The model also provides a convenient rationalization of the reactivity differences in the series of *o*-quinonoidal heterocycles. The activation energy for Diels-Alder reaction can be considered to involve two contributions: an endothermic contribution due to disruption of the π system in the five-membered heterocyclic ring, and an exothermic one due to simultaneous formation of a benzene ring. The degree of cancellation determines the height of the activation barrier. The greater the resonance stabilization of the "parent" five-membered heterocycle, the less reactive should be the bicyclic heterocycle. Thus isobenzofuran, derived from the nonaromatic or weakly aromatic furan (DRE = 1.6 kcal/mol[4b]), is much more reactive than either isothianaphthene or isoindole, both of which are derived from aromatic monocycles (DRE's of 6.5[4c] and 8.4 kcal/mol,[4b] respectively).

Conclusion

On the basis of our experimental results, our perturbation calculations, and our analysis of the published SCF calculations of Dewar et al., we suggest the heterocycles **1** to consist of contiguous but virtually noninteracting π systems, with their aromaticities deriving largely from the five-membered ring and their reactivity stemming from the adjacency of the butadiene moiety. This structural feature allows synchronous disruption of the π system in the heterocyclic ring and formation of a benzene ring during dienophile addition, leading to the observed hyperreactivity.

References and Notes

(1) Taken in part from the Ph.D. Thesis submitted by E.C. to the Graduate School of Arts and Sciences, 1976.

(2) (a) Isoindole: J. D. White and M. E. Mann, *Adv. Heterocycl. Chem.*, **11**, 113 (1969). (b) Isobenzofuran: R. N. Warrener, *J. Am. chem. Soc.*, **93**, 2345 (1971). (c) Isothianaphthene: B. Iddon, *Adv. Heterocycl. Chem.*, **14**, 331 (1972). (d) Benzo[*c*]selenophene: L. E. Saris and M. P. Cava, *J. Am. Chem. Soc.*, **98**, 867 (1976).

(3) (a) M. H. Palmer and S. M. F. Kennedy, *J. Chem. Soc., Perkin Trans. 2*, 81 (1976); (b) W. Rettig and J. Wirz, *Helv. Chim. Acta*, **59**, 1054 (1976).

(4) (a) J. Kopecky, J. Shields, and J. Bornstein, *Tetrahedron Lett.*, 3669 (1967); (b) M. J. S. Dewar, A. J. Harget, N. Trinajstic, and S. D. Worley, *Tetrahedron*, **26**, 4505 (1970); (c) M. J. S. Dewar and N. Trinajstic, *J. Am. Chem. Soc.*, **92**, 1453 (1970); (d) B. A. Hess, L. J. Schaad, and C. W. Holyoke, *Tetrahedron*, **28**, 3657 (1972); (e) B. A. Hess and L. J. Schaad, *Tetrahedron Lett.*, 535 (1977).

(5) E. Chacko, J. Bornstein, and D. J. Sardella, *Tetrahedron Lett.*, 1095 (1977).

(6) This question has been formulated by various authors (e.g., ref 1a, 3a,b, and 5), with Rettig and Wirz[3b] coming closest to our proposed structure.

(7) The 60-MHz NMR spectrum of benzo[*c*]selenophene was graciously supplied by Professor Cava.

(8) (a) M. J. S. Dewar, "Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, Chapter 5; (b) L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, New York, N.Y., 1966, Chapter 8.

(9) D. J. Sardella, T. Holak, and G. Vogel, *Orgn. Mag. Reson.*, **7**, 355 (1975).

(10) LAOCN3; Program 111, Quantum Chemistry Program Exchange; average deviation between experimental and calculated line positions.

(11) P. Crews, R. R. Kintner, and H. C. Padgett, *J. Org. Chem.*, **38**, 4391 (1973).

(12) (a) Indole: P. J. Black and M. L. Heffernan, *Aust. J. Chem.*, **18**, 353 (1968); $J_{\mathrm{ratio}} = 0.92$. (b) Benzothiophene: K. Takahashi, I. Ito, and Y. Matsuki, *Bull. Chem. Soc. Jpn.*, **39**, 2316 (1968); $J_{\mathrm{ratio}} = 0.88-1.00$. (c) Benzofuran: no data are available; however, Okuyama and Fueno [*Bull. Chem. Soc. Jpn.*, **47**, 1263 (1974)] report values of 8.1 and 8.4 Hz for J_{45} in 6-methyl- and 6-methoxybenzofuran, respectively, which bracket the value for the corresponding coupling in naphthalene (8.3 Hz).

(13) Reference 8a, p 173 ff.

(14) M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.*, **91**, 6325 (1969).

(15) Coupling constants were taken from ref 10 and 13.

(16) π bond orders were taken from (a) C. A. Coulson and A. Streitwieser, "Dictionary of π-Electron Calculations", W. H. Freeman, San Francisco, Calif., 1965; (b) A. Streitwieser and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations", Pergamon Press, Elmsford, N.Y., 1965.

