

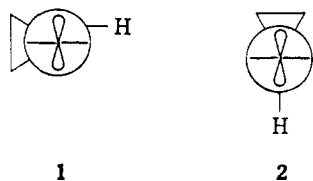
Conformational Analysis of Cyclopropyl Groups Attached to Trigonal Carbon in Organic Radicals¹

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Abstract: Several organic π radicals having cyclopropyl substituents have been studied by means of esr and endor spectroscopy. Through the cyclopropyl methine β hyperfine splittings it was determined that the cyclopropyl group preferentially adopts a bisected conformation except in sterically crowded environments. The preference is rather powerfully attenuated by negative and accentuated by positive charge on the attached trigonal carbon. The β hfs have been quantitatively related to potential barriers to internal rotation by means of quantum mechanical calculations.

The propensity of cyclopropyl groups for bisected (1), as opposed to symmetrical (2), conformations when attached to trigonal carbon appears, from several



published examples,⁴⁻⁸ to be reasonably general. However, attention has focused mainly on systems in which cyclopropyl is bound to electron-deficient carbon, *i.e.*, on carbonium ions and carbonyl compounds. Nevertheless, phenyl cyclopropane⁹ and vinyl cyclopropanes^{10,11} have also been reported to have the usual bisected conformational bias. At the start of this work, no conformational analyses had been reported for systems having cyclopropyl attached to electron-affluent trigonal carbon nor for cyclopropyl substituted free radicals. The use of esr spectroscopy for qualitative and approximate quantitative conformational studies in radical systems has been reported,¹² though not for the cyclopropyl group specifically. Since negatively charged, as well as neutral and cationic, free radicals are known, an esr study of cyclopropyl derivatives in such systems presented an appealing opportunity to study the effect of charge and other factors upon cyclopropyl conformations. While this research was in progress, two pertinent communications appeared,^{8,13} one of them from this laboratory.¹³

(1) A small portion of this work has been published previously as a communication: N. L. Bauld, R. Gordon, and J. Zoeller, Jr., *J. Amer. Chem. Soc.*, **89**, 3948 (1967).

(2) To whom correspondence should be addressed.

(3) Alfred P. Sloan Foundation Fellow, 1966-1968.

(4) C. U. Pittman, Jr., and G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 2998 (1965).

(5) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647 (1965).

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(8) G. A. Russell and H. Malkus, *J. Amer. Chem. Soc.*, **89**, 160 (1967).

(9) G. L. Closs and B. Klinger, *ibid.*, **87**, 3265 (1965).

(10) H. Gunther and D. Wendisch, *Ann. Chem.*, **5**, 251 (1966).

(11) G. R. DeMare and J. S. Martin, *J. Amer. Chem. Soc.*, **88**, 5033 (1966).

(12) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962).

(13) See ref 1.

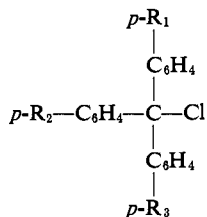
Results

The radicals included in this study are structurally rather diverse and reasonably numerous. They include four neutral radicals, five anion radicals, one dianion radical, and one cation radical. All but two are hydrocarbons, since we knew that charge and spin densities would be less subject to uncertainty in systems devoid of heteroatoms, one of our primary aims being to learn the effect of charge density on cyclopropyl conformation and conjugation. The radicals may be recognized as especially stable ones, a compromise made in favor of ease of generation of a large number of radicals over the widest feasible range of temperatures. The esr spectra will not be reproduced but have been made available to referees for inspection, along with computer simulations.

The Triphenylmethyl System. *p*-Cyclopropyl derivatives of the trityl radical aroused our interest because steric repulsions between the cyclopropyl group and the phenyl ring protons *ortho* to it should be rather small. As a practical matter, there are not many common systems having cyclopropyl attached to trigonal carbon which would be significantly less hindered. The cyclopropyl carbonyl radical is an outstanding exception but would have presented rather formidable experimental difficulties.^{13a} By comparing the conformational findings in the trityl and sterically similar systems with those from systems having *peri* or larger steric interactions, some insight into steric effects on the conformational bias of the cyclopropyl group could reasonably be expected. The *para* derivatives, rather than the *meta*, were preferred because of the much larger spin density at the former position, a circumstance favorable to more precise measurement of the hyperfine splittings of interest.

Chlorides **3a-d** were synthesized *via* the usual Grignard route, the methyl derivatives being necessary to establish the free rotation value for the β hyperfine splitting constant of interest, as will be discussed in the next section. The corresponding radicals were generated from the chlorides in a vacuum system using toluene and zinc dust.

(13a) NOTE ADDED IN PROOF. J.K. Kochi, P. J. Krusic, and D. R. Eaton [*J. Amer. Chem. Soc.*, **91**, 1877 (1969)] have recently reported the esr spectrum of the cyclopropyl carbonyl radical at 150° generated by the action of *t*-butoxy radicals on methylcyclopropane.



- 3a**, $R_1 = R_2 = R_3 =$ cyclopropyl
b, $R_1 = R_2 = R_3 =$ methyl
c, $R_1 =$ cyclopropyl; $R_2 = R_3 =$ H
d, $R_1 =$ methyl; $R_2 = R_3 =$ H

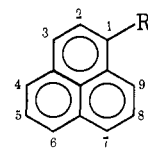
Tetrahydrofuran was also tried as solvent but it gave much more poorly resolved spectra. In toluene, all four radicals yielded well-resolved esr spectra, but, even so, the spectra were so complex as to defy completely unequivocal assignments of coupling constants. In some cases guesses were ventured which later proved to be correct, but the assignments were not satisfactorily definitive. Fortunately, the simplifying power of endor spectroscopy¹⁴ could be brought to bear on the problem, and it was by this means that the hyperfine splittings (hfs) were unraveled (Table I).

