zeolite (Na ZSM-5). The spectrum is identified as that of anethole radical cation ($2^{\bullet+}$).

In summary, we have delineated the structure and spin density distribution of phenylcyclopropane radical cation, $1^{\bullet+}$, by CIDNP experiments and ab initio calculations. The most significant feature is the stereoelectronic effect deduced for the β-nuclei of the cyclopropane ring. The positive hfcs of the $H_{\beta,trans}$ nuclei, assigned on the basis of CIDNP results and reproduced by ab initio calculations, reflect the delocalization of spin density onto these nuclei (cf., Figure 2). These results delineate the structure and spin density distribution of phenylcyclopropane radical cation, $1^{\bullet+}$, and establish it as an example of a structure type for which only two examples were known previously.[5c,7]

Acknowledgment. Financial support of this work by the National Science Foundation through grant CHE-9714840 and an equipment grant, CHE-9520633, is gratefully acknowledged.

References and Notes

(1) (a) Forrester, R. A.; Ishizu, K.; Kothe, G.; Nelsen, S. F.; Ohya-Nishiguchi, H.; Watanabe, K.; Wilker, W. Organic Cation Radicals and Polyradicals. In *Landolt Börnstein, Numerical Data and Functional Relationships in Science and Technology*; Springer-Verlag: Heidelberg, 1980; Vol. IX, Part d2. (b) Yoshida, K. *Electrooxidation in Organic Chemistry: The Role of Cation Radicals as Synthetic Intermediates*; Wiley: New York, 1984. (c) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988. (d) *Radical Ionic Systems*; Lund, A.; Shiotani, M., Eds., Kluwer Academics: Dordrecht, 1991. (e) Roth, H. D. *Top. Curr. Chem.* **1992**, *163*, 133−245.

(2) (a) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133. (b) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180−186. (c) Nelsen, S. F. *Acc. Chem. Res.* **1987**, *20*, 269−276. (d) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343−350. (e) Bauld, N. L.; Bellville, D. J.; Harirchian, B.; Lorenz, K. T.; Pabon, R. A.; Reynolds, D. W.; Wirth, D. D.; Chiou, H.-S.; Marsh, B. K. *Acc. Chem. Res.* **1987**, *20*, 371. (f) Yoon, U. C.; Mariano, P. S. *Acc. Chem. Res.* **1992**, *25*, 233. (d) Gerson, F. *Acc. Chem. Res.* **1994**, *27*, 63. (g) Bauld, N. L. *Adv. Electron Transfer Chem.* **1992**, *2*, 1−66.

(3) Smith, R. L.; Chou, P. K.; Kenttämaa, H. I. In *The Structure, Dynamics of Organic Ions*; John Wiley & Sons: New York, 1996; 197−261.

(4) (a) Buenker, R. J.; Peyerimhoff, S. D. *J. Phys. Chem.* **1969**, *73*, 4425. (b) Cochanski, E.; Lehn J. M. *Theor. Chim. Acta* **1969**, *14*, 281. (c) Haselbach, E. *Chem. Phys. Lett.* **1970**, *7*, 428. (d) Rowland, C. G. *Chem. Phys. Lett.* **1971**, *9*, 169. (e) Collins, J. R.; Gallup, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 1530. (f) Bouma, W. J.; Poppinger, D.; Radom, L. *Isr. J. Chem.* **1983**, *23*, 21. (g) Wayner, D. D. M.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 3283. Wayner, D. D. M.; Boyd, R. J.; Arnold, D.

R. *Can. J. Chem.* **1983**, *61*, 2310. (h) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 3405. (i) Krogh-Jespersen, K.; Roth, H. D. *J. Am. Chem. Soc.* **1992**, *114*, 8388−8394.

(5) (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.* **1983**, *105*, 6805. (c) Roth, H. D.; Schilling, M. L. M. *Can. J. Chem.* **1983**, *61*, 1027. (d) Haddon, R. C.; Roth, H. D. *Croat. Chem. Acta* **1984**, *57*, 1165.

(6) (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.

(7) Herbertz, T.; Blume, F.; Roth, H. D. *J. Am. Chem. Soc.* **1998**, *120*, 4591−4599.

(8) Herbertz, T.; Roth, H. D. *J. Am. Chem. Soc.* **1998**, *120*, 11904−11911.

(9) Dinnocenzo, J. P.; Zuilhof, H.; Lieberman, D. R.; Simpson, T. R.; McKechney, M. W. *J. Am. Chem. Soc.* **1997**, *119*, 994−1004.

(10) Acetone-d_6 solutions containing 10^{-2} M each of phenylcyclopropane (**1**) and chloranil (bottom) were irradiated in the probe of a Bruker 60 MHz NMR spectrometer by the collimated beam of a Hanovia 1000-W high-pressure Hg−Xe lamp through a fused silica light pipe.

(11) Carrington, A.; McLachlan, K. D. *Introduction to Magnetic Resonance*; Harper & Row Publishers: New York, 1967; p 72−98.

(12) Krusic, P. J.; Rettig, T. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 995−997.

(13) Williams, F.; Guo, Q.-X.; Petillo, P. A.; Nelsen, S. F. *J. Am. Chem. Soc.* **1988**, *110*, 7887−7888.

(14) (a) Lakkaraju, P. S.; Zhang, J.; Roth, H. D. *J. Phys. Chem.* **1994**, *98*, 2722−2725. (b) Jaszewski, A. R.; Jezierska, J.; Jezierski, A. *Spectrochim. Acta A* **1999**, 1699−1709.

(15) (a) Ramamurthy, V.; Casper, C. V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 594−599. (b) Ramamurthy, V.; Casper, C. V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600−605. (c) Chen, F. R.; Fripiat, J. J. *J. Phys. Chem.* **1992**, *96*, 819−823. Chen, F. R.; Fripiat, J. J. *J. Phys. Chem.* **1993**, *97*, 5796−5797. (d) Rhodes, C. J.; Reid, I. D.; Roduner, E. *J. Chem. Soc., Chem. Commun.* **1993**, 512−513. (e) Roduner, E.; Crockett, R.; Wu, L. M. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2101−2105. (f) Corma, A.; Fornes, V.; Garcia, H.; Marti V.; Miranda, M. A. *Chem. Mater*. **1995**, *7*, 2136.

(16) Roth, H. D.; Weng, H.; Zhou, D.; Lakkaraju, P. S. *Acta Chem. Scand.* **1997**, *51*, 626−635.

(17) Lakkaraju, P. S.; Zhou, D.; Roth, H. D. *Chem. Commun.* **1996**, 2605.

(18) Roth, H. D.; Shen, K.; Lakkaraju, P. S.; Fernández, L. *Chem. Commun*. **1998**, 2447−2448.

(19) ESR samples were prepared by stirring 2−3 mg of phenylcyclopropane with 50−70 mg of zeolite (Na−ZSM-5, thermally activated by calcination at 500 °C for 12 h and stored under argon) in 10 mL of 2,2,4-trimethylpentane for 2 h. The loaded zeolite is collected by filtration, washed with *n*-hexane, and dried under vacuum (0.001Torr).

(20) The incorporation and reactions of several mono- and di-substituted cyclopropanes in ZSM-5 will be reported elsewhere.