(17) A least-squares fit yielded the equation $J_{\mathrm{ratio}} = 0.954P_{\mathrm{ratio}} + 0.037$, with a correlation coefficient of 0.992.

(18) $P_{\mathrm{ratio}} = 0.70$ in *o*-xylylene: C. R. Flynn and J. Michl, *J. Am. Chem. Soc.*, **96**, 3280 (1974).

(19) Reference 8a, Chapter 6.

(20) Calculations were done using wave functions and energies given in ref 16a; the parameters are not the best values suggested by Streitwieser,[21] and no quantitative significance is intended to be attached to the results.

(21) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961, Chapter 4.

(22) K. Fukui, *Acc. Chem. Res.*, **4**, 57 (1971), and references cited therein.

(23) Reference 8a, Chapter 8.

Stereochemistry of Cyclopropyl Radicals by Electron Spin Resonance[1]

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Abstract: ESR spectra are examined for cyclopropyl radicals including 1-fluoro analogues and the *exo*-tricyclo[3.2.1.$0^{2,4}$]octan-3-yl radical in cyclopropane or ethane solutions. The rate of inversion at the pyramidal tervalent carbon atoms of cyclopropyl radicals with an α hydrogen atom is rapid ($k > 8 \times 10^7\ \mathrm{s}^{-1}$), whereas the pyramidal geometry of 1-fluorocyclopropyl radicals is static on the ESR time scale. The hfsc of the β proton cis to the odd electron orbital is larger than that of the trans β proton. The β-methyl proton hfsc trans to the odd electron orbital is larger than the cis one. The 2,3-*cis*-dimethylcyclopropyl radical is slightly more stable in the structure where the odd electron orbital is trans to the methyl substituents. The stable geometry of 2-bicyclobutyl radical is also discussed.

Fessenden and Schuler[2] have shown on the basis of ESR results that the trigonal carbon atom of the cyclopropyl radical is pyramidal and is undergoing a rapid inversion from one pyramidal form to another. Since then the pyramidal geometry and the configurational stability of cyclopropyl radicals have been a subject of theoretical investigations[3] and of product studies.[4] Molecular orbital calculations[3b,c] predicted conflicting geometrical dependences of β-proton hfsc's for the nonplanar cyclopropyl radical. The β-proton hfsc's arise predominantly from hyperconjugation. To our knowledge, no experimental study has been reported on this subject, although such a study is important in order to understand the stereochemistry of cyclopropyl radicals.

Ando and his co-workers[4a,b] have demonstrated that the geometry of the fluorine atom is retained in the homolytic reduction of *gem*-halogenofluorocyclopropanes with a tin hy-

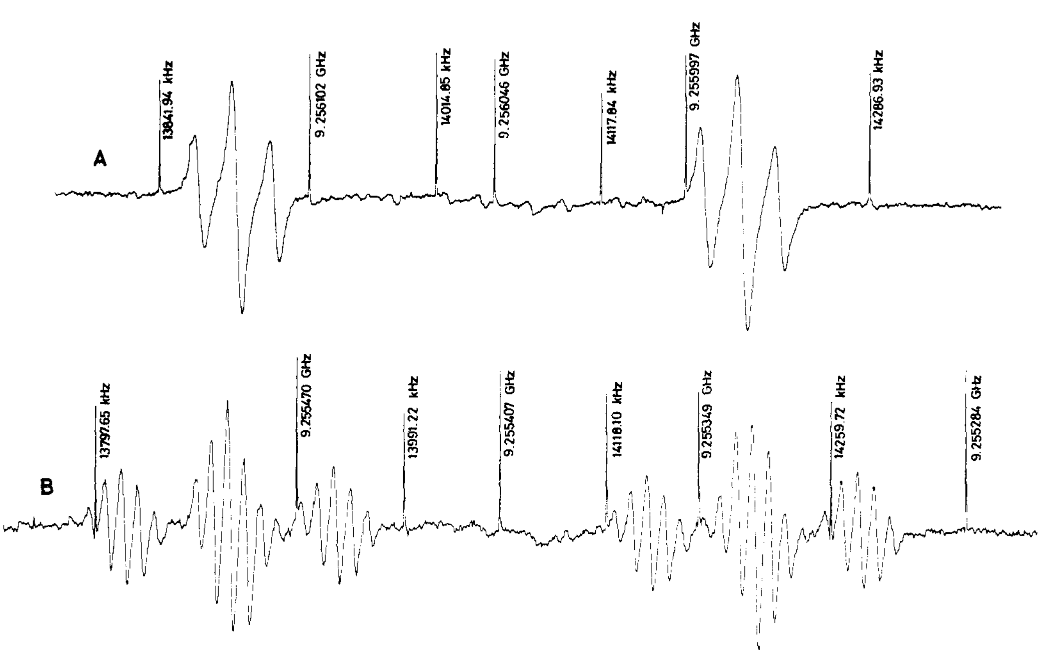
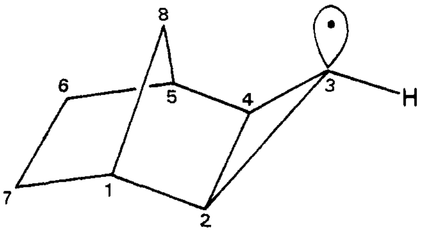