Table I. Esr and Endor Hfs of Substituted Trityl Radicals (Gauss, in Toluene Solution)

$p,p',p''\text{-R}_1,R_2,R_3\text{-trityl}$	$T, ^\circ\text{C}$	a_β	a_γ	a_o	a_m	a_p
$R_1 = R_2 = R_3 =$ H	-20			2.53	1.11	2.77
$R_1 = \text{CH}_3$; $R_2 = R_3 =$ H	Ambient	2.90		2.53	1.10	2.78
$R_1 = R_2 = R_3 = \text{CH}_3$	-80	3.035		2.60	1.14	
$R_1 = R_2 = R_3 =$ cyclopropyl	-10	0.752		2.60	1.14	
	-20	0.711	0.224	2.60	1.14	
	-30	0.678	0.232			
	-40	0.621	0.241			
	-50	0.588	0.244			
	-60	0.538	0.250			
	-70	0.498	0.254			
	-80	0.455	0.258			
	-90	0.418	0.264			

It is of incidental interest that, although the mono-substituted trityl radicals tended to dimerize at the lower temperatures, as shown by attenuation of the esr signal, the trisubstituted ones did not. This observation is in accord with the recent discovery that trityl radicals do not, as was previously believed, couple symmetrically to give hexaphenylethane, but that they couple unsymmetrically, at one benzylic and one *para* position, to give a triene.¹⁵ Presumably, the blocking of all three *para* positions prevents such a coupling mode.

The Phenalenyl System. The 1-cyclopropyl- and 1-methylphenalenyl radicals are another pair of neutral hydrocarbon radicals of interest. The parent phenalenyl (perinaphthenyl) radical has an exceptionally high spin density (corresponding to a hfs of 6.30 G) at the 1 and equivalent positions. Therefore, the 1-substituted derivatives were preferable. This system also presented an opportunity to observe the effect of steric interactions since in one of the bisected conformations of the 1-cyclopropyl phenalenyl radical, the cyclopropyl methine hydrogen sustains a *peri* interaction with the



$R = \text{CH}_3, \text{cyclopropyl}$

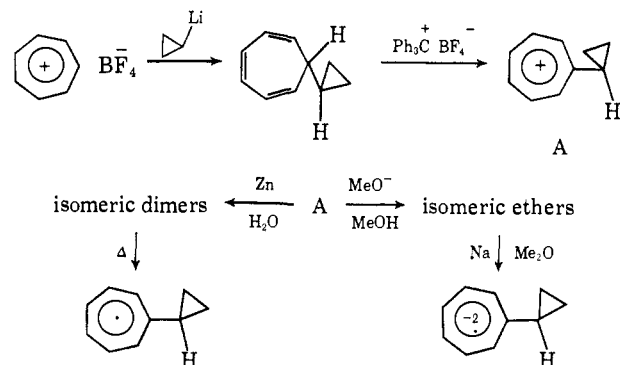
proton at the 9 position, and in the other bisected conformation the cyclopropyl group is fairly close to this proton. Addition of cyclopropyllithium and of methylmagnesium iodide to 1-phenalanone, followed by POCl_3 -pyridine dehydration, gave mixtures of the various position isomers of cyclopropyl- and methylphenalene, respectively. These were converted directly into the corresponding 1-substituted phenalenyl radicals by sodium methoxide in 98% THF-ethanol, a procedure we had found to lead to excellent esr spectra of the known parent phenalenyl radical. These esr spectra were interpretable, and the hfs are given in Table II.

Table II. Esr Hfs of Substituted Phenalenyl Radicals (98% THF-Ethanol)

1-R-Phenalenyl radical	Temp, $^\circ\text{C}$	a_β	a_γ	$a_{3,4,6,7,9}$	$a_{2,5,8}$
$R = \text{H}$	Ambient			6.30	1.82
$R = \text{CH}_3$	Ambient	6.0		6.0	1.7
$R = \text{cyclopropyl}$	-50 to +50	5.28	0.28	5.99	1.70

Tropenyl Radical-Tropenide Dianion Radical Systems. The tropenyl radical, though not as stable to dimerization as the trityl and phenalenyl radicals, is apparently more stable toward destructive side reactions and has been generated thermally over the temperature range 80–210 $^\circ$.¹⁶ Our interest in this ring system was reinforced by the observation made earlier in this laboratory that the tropenide dianion radical is also easily generated and is stable over a wide temperature range.¹⁷ The syntheses involved are shown in Scheme I.

Scheme I



The neutral radicals were generated by heating the appropriate dimer either in the neat condition or in molten naphthalene in a degassed, sealed, esr tube. In neither the cyclopropyl nor methyl case was the radical as stable as the parent tropenyl radical. In fact, the substituted radicals were readily generated only over a rather small temperature range, so that useful tempera-

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(15) H. Lankamp, W. Th. Nauta, and C. McLean, *Tetrahedron Lett.*, 249 (1968).

(16) G. Vincow, M. L. Morrell, W. V. Volland, H. J. Dauben, and R. Hunter, *J. Amer. Chem. Soc.*, **87**, 3529 (1965).

(17) N. L. Bauld and M. S. Brown, *ibid.*, **89**, 5417 (1967).

Table III. ESR Hfs of Tropenyl Radicals and Tropenide Dianion Radicals

Radical	Metal	Solvent	T , °C	a_{β}	a_{γ}	a_{ring}	a_{2M^+}
Tropenide dianion	Na	THF	-90			3.48 (7)	1.74
	K	THF	-90			3.48 (7)	
Methyltropenide dianion	Na	THF	-90	6.96		2.77 (6)	1.42
Cyclopropyltropenide dianion	Na	Me ₂ O	-130	3.08		2.78 (6)	1.57
	K	Me ₂ O	-130	3.22		2.70 (6)	0.55
Tropenyl		None	190			3.62 (7)	
Methyltropenyl		None	190	1.95		3.90 (6)	
Cyclopropyltropenyl		None	190	1.64		4.92 (2)	
						4.00 (2)	
						2.46 (2)	

Table IV. ESR Hfs of p,p' -Disubstituted Biphenyl Anion Radicals

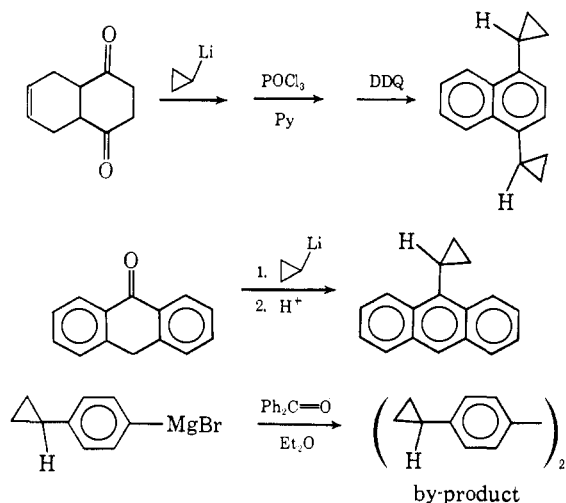
Substituents	Metal	Solvent	T , °C	a_{β}	a_{γ}	a_o	a_m	a_p
H, H	K	DME				2.73	0.43	5.46
CH ₃ , CH ₃	K	THF		5.63		2.66	0.51	
Dicyclopropyl	Na	THF	-80	3.27		2.01	0.46	

ture dependence data could not be gathered for this system. It was interesting to note, in the case of cyclopropyl tropenyl, that the polymeric product which results from sustained (say 0.5 hr) heating of the dimer at about 200° had the cyclopropyl group largely intact. Polymerization must have occurred *via* the triene moiety, at least in large part.

The substituted tropenide dianion radicals were generated similarly to the parent dianion radical, except that dimethyl ether had to be used as the solvent for the cyclopropyl tropenide dianion radical, which proved unstable above about -100°. The latter observation is consistent with the known instability of the (analogous) cyclopropyl carbinyl anion. The hfs obtained are listed in Table III.

Hydrocarbon Ion Radicals. Three hydrocarbon anion radicals were investigated, namely those of p,p' -dicyclopropylbiphenyl, 1,4-dicyclopropylnaphthalene, and 9-cyclopropylanthracene. These are, along with the tropenide dianion radical, the first systems to be reported in which the relevant trigonal carbon is negatively charged. In addition, steric effects increase in the order of listing. The syntheses involved are given in Scheme II. The anion radicals were generated using

Scheme II



alkali metal-etheral solvent combinations in all three cases. Because of rapidly deteriorating resolution

above and below the optimum temperatures for the individual esr measurements, useful temperature dependencies were again precluded. The hfs of these three anion radicals, along with those of the cation radical of 9-cyclopropylanthracene, prepared in sulfuric acid, are listed in Tables IV, V, and VI.

Anion Radicals of Heteroatom Systems. In addition to the hydrocarbon species already described, the anion radicals of two systems containing heteroatoms were also studied. These were systems in which, although the exact magnitude of the charge density at the trigonal center was in doubt, there was little doubt that it was slightly electron rich. This permitted conformational analyses in two additional systems of the type in which we had a special interest.

p -Cyclopropylnitrobenzene was prepared by nitrating phenylcyclopropane and separating the *o* and *p* isomers by preparative vpc. The anion radical of the *para* isomer was formed by two different routes, *viz.*, the *intra muros* electrochemical method of Geske and Maki,¹⁸ using tetrabutylammonium iodide in DMF, and by the alkali metal method, using potassium in DME. The results are listed in Table VII.

The anion radical of phenylcyclopropyl ketone was also prepared using potassium in DME, for comparison with the known acetophenone ketyl.¹⁹ A well-resolved spectrum resulted, but it was too complex to analyze completely. However, an approximate value for the hfs of the cyclopropyl methine proton was obtained as follows. Cyclopropylphenyl ketone was deuterated at the cyclopropyl methine by refluxing it in D₂O-DME-potassium *t*-butoxide for about 7 days (isotopic purity >95%, nmr). The anion radical of the deuterated ketone was generated as before and also gave a rich, well-resolved esr spectrum, very similar to that of the undeuterated ketyl. Several independent determinations of the spectrum length indicated the spectrum of the deuterated ketyl to be 0.60 G shorter than that of the undeuterated one. Since substitution of deuterium for a proton should shorten the spectrum by an amount equal to 0.694 times the hfs of the replaced proton, the cyclopropyl methine splitting must have been 0.86 G. Despite the special care taken in measuring the spectral

(18) D. H. Geske and A. H. Maki, *J. Amer. Chem. Soc.*, **82**, 2671 (1960).

(19) N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964).

Table V. ESR Hfs of 1,4-Disubstituted Naphthalene Anion Radicals

Substituents	Metal	Solvent	Temp, °C	a_β	a_γ	a_2	a_5	a_8
H, H	Na	DME	Ambient			1.87	4.95	1.87
CH ₃ , CH ₃	Na	DME	-70	3.26		1.63	5.17	1.79
Dicyclopropyl	K	THF	-70	4.76	0.18	1.59	5.10	1.76

Table VI. ESR Hfs of 9-Substituted Anthracene Anion and Cation Radicals

Substituent, charge type	Metal	Solvent	Temp, °C	a_β	a_γ	a_1	a_2	a_3	a_4	a_{10}
H, anion	K	DME				2.74	1.57			5.56
CH ₃ , anion	K	DME		4.27		2.94	1.39	1.73	2.77	5.16
Cyclopropyl, anion	K	THF	-100	6.64	0.17	2.74	1.2	1.66	2.44	5.72
H, cation		H ₂ SO ₄				3.11	1.4			6.69
CH ₃ , cation		H ₂ SO ₄		7.79		2.81	1.46	1.19	2.85	7.03
Cyclopropyl, cation		H ₂ SO ₄	Ambient	4.0	0.26	2.64	1.36	1.29	2.64	7.66

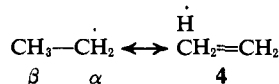
Table VII. ESR Hfs of *para*-Substituted Nitrobenzene Anion Radicals

Substituent	Solvent	Temp, °C	a_N	a_β	a_o	a_m	a_p
H	CH ₃ CN	Ambient	10.32		3.39	1.09	3.97
CH ₃	CH ₃ CN	Ambient	11.0	3.90	3.31	1.14	
Cyclopropyl	DMF	Ambient	9.76	1.61	3.28	1.07	

lengths and the reproducibility of the results under a variety of conditions, the risk in determining hfs in this indirect manner is appreciable. Nevertheless, some confidence is justified in the above answer, especially in view of its consistency with values from other ketyls.⁸ In any case, the qualitative conformational bias, as discussed later, would be unaffected.