Figure 1. ESR spectra of 4 (A) and 5 (B); the numbers at the markers in kHz and GHz units are ^{1}H NMR frequency and ESR microwave frequency, respectively.

dride. Freeman and his collaborators[5] have shown that the *exo*-tricyclo[3,2.1.0^{2,4}]octan-3-yl radical (**1**) has the C$_3$-H bond located trans to the nonbornane moiety in the stable geometry. These results of product studies stimulated us to perform an ESR study of 1-fluorocyclopropyl radicals and **1** to elucidate the stereochemical dependences of proton hfsc's of cyclopropyl radicals "frozen" in a pyramidal geometry at the trigonal carbon atom.



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Results

1-Fluorocyclopropyl Radicals. Figure 1A shows the ESR spectrum observed during photolysis of a cyclopropane solution of a mixture of (*Z,Z*)-1-bromo-1-fluoro-2,3-dimethylcyclopropane (**2**), triethylsilane, and di-*tert*-butyl peroxide at −108 °C. The spectrum is a doublet (74.8 G) of triplets (5.53 G) with a *g* factor of 2.0040. Figure 1B shows the spectrum of the radical generated by homolytic bromine atom abstraction from (*E,E*)-1-bromo-1-fluoro-2,3-dimethylcyclopropane (**3**) at −108 °C. The latter spectrum consists of a doublet (77.6 G), a triplet (15.6 G), and a septet (2.43 G) with a *g* factor of 2.0040. The spectra in Figure 1A and 1B are attributed to (*E,E*)-1-fluoro-2,3-dimethylcyclopropyl (**4**) and (*Z,Z*)-1-fluoro-2,3-dimethylcyclopropyl (**5**) radicals, respectively, on the basis of the product studies of Ando and his co-workers.[4a,b] Only the spectrum of **4** was observed during the photolysis of the reaction mixture containing **2**, and **5** could be detected only from **3**. These results show that the rate of inversion at the pyramidal radical center is quite slow on the ESR time scale. The doublet splittings of 74.8 and 77.6 G of the present species are reasonable for hfsc's of fluorine nuclei bonded to pyramidal tervalent carbon atoms.[6] The hfsc's of **4** and **5** are assigned as shown below:

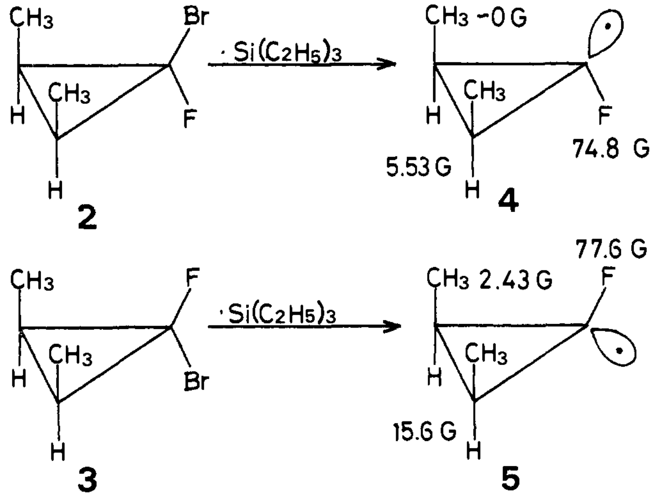
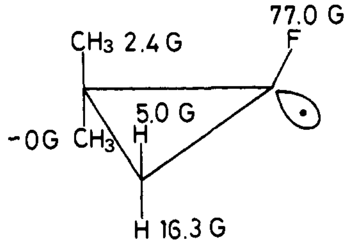


Figure 2A shows the spectrum observed during photolysis of a cyclopropane solution containing di-*tert*-butyl peroxide, triethylsilane, and 1-bromo-1-fluoro-2,2-dimethylcyclopropane at −108 °C. The spectrum consisted of three sets of doublets of 77.0, 16.3, and 5.0 G and a 1:3:3:1 quartet of 2.4 G with a *g* factor of 2.0039. Figure 2B shows a computer simulation based on these parameters. We attribute the spectrum to the 1-fluoro-2,2-dimethylcyclopropyl radical (**6**) "frozen" in one