Calculations

In organic π radicals (*i.e.*, those in which the electron spin density is found primarily in a p orbital or a π electronic system), protons either attached (α) to or one carbon removed (β) from a trigonal carbon atom may produce relatively large hyperfine splittings (hfs). Those protons more remote than this usually cause much smaller splitting except in some rigid systems,²⁰ as is also the case in nmr spectroscopy. The ethyl radical, for example, has both major types of splitting. The two



equivalent α protons have hfs of 22.5 G. The three equivalent β protons have $a_\beta = 27.1$ G. It is the latter, β , hfs which are of primary interest for the present purposes. They are generally ascribed to hyperconjugative interactions (4) which place electron spin on the β hydrogen nucleus where it can interact with the proton's nuclear magnet. In accordance with the hyperconjugative mechanism, β splittings have been found to have a pronounced orientation dependence, of the form given in eq 1.²¹ Here, ρ_i represents the spin density at the

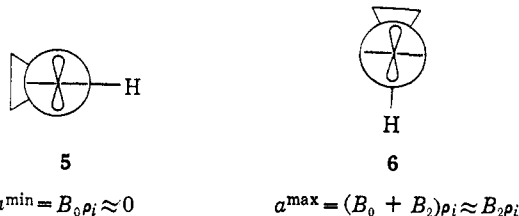
$$a_\beta = (B_0 + B_2 \cos^2 \theta) \rho_i \quad (1)$$

trigonal carbon (i) of the attachment, θ the dihedral angle between the C-H β bond and the 2p orbital on the i th carbon, and B_0 and B_2 are constants. Note that the

splitting is maximized where the p orbital and C-H β are "parallel" and thus optimally aligned for overlap. B_2 may be viewed as a measure of the efficiency of transmission of spin density to the β hydrogens, per unit spin density, whereas B_0 is a residual splitting which persists even when the orbitals are orthogonal and unsuited to overlap. It appears general that $B_2 \gg B_0$,²² as might be expected, and thus eq 2 is often used as an approximation.

$$a_\beta = (B_2 \cos^2 \theta) \rho_i \quad (2)$$

Applying these equations to the bisected (B) and symmetrical (S) conformations of a generalized system having a cyclopropyl group attached to a trigonal carbon, the results shown under structures 5 and 6, re-



spectively, are obtained. The B conformation has a minimum (near zero) hfs, and the S one a maximum. Any system in which internal rotation is merely restricted and not actually "frozen out" into one of these idealized structures will have an intermediate value of a_β , corresponding to a time average $\cos^2 \theta$ between zero and unity. For ideally free rotation (FR), where no conformational preference exists, the time average value of $\theta(\langle \theta \rangle_{av})$ is 45° and $\langle \cos^2 \theta \rangle_{av} = 1/2$. It follows that $a^{\min} < a_\beta < a^{\text{FR}} = 1/2 a^{\max}$ indicates a B and $1/2 a^{\max} < a_\beta < a^{\max}$ an S preference. If one is prepared to assume $a^{\min} = 0$ (eq 2) and has either a^{FR} or a^{\max} , a qualitative decision as to conformational bias is possible. Unfortunately, neither of these is known exactly for any case. Since rigid systems having constrained cyclopropyl S conformations are difficult to imagine, it seemed futile to try to find a^{\max} by any direct measurement. However, an approximate value of a^{FR} can be found indirectly, as follows. Methyl groups which are rapidly rotating, accurately have $\langle \cos^2 \theta \rangle_{av} = 1/2$, even where rotation is not completely free, owing to their cylindrical symmetry. The methyl hfs of the corre-

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(21) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960),

(22) A. Horsfield, J. R. Morton, and D. H. Whiffen, *Mol. Phys.*, **4**, 425 (1961).

sponding radical in which cyclopropyl is replaced by methyl is therefore, according to eq 2, a^{FR} , if ρ_i and B_2 are identical for both radicals. That ρ_i is indeed the same, to within just a few per cent, is reasonably certain from the fact that the ring (α) proton hfs are virtually the same in the cyclopropyl and methyl substituted radicals in all cases studied except the tropanyl systems, where the problem of doubly degenerate orbitals is encountered (see Tables I-VII and later discussion). These α splittings are also very close to those of the parent, unsubstituted, radicals. Apparently, and plausibly, cyclopropyl and methyl represent very small and quite similar perturbations upon the basic π systems, resulting in spin-density distributions which are almost identical with each other and very similar to that in the parent radical.

The quantity B_2 , as mentioned, is a measure of the efficiency of the hyperconjugative interaction with the β C-H bond. As such, one might expect it to be similar in magnitude for any C-H bond. This seems especially probable upon reflecting upon the fact that esr (and other) measurements have established even C-C bond hyperconjugation to be about 80% as efficient as C-H hyperconjugation.²³ Moreover, direct experimental evidence bearing on the point is available from this work. The cyclopropyl methine hfs (a_β) in 1-cyclopropylphenalenyl (5.3 G) is essentially temperature independent from +50 to -50° (to within *ca.* 0.1-0.2 G). The rotational barriers must therefore be very small, *i.e.*, the system is essentially freely rotating. As expected, the value of a_β here is not very different from $a_\beta^{\text{CH}_3}$ (6.0 G) in the 1-methylphenalenyl radical. The ratio is 0.88. Applying a correction for the negative B_0 found for cyclopropyl and discussed further on raises this to 0.97. For these reasons we feel that the assumption of equal B_2 's, while perhaps not perfectly accurate, is a good one, not subject to serious error. It was thus convenient to define an experimental quantity $C(R)$ as in eq 3. Applying eq 2 and invoking the

$$C(R) = a_\beta/a_\beta^{\text{CH}_3} \quad (3)$$

foregoing assumptions, this is equal to $2\langle \cos^2 \theta \rangle_{\text{av}}$. As such $C(R)$ is < 1 for a B, and > 1 for an S, preference. Its range is 0-2. In other words $C(R)$ is a qualitative index of conformational preference.