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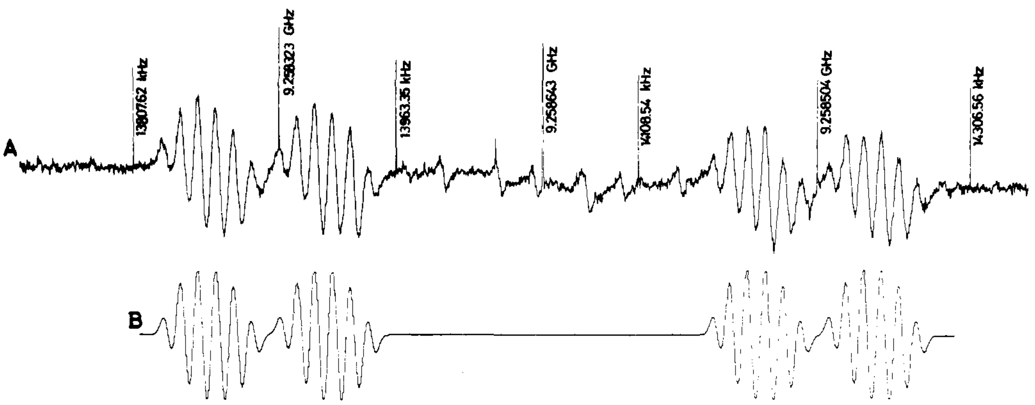


Figure 2. Observed (A) and simulated (B) spectra of **6**; the numbers at the markers have the same significance as in Figure 1.

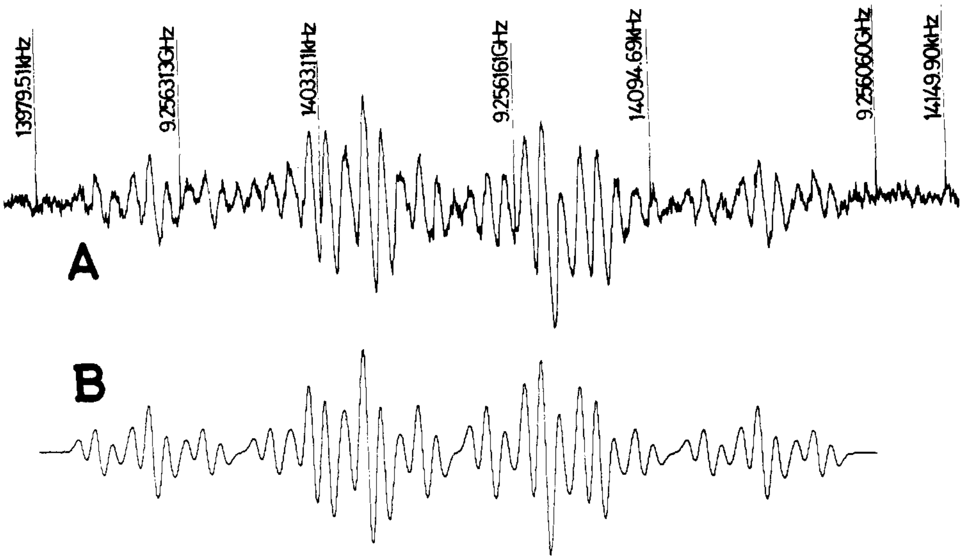


Figure 3. Observed (A) and simulated (B) spectra of **1**; the numbers at the markers have the same significance as in Figure 1.

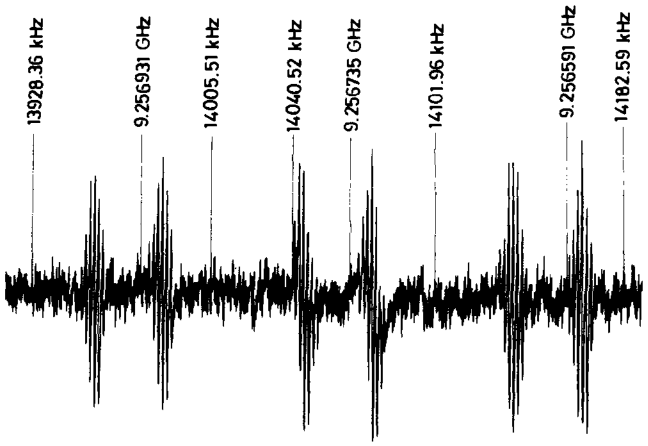
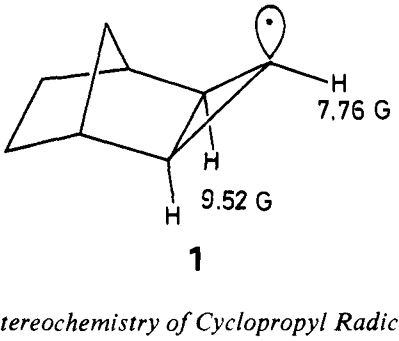


Figure 4. ESR spectrum of **7**. The central two groups of absorptions are broadened by partially resolved second-order splittings. The numbers at the markers have the same significance as in Figure 1.

pyramidal form, and the hfsc's of **6** are assigned as shown below from the comparison of its hfsc's with those of **4** and **5**. The average of the observed cis and trans (relative to the odd electron orbital) β-proton hfsc's of the present 1-fluorocyclopropyl radicals are much smaller than that of the cyclopropyl radical (23,42 G),[2] which suggests that the geometry around the tervalent carbon atom of the former radicals may be more pyramidal than that of the cyclopropyl radical. There was no indication of line width alternation phenomena in the spectrum of **6**, which indicates that the rate of inversion of the pyramidal α-carbon atom of **6** is slower than 7×10^6 s^{-1} at −108 °C.

***exo*-Tricyclo[3.2.1.0^{2,4}]octan-3-yl Radical.** Photolysis of the bis(*exo*-tricyclo[3.2.1.0^{2,4}]octane-3-carbonyl) peroxide in a cyclopropane solution at −82 °C gave the ESR spectrum shown in Figure 3, which consisted of three sets of triplets of 9.52, 2.38, and 0.72 G and a doublet of 7.76 G with a g factor of 2.0029. We attribute this to the *exo*-tricyclo[3.2.1.0^{2,4}]octan-3-yl radical (**1**). The doublet splitting of 7.76 G is similar to the α-proton hfsc of the cyclopropyl radical (6.51 G)[2] and is ascribed to the α proton. This assumes that the pyramidal nature of the α carbon atom of **1** is similar to that of the cyclopropyl radical. The largest triplet splitting of 9.52 G is tentatively attributed to the two β protons as shown below:



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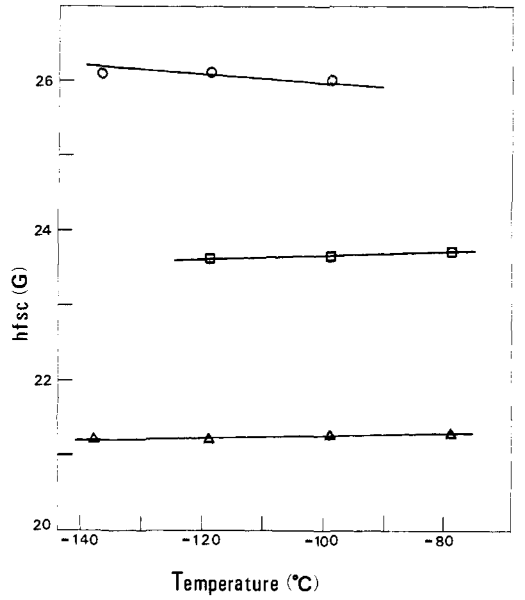
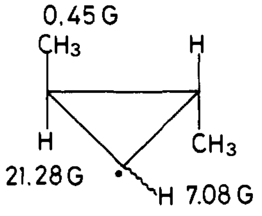


Figure 5. Temperature dependence of β-proton hfsc's: △, 7; □, 8; ○, 9.

The interesting point is that these hfsc's of the β protons, which are located mostly trans to the odd electron orbital,[5] are much smaller than the β-proton hfsc of the cyclopropyl radical (23.42 G).[2]

Cyclopropyl Radicals with an α Hydrogen Atom. We have also examined 2,3-*trans*-dimethylcyclopropyl (**7**), 2,2-dimethylcyclopropyl (**8**), and 2,3-*cis*-dimethylcyclopropyl (**9**) radicals generated as before by homolytic bromine atom abstraction from the corresponding 1-bromocyclopropanes in ethane solutions. Figure 4 shows the ESR spectrum of **7** at −99 °C, which is readily analyzed in terms of a doublet (7.08 G), a triplet (21.28 G), and a small septet (0.45 G) with a g factor of 2.0028. The radicals **8** and **9** at −99 °C gave ESR spectra similar to that of **7**. The spectrum of **8** consisted of a doublet (6.47 G), a triplet (23.66 G), and a septet (0.97 G) with a g factor of 2.0027. The spectrum of **9** was analyzed as a doublet (7.09 G), a triplet (26.04 G), and a septet (1.58 G) with a g factor of 2.0027. These hfsc's[7] are assigned straightforwardly as shown below on the basis of time-averaged molecular symmetries:



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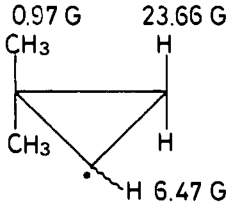

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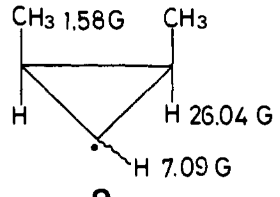

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The α-proton hfsc's of radicals **7**, **8**, and **9** are quite similar to that of the cyclopropyl radical, which indicates that the pyramidal nature of the tervalent carbon atoms of the former radicals are similar to that of the latter radical. The two β protons and the six γ protons of **7** and **8** appeared equivalent, and there was no indication of line width alternation phenomena in the spectra of **7** (as shown in Figure 4) and **8**. These results show that inversion at the α carbon atoms of **7** and **8** occurs at a high frequency ($k > 8 \times 10^7\ s^{-1}$) at −99 °C.