In order to utilize $C(R)$ for quantitative purposes it is necessary to relate it, *via* $\langle \cos^2 \theta \rangle_{\text{av}}$, to a rotational barrier, V_0 . This is done through eq 4, which sums the

$$\langle \cos^2 \theta \rangle_{\text{av}} = \frac{\sum_{j=0}^{\infty} g_j \langle \cos^2 \theta \rangle_j \exp(-E_j/kT)}{\sum_{j=0}^{\infty} g_j \exp(-E_j/kT)} \quad (4)$$

expectation values of $\cos^2 \theta$ ($\langle \cos^2 \theta \rangle_j$) for all torsional quantum states (j), properly weighted according to their populations. The eigenvalues, E_j , are needed for the latter and the eigenfunctions, Ψ_j , for the calculation of the $\langle \cos^2 \theta \rangle_j$, the latter by eq 5. The g_j are the

$$\langle \cos^2 \theta \rangle_j = \frac{\int \Psi_j^* \cos^2 \theta \Psi_j \, d\tau}{\int \Psi_j^* \Psi_j \, d\tau} \quad (5)$$

(23) L. M. Stock and J. Suzuki, *J. Amer. Chem. Soc.*, **87**, 3909 (1965).

degeneracies of the states. The E_j and Ψ_j must be obtained by solving the Schrodinger equation for internal rotation. This has been written down before^{24,25} (eq 6) and may be seen to be a Mathieu equation where $B = 2IE/\hbar^2$, $S = 2IV_0/\hbar^2$, and $I =$ reduced moment of iner-

$$d^2\Psi/d\theta^2 + (B - S \cos^2 \theta)\Psi = 0 \quad (6)$$

tia. It was not solved in the previous work by Stone and Maki, who, instead, used harmonic oscillator E_j and Ψ_j below the barrier ($B \ll S$) and rigid rotor ones above ($B \gg S$). We were fortunate enough to have available a computer program for solving the Mathieu equation for accurate E_j and Ψ_j , the latter as complex Fourier series (eq 7).²⁶ The angle θ is related to the α of eq 7

$$\Psi_j = \sum_{k=-\infty}^{+\infty} A_k \exp(i2k\alpha) \quad (7)$$

by $\theta = \alpha + \pi/2$. In the calculations to be discussed, 67 terms were retained in the series.

The criterion for convergence to the eigenvalues was 9 decimal places. The reduced moment of inertia was assigned the value 5×10^{-39} g cm², but the calculation was essentially insensitive to values of I between 3 and 7×10^{-39} , as had been found in Stone and Maki's work.²⁵

With the E_j and Ψ_j in hand, the $\langle \cos^2 \theta \rangle_j$ were then computed for each quantum state *via* eq 5. It may be worthwhile to note the behavior of $\langle \cos^2 \theta \rangle_j$ as a function of E_j (Figure 1). The quantum states of lowest energy have very small $\langle \cos^2 \theta \rangle_j$, as expected for a harmonic oscillator in the present system. The states well above the barrier have $\langle \cos^2 \theta \rangle_j$ asymptotically approaching 0.500, as behooves a rigid rotor. However, the behavior of $\langle \cos^2 \theta \rangle_j$ near the barrier (either above or below) is quite different from the idealized cases. Hence the results of Stone and Maki, though qualitatively similar, are quantitatively substantially disparate from those obtained in the above manner.

Above the barrier, the states begin pairing up and fairly quickly become essentially doubly degenerate, also as expected for a rigid rotor. At energies reasonably well above the barrier the eigenvalues are essentially those of a rigid rotor. This is fortunate, because program MATHIEU fails to converge for states substantially above the barrier. In order to estimate the contributions to $\langle \cos^2 \theta \rangle_{\text{av}}$ from these relatively high energy states it is necessary to use the rigid rotor eigenvalues and to obtain $\langle \cos^2 \theta \rangle_j$ by extrapolation of curves such as those in Figure 1. Even in the worst case for which calculations were made ($V_0 = 1.9$ kcal, 263°K) it was possible to account for 98.5% of the population before convergence was lost. The relatively good approximation method was therefore never applied to more than 1.5% of the population, so that the over-all error should

(24) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1944, p 358.

(25) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962).

(26) Program MATHIEU was obtained from Dr. Ann Tipton, then a postdoctoral associate of Dr. James Boggs of this department. It is essentially based upon a computational scheme recorded in the literature²⁷ and has been checked for accuracy against values obtained by other workers using various methods.^{28,29} We thank Professor Boggs and Dr. Tipton for their cooperation.

(27) D. R. Herschbach, "Tables for the Internal Rotation Problem," Department of Chemistry, Harvard University, Boston, Mass., 1957.

(28) G. Blanch and I. Rhodes, *Wash. Acad. Sci.*, **45**, 166 (1955).

(29) "Tables Relating to Mathieu Functions," Columbia University Press, New York, N. Y., 1951.

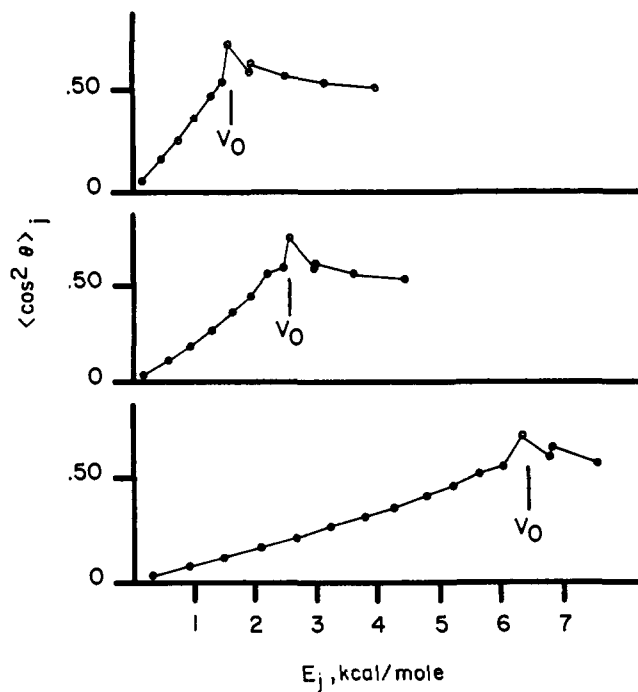


Figure 1.

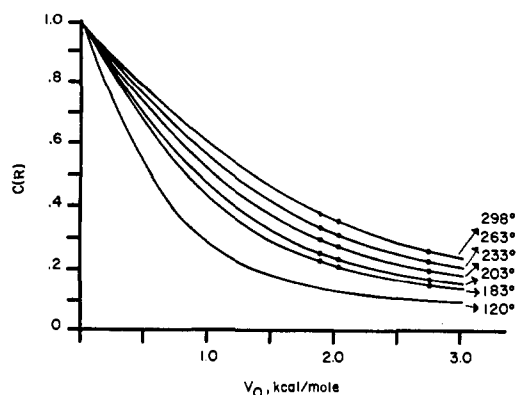


Figure 2.

be quite small. Higher barriers and lower temperatures are favorable to convergence.

Substituting these $\langle \cos^2 \theta \rangle_j$ and E_j into eq 4, it was possible to calculate $\langle \cos^2 \theta \rangle_{av}$ and, hence, $C(R) = 2 \langle \cos^2 \theta \rangle$. Some $C(R)$ vs. V_0 isotherms are shown in Figure 2. These are (somewhat surprisingly) in excellent agreement with $C(R)$ values calculated using a simple approximation method previously suggested by us,¹³ in which a continuum of states was assumed and the kinetic energy of internal rotation neglected. The points not explicitly drawn in Figure 2 were obtained in this way. Obviously, the results are essentially identical. Therefore, despite its lack of theoretical rigor, this much simpler procedure can be recommended, at least for the range of temperature and V_0 for which the correspondence has been verified (see Figure 2).

The measurement of a $C(R)$ value at a single temperature is thus sufficient to allow a determination of V_0 . However, for one radical, the p,p',p'' -tricyclopropyltrityl radical, a rather precise temperature dependence study of $C(R)$ was available, permitting a check of our calculations. Figure 3 is a plot of $C(R)$

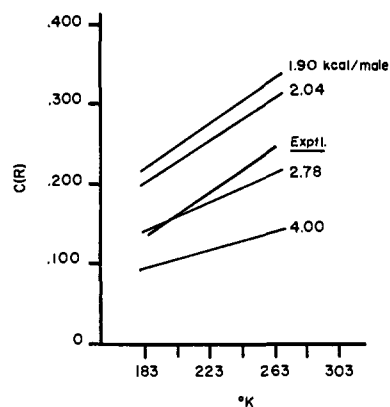


Figure 3.

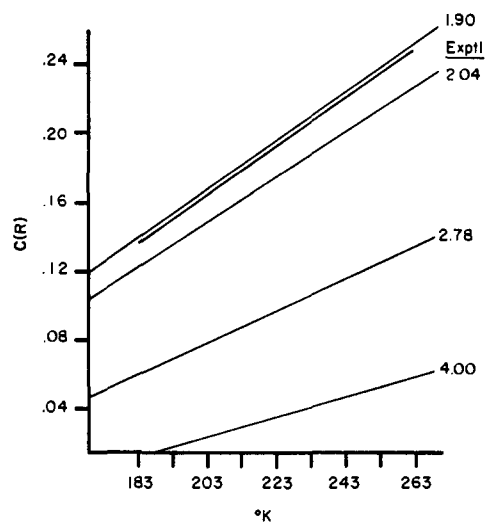


Figure 4.

vs. T for various V_0 ; the boldface line represents the experimental points. The agreement is rather alarmingly bad, despite the apparent rigor of the calculation. If, however, eq 2 is replaced by the more accurate eq 1, with $B_0/B_2 = -0.043$, excellent correspondence is achieved, with $V_0 = 1.91$ kcal/mol (Figure 4). In the case of a two parameter equation such as eq 1, the temperature dependencies do not constitute a check, but instead enable one to determine the parameter ratio. The observed ratio is quite reasonable in magnitude but is of opposite sign to those previously obtained.²² The B_0 term should be especially important in this system because, although it is indeed small compared to B_2 , it is not nearly so small in comparison to $B_2 \langle \cos^2 \theta \rangle_{av}$ where, as in the trityl system, $\langle \cos^2 \theta \rangle_{av}$ is small. Therefore, in systems where the B preference is large, it is especially advisable to replace eq 8 by eq 9. Thus, B_0 for the methyl group is still neglected. When more reliable values of $B_0^{CH_3}$ become available, a further small correction for this will be desirable.

$$C(R) = 2 \langle \cos^2 \theta \rangle_{av} \quad (8)$$

$$C(R) = a_\beta / a_\beta^{CH_3} = \frac{B_0 + B_2 \langle \cos^2 \theta \rangle_{av}}{B_0^{CH_3} + B_2 \langle \cos^2 \theta \rangle_{av}^{CH_3}} = \frac{2B_0/B_2 + 2 \langle \cos^2 \theta \rangle_{av}}{2} \quad (9)$$

Critique. Presumably, the theoretical $C(R)$ values, obtained as described above, are correct, but it is con-

ceivable that, through the use of some fallacious assumption(s), these might not correspond quantitatively with the experimental $C(R)$ (the qualitative conformational criterion seems well entrenched). One possible source of such a disparity is the following. The procedure assumes an assembly of radicals which do not interact with other molecules, such as solvent molecules or metal ions. Since the cyclopropyl group is by no means cylindrically symmetrical, an ambient solvent shell could superimpose its own conformational bias upon the inherent internal one and thus make a spurious, solvent-dependent contribution to V_0 . A small effect of this kind cannot be ruled out, but a contribution which we would consider to be seriously damaging to the accuracy of the V_0 's seems unlikely. This is especially true for the neutral radicals, which should not be strongly solvated. We are now investigating solvent effects on V_0 in anion radicals, and it appears that such effects are finite but small. The studies will be reported at a later date.