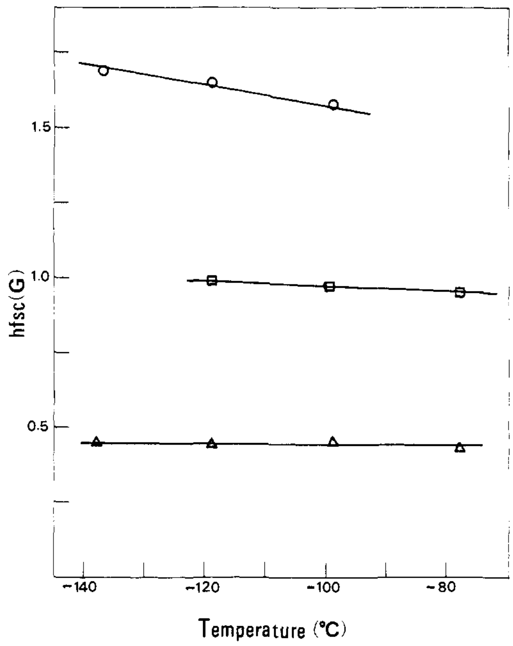


Figure 6. Temperature dependence of proton hfsc's of β-methyl groups: △, 7; □, 8; ○, 9.

Table I. β-Proton Hfsc's of Cyclopropyl Radicals (G)

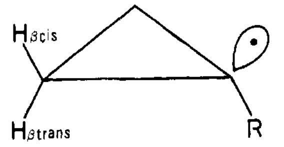
<table>
<tr><th>Radical</th><th>$H_{\beta cis}$[a]</th><th>$H_{\beta trans}$[a]</th></tr>
<tr><td>4</td><td>b</td><td>5.53</td></tr>
<tr><td>5</td><td>15.6</td><td>b</td></tr>
<tr><td>6</td><td>16.3</td><td>5.0</td></tr>
<tr><td>1</td><td>b</td><td>9.52[c]</td></tr>
<tr><td>9</td><td colspan="2">26.04[d]</td></tr>
<tr><td>7</td><td colspan="2">21.28[e]</td></tr>
<tr><td>8</td><td colspan="2">23.66[e]</td></tr>
<tr><td>10[f]</td><td colspan="2">23.42[e]</td></tr>
</table>

[a] $H_{\beta cis}$ and $H_{\beta trans}$ designate the β protons cis and trans to the odd electron orbital, respectively. [b] Not applicable. [c] This may not be $a(H_{\beta trans})$ in a strict sense, because this is not the "frozen" value but a time-average value. [d] Weighted mean of $a(H_{\beta cis})$ and $a(H_{\beta trans})$. [e] The average value of $a(H_{\beta cis})$ and $a(H_{\beta trans})$. [f] The cyclopropyl radical; ref 2.

Figures 5 and 6 show the temperature dependences of the β- and γ-proton hfsc's of **7**, **8**, and **9**, respectively. The temperature dependence for **9** is rather different from that for **7** and **8**. This will be discussed in a later section.

Discussion

β-Proton Hfsc. Table I summarizes the observed β-proton hfsc's of cyclopropyl radicals. In the "frozen" 1-fluorocyclopropyl radicals, the hfsc of $H_{\beta cis}$ is about three times larger than that of $H_{\beta trans}$. The α fluorine substituent seems to have only a minor effect on the relative magnitudes of hfsc's of $H_{\beta cis}$ and $H_{\beta trans}$, considering the results for **1**. The β-proton hfsc of



1, in which the odd electron orbital extends mostly trans to the two β hydrogen atoms,[5] is much smaller than those of the cy-

Table II. Calculated β-Proton Hfsc's of Cyclopropyl (**10**) and 1-Fluorocyclopropyl (**11**) Radicals[a] (G)

Radical	Method	$a(H_{\beta cis})$	$a(H_{\beta trans})$
10	EH	15.0	17.8
10	INDO	21.2	21.4
10[b]	INDO	15.3	14.2
10	Ab initio[c]	16.4	12.1
11	EH	12.3	15.7
11	INDO	14.4	15.2

[a] The angle between the ring plane and the C_1–H or C_1–F bond is assumed as 30°. [b] With the geometry in which the hydrogen atom is simply removed from the cyclopropane; the angle was 59.1°. [c] Reference 3b.