A second point to consider is the shape of the potential function for internal rotation (eq 10). This function

$$V = V_0 \cos^2 \theta \quad (10)$$

is appropriate for barriers of either conjugative or torsional origin, but may well be less satisfactory for those of steric origin. The calculations as applied to the phenalenyl, naphthalene, and anthracene systems may thus be criticized. The criticism is somewhat mollified by the fact that steric effects are relatively small, so that the steric potential function may not deviate too greatly from $\cos^2 \theta$, but rigor cannot be claimed for these systems. This applies especially to the former two systems, where there are two non-equivalent B forms and hence two barriers. The calculated V_0 must therefore be a compromise value and should be thought of as an index of the over-all conformational bias of the system.

The assumption of equal B_2 's and ρ_i 's for the cyclopropyl and methyl systems was brought out previously and supported. One final point should be made in this general connection, namely, that B_0 for the cyclopropyl group is probably not a constant, for reasons to be discussed later, but would be better represented by $B_0 \sin^2 \theta$. The V_0 are not affected dramatically by this, but it seems desirable to include a correction of this type. This was done approximately, by taking $\langle \cos^2 \theta \rangle_{av}$ as $1/2 C(R)$ and thus obtaining $\langle \sin^2 \theta \rangle_{av}$. The correction $2B_0 (\sin^2 \theta)$ was then applied to the experimental $C(R)$ values before reading V_0 from charts such as Figure 2. The corrections were not more than 0.1 kcal/mol.

Discussion

All of the experimental $C(R)$ and calculated V_0 values obtained in this work are assembled in Table VIII. The p,p',p'' -tricyclopropyltrityl radical has the symmetry appropriate to a twofold potential.³⁰ It is a neutral, nonpolar radical (minimum solvent and charge density effects, respectively), and B_0/B_2 was determined specifically for it (no approximate B_0 correction required). Therefore, the potential barrier, $V_0 = 1.91$ kcal, should be quite accurate (it seems unlikely to be in error by as much as 0.10 kcal) and should represent a

(30) The S conformation should have C_s symmetry.

Table VIII. Potential Barriers (V_0) of Various Radicals

Radical	V_0 , kcal
p,p',p'' -Tricyclopropyltrityl	+1.91
Cyclopropyltropylenyl	+1.5
1-Cyclopropylphenalenyl	+0.15
p,p' -Dicyclopropylbiphenyl	+0.58
Cyclopropyltropenide dianion	+0.60
p -Cyclopropylnitrobenzene	+1.64
1,4-Dicyclopropylnaphthalene	-1.00
9-Cyclopropylantracene anion	-1.25
9-Cyclopropylantracene cation	+1.12
Cyclopropyl phenyl ketyl	+2.22

true internal barrier. An essentially identical barrier was found for the monocyclopropyl derivative. The β hfs of the trimethyl derivative was, as expected, temperature independent (-10 to -90°). The B conformations of the cyclopropyl substituted radicals are thus appreciably preferred, and the V_0 value of 1.91 invites comparison with the 1.4-kcal barrier estimated for phenylcyclopropane.⁹ The difference could plausibly be ascribed to greater conjugative interaction of the cyclopropyl group with a trigonal carbon having radical character than with one not having net spin density. However, the uncertainty in the phenylcyclopropane barrier appears to be rather large, so that we are not inclined to emphasize the disparity. It is pertinent that $\rho_i \approx 0.11$ at the *para* carbon of the trityl radicals, *i.e.*, the spin density is far from a full unit. As a result the radical stabilizing effect of cyclopropyl and its conformational concomitants may not be as dramatic here as for, say, the cyclopropylcarbiny radical. The B conformation is also preferred, apparently, in the tricyclopropyltrityl cation, but the barrier is not known.³¹

The cyclopropyltropylenyl (neutral) radical shows a similar, $V_0 = 1.5$ kcal, B preference, but a few additional remarks about $C(R)$ are appropriate in this case. To the Hückel approximation, the odd electron of the tropylenyl radical is considered to enter either of a degenerate pair of antibonding MO's. However, in a substituted tropylenyl radical the degeneracy is lifted, and, unlike the other radicals of this study, even an alkyl group modifies the spin distribution drastically away from that of the parent. A corollary effect is that the cyclopropyl and methyl groups are more sensitively distinguished, in terms of spin density distribution, than in the other systems. Hence the assumption of equal ρ_i for the two substituted radicals loses some validity. This can be shown and corrected for as follows. The total α hfs in the parent tropylenyl radical, from the seven equivalent ring protons, is 25.34 G at 190° . The total splitting of all six ring protons in the cyclopropyltropylenyl radical at this temperature is 22.76 G. The equivalent, in spin density of the remaining 2.58 G, must reside primarily at the remaining ring carbon (*i*), to which the cyclopropyl group is attached. In the same way, $\rho_i = 1.94$ G is estimated for the methyltropylenyl case. It should now be apparent that cyclopropyl substitution does give rise to a different spin distribution than does methyl substitution in this system, in particular with the former being less electron repelling than the latter. The disparate ring splittings also provide confirmation of the different spin distributions in the two

(31) T. Sharpe and J. C. Martin, *J. Amer. Chem. Soc.*, **88**, 1815 (1966).

cases. Fortunately, $C(R)$ can still be found. In fact, because the actual ratio of the ρ_i 's is now known, it becomes unnecessary to assume this ratio to be unity. It is conceded that part of the defect spin densities used above actually resides on the substituent group, but this should be a relatively small fraction of ρ_i and, in any case, roughly proportional to it.

In this manner, the barrier $V_0 = 1.5$ kcal was found, which is pleasingly similar to the trityl barrier. That it is slightly smaller than the latter might have been anticipated for two reasons. First, ρ_i (2.54 G) is slightly smaller than for the trityl case (3.0 G). Second, steric or torsional effects might be slightly larger in the tropanyl system, in which the internal C-C angles are spread more than in a phenyl ring. As mentioned earlier, the tropanyl system is nonalternant and hence not necessarily nonpolar. In fact, the ρ_i calculation mentioned above can be used to show that $q_i \geq +0.04$. The polarity is thus rather small and, even though it may influence V_0 somewhat, the effect should be to increase rather than decrease it.

Standing in vivid contrast to these results are those for the phenalenyl system. The barrier here is only $V_0 = 0.15$ kcal. The absence of a perceptible temperature dependence of the hfs corroborates a very small barrier. Since the radical is neutral and essentially nonpolar, the dissimilarity to the trityl results cannot be a charge density effect nor, since $\rho_i \approx 0.22$, can it be attributed to diminished conjugation resulting from a smaller ρ_i . Apparently, one must invoke *peri* steric repulsions in the B conformations, which almost nullify the inherent, presumably conjugatively based, B preference already established in the two previous, unhindered, cases. A steric effect of *ca.* 1.7–1.8 kcal would be sufficient, assuming the conjugative effect to be equal to that in the trityl series. This seems to be in the right neighborhood for such a *peri* interaction.³² Models indicate that the S conformation would be much freer of steric repulsions than the B conformations. The phenalenyl system is, incidentally, one of those in which the assumption of a twofold barrier is inappropriate, and the cited V_0 value is therefore less meaningful than for the trityl and tropanyl cases.

Comparison of these three sets of results with those for the anionic radicals helps illuminate the effect of charge density on V_0 and provides further evidence to support the proposals concerning *peri* steric effects. Before discussing these results, however, a brief commentary on the methods used to estimate q_i seems desirable. For the alternant hydrocarbon ion radicals (the biphenyl, naphthalene, and anthracene radicals) the approximation $q_i \approx \rho_i$ should be moderately good. The ρ_i , in turn, are calculable from their McConnell-Weissman proportionality to the β hfs of the corresponding methyl derivative. The assumption, implicit in the above, that all of the excess charge density can be attributed to the singly occupied MO, while appropriate for alternant hydrocarbon systems, is worse for nonalternant ones or heteroatom-containing systems. Several different procedures were followed. For the cyclopropyl tropanyl dianion radical, correction was made for contributions to q_i from filled MO's by estimating q_i for the tropanyl anion and then adding this

to the q_i contribution from the odd electron in the dianion radical. The latter was obtained through its proportionality to the β hfs of the methyl derivative, *via* ρ_i . The former can be estimated roughly by subtracting ρ_i for the cyclopropyl tropanyl radical from the q_i already calculated for the latter radical. The correction is, fortunately, small in comparison to the odd electron contribution. Similarly, in the nitrobenzene case, q_{para} was estimated for nitrobenzene itself, and this closed shell contribution added to the open shell ($q_i \approx \rho_i$) one. For the ketyl case, an HMO calculation had to suffice. These q_i are therefore, emphatically, estimates, but are probably correct to within $\pm 25\%$.

The *p,p'*-dicyclopropylbiphenyl anion radical has $V_0 = 0.58$ kcal, still reflecting a B preference, but one which is considerably dampened in comparison to the trityl series, which is sterically comparable. Negative charge obviously attenuates the B preference rather powerfully ($q_i \approx -0.20$). For the cyclopropyl tropanyl dianion radical, V_0 is very similar to that in the biphenyl series ($V_0 = 0.60$ kcal) and a good deal smaller than for the neutral cyclopropyl tropanyl radical, both of which results should be expected. The barrier for the *p*-cyclopropylnitrobenzene anion radical ($V_0 = 1.64$) is also less than in the trityl series, but, as might be expected from its relatively small q_i (-0.05 to -0.10), the reduction is considerably less than for the previous two anionic hydrocarbon radicals.

The 1,4-dicyclopropylnaphthalene and 9-cyclopropylanthracene anion radicals actually have S preferences ($V_0 = -1.00$ and -1.25 , respectively), and are the first such instances to be recognized. Undoubtedly, *peri* steric effects are at work again. The 1,4-dicyclopropylnaphthalene anion radical and the 1-cyclopropylphenalenyl radical should have very similar *peri* steric effects. Assuming $V_0 = V(\text{steric}) + V(\text{conj})$ and using $V(\text{steric}) = -1.75$ from the phenalenyl series and $V_0 = -1.00$, one finds $V(\text{conj}) = +0.75$, *i.e.*, a small bisected preference of about the same size as for the unhindered anionic radicals (biphenyl anion radical and tropanyl dianion radical). The mutual consistency of these results lends additional credence to the suggested interpretations. It is interesting that a *peri* steric repulsion overwhelms the conjugative effect in an anionic radical, thus producing an S preference, but just about cancels the larger conjugative effect in a neutral radical, leading to only a very small net conformational bias.

The effect of charge on the magnitude of the conjugative interaction is further evident from a comparison of the data for the 9-cyclopropylanthracene cation radical with those for the corresponding anion radical, which radicals should have at least similar steric effects. The cation has a B preference ($V_0 = 1.12$ kcal) in contrast to the S preference ($V_0 = -1.25$) of the anion. The difference (2.37 kcal) should represent the difference in conjugative contributions to the two barriers. Using $V(\text{conj})$ for the 1,4-dicyclopropylnaphthalene anion radical (-0.75 kcal) as an estimate of $V(\text{conj})$ for the 9-cyclopropylanthracene anion radical, the value $V(\text{conj}) = +3.12$ emerges for the cation radical, a larger number than for any of the anionic or neutral cases. The *peri* steric effect which dominated $V(\text{conj})$ in the anion radical is, in turn, dominated by the larger conjugative interaction in the cation radical.

The final radical, cyclopropyl phenyl ketyl has