Table III. β-Methyl Proton Hfsc's of Cyclopropyl Radicals (G)

Radical	Cis[a]	Trans[a]
4	<1	*b*
5	*b*	2.43
6	<1	2.4
9	1.58[c]	
7	0.45[d]	
8	0.97[d]	
12[e]	0.78[d]	

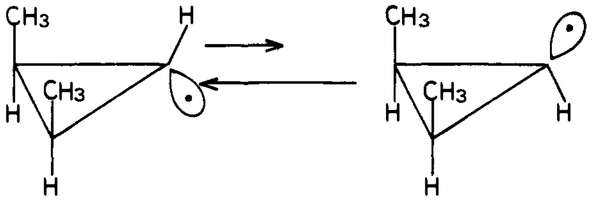
[a] This designates the location of the β-methyl group relative to the odd electron orbital. [b] Not applicable. [c] Weighted mean of cis and trans values. [d] The average of the cis and trans values. [e] 2,2,3,3-Tetramethylcyclopropyl radical; ref 13.

clopropyl radical, **7** and **8**; the latter values are the average of $a(H_{\beta cis})$ and $a(H_{\beta trans})$. The β-proton hfsc of **1** is, therefore, an upper limit of $a(H_{\beta trans})$ for cyclopropyl radicals without an α substituent. Consequently, the hfsc of $H_{\beta cis}$ of a cyclopropyl radical without an α substituent is estimated as larger than 30 G. On the basis of these results it is concluded that the hfsc of the β proton cis to the odd electron orbital is much larger (more than three times) than that of the trans β proton in cyclopropyl radicals. Thus we can conclude that the sp^n-hybridized odd electron orbital of a cyclopropyl radical is hyperconjugatively coupled more strongly with a neighboring σ bond of a cis arrangement than with a trans bond. The present ESR results fit the monotonic correlation[9] between ESR and NMR couplings, i.e., vicinal cis couplings in NMR spectra of cyclopropanes are larger than trans couplings.[10] We also point out that the C_β–$H_{\beta cis}$ bond is more eclipsed with the odd electron orbital than the C_β–$H_{\beta trans}$ bond is.

Proton hfsc's of the cyclopropyl (**10**) and the 1-fluorocyclopropyl (**11**) radicals were calculated using the extended Hückel (EH)[11] and UHF-INDO[12] methods. Table II summarizes calculated hfsc's of $H_{\beta cis}$ and $H_{\beta trans}$ together with those obtained with an ab initio method.[3b] The results of EH and UHF-INDO methods are not satisfactory and it is advised that caution should be exercised in applying semiempirical molecular orbital methods to cyclopropyl radicals (and probably also ions).

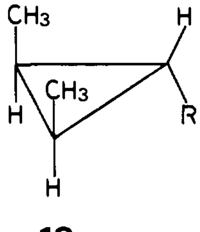
β-Methyl Proton Hfsc. Table III summarizes hfsc's of β-methyl groups. In "frozen" 1-fluorocyclopropyl radicals, the proton hfsc's of trans (relative to the odd electron orbital) β-methyl groups are around 2.4 G, while those of cis β-methyl groups are less than the line widths (~1 G). The observed average values of hfsc's of cis and trans β-methyl groups are 0.4–1.0 G for the 2,2,3,3-tetramethylcyclopropyl radical (**12**),[13] **7**, and **8**. These are smaller than the hfsc's of trans β-methyl groups in 1-fluorocyclopropyl radicals. These results reasonably suggest that the trans β-methyl proton hfsc is larger than that of the cis β-methyl group in cyclopropyl radicals.

Stable Inversion Isomers. ESR results show that **9** is rapidly inverting between **9a** and **9b**. First we examine here the relative stability of these isomers. The conclusion in the preceding two sections indicates that both β-proton and β-methyl proton hfsc's are larger in the structure of **9a** than **9b**. The observed β-proton and β-methyl proton hfsc's of **9** are larger than those of **7**, **8**, **10**, and **12**, showing that **9a** is slightly more stable than **9b** in spite of the larger steric repulsion between the α hydrogen atom and the methyl substituents in the former geometry. This is further supported by the temperature dependences of these hfsc's. The lowering of the temperature induced an increase in the β-proton hfsc of **9** in contrast with decreases of those of **7** and **8** (Figure 5). The β-methyl proton hfsc of **9** showed a larger negative temperature dependence than those of **7** and **8** (Figure 6). These trends are reasonably explained, i.e., the decrease in the temperature induces the increase in the population of the more stable structure **9a**, resulting in the increase of hfsc's of β proton and β-methyl proton.



9a **9b**

Dewar and Harris[14] observed the conversion of the bromides **13a** and **14a** to lithio derivatives **13b** and **14b** with metallic lithium via the radical **9** with partial retention of configuration; the conversion of the bromide **13a** was more retentive. The present conclusion on the more stable geometry of the radical **9** is consistent with their observations if the radical is assumed to abstract lithium atom from the front side of the odd electron orbital and the rate constants of lithium atom abstraction by **9a** and **9b** were equal.



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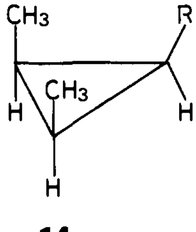

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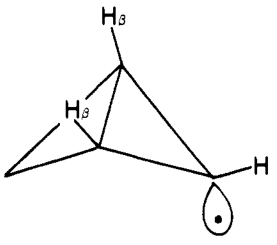
a, R=Br; **b**, R=Li

Krusic, Jesson, and Kochi[15] observed a small triplet of 4.40 G due to the two β protons in the ESR spectrum of the 2-bicyclobutyl radical (**15**). They discussed their results in terms of the geometry shown below:



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This stable geometry is consistent with the present conclusion on the stereochemistry of β-proton hfsc's, that is, the observed small β-proton hfsc indicates that the odd electron orbital is directed mostly trans to the β hydrogen atoms. The stabilization of this geometry is possibly due to the interaction between the odd electron orbital and one of the almost degenerate doubly occupied in-plane Walsh orbitals in the cyclopropane ring located cis to the odd electron orbital; this interaction is expected to be more favorable in this cis arrangement than in the trans one (vide supra).

Experimental Section

ESR Measurements. ESR spectra were measured on a JEOL PE-2X spectrometer modified with a JEOL ES-SCXA gunn diode X-band microwave unit equipped with a cylindrical mode cavity with slits for UV irradiation. Accumulations and simulations were performed with a JEOL JEC-6 minicomputer. The field sweep was monitored with ^{1}H NMR using a water sample, which was set just outside the ESR cavity and applied with an 80-Hz field modulation through a coil wound beside the NMR sample. A tunable NMR radio frequency was supplied from a JEOL ES-FC3 oscillator and the NMR output was amplified and detected with an 80-Hz amplifier unit in the ESR spectrometer and monitored on an oscilloscope during ESR measurements. The ^{1}H NMR frequency was counted on a Takeda-Riken TR-5501 frequency counter. The magnetic field difference between the ESR and NMR sample position was calibrated daily with perylene cation in concentrated sulfuric acid ($g = 2.002583$).[16] In the present type of ESR experiments, the drift of ESR microwave frequency can be as large as 0.0007 GHz which corresponds to an error of 0.00015 in g factor or 0.25 G in magnetic field strength. The drift may result from the heating of the cavity by radiation and/or the change of chemical constituents in the sample through photochemical reactions. To avoid these types of inaccuracies, the ESR microwave frequency was monitored with a Takeda-Riken TR-5501 frequency counter equipped with a TR-5023 frequency converter, and the g factors and the hfsc's were corrected against the microwave frequency drift.

UV irradiation was performed with a Philips SP-500 super-high-pressure mercury lamp focused with two quartz lenses and filtered through a distilled water cell of 45 mm path length.

The ESR samples were cooled with a cold nitrogen gas flow controlled by a JEOL JES-VT-3A temperature controller. The heating of samples by radiation was calibrated by measuring the temperature of liquid cyclopropane in a sample tube during irradiation and the temperature of the cooling nitrogen gas.

***gem*-Bromofluorocyclopropanes.** 1-Bromo-1-fluoro-2,3-*cis*-dimethylcyclopropanes and 1-bromo-1-fluoro-2,2-dimethylcyclopropane was obtained by the reaction[17] of *cis*-2-butene and isobutene, respectively, with bromofluorocarbene generated by basic decomposition of dibromofluoromethane.[18] The two isomers (**2** and **3**) of 1-bromo-1-fluoro-2,3-*cis*-dimethylcyclopropane were separated by VPC on a glass column packed with 20% DEGA on Celite 545. The ^{19}F NMR data of **2**: shift 42.3 ppm upfield from external CF_3COOH; $^3J(HF_{cis}) = 19.9$ and $^4J(HF_{trans}) = 2.8$ Hz. Those of **3**: shift 82.4 ppm upfield from external CF_3COOH; $^3J(HF_{trans}) = 4.2$ and $^4J(HF_{cis}) = 1.4$ Hz. The ^{13}C NMR data of **2**: shifts of C_1, C_2, and CH_3 are 96.5, 22.8, and 10.0 ppm downfield from internal $(CH_3)_4Si$, respectively; $^1J(CF) = 301$, $^2J(CF) = 10$, $^3J(CF) < 4$ Hz. Those of **3**: shifts of C_1, C_2, and CH_3 are 84.5, 24.9, and 5.4 ppm downfield from internal $(CH_3)_4Si$, respectively; $^1J(CF) = 302$, $^2J(CF) = 10$, $^3J(CF) = 7$ Hz.

Bis(tricyclo[3.2.1.0^{2,4}]octane-3-carbonyl) Peroxide. *exo*-Tricyclo[3.2.1.0^{2,4}]octane-3-*anti*-carboxylic acid[19] was converted into the corresponding acid chloride with excess thionyl chloride. Bis(tricyclo[3.2.1.0^{2,4}]octane-3-carbonyl) peroxide was prepared in ether in the presence of a few drops of water.[20]

1-Bromocyclopropanes. 1-Bromo-2,2-dimethylcyclopropane, 1-bromo-2,3-*trans*-dimethylcyclopropane, and 1-bromo-2,3-*cis*-dimethylcyclopropane were kindly offered by Dr. S. Terabe.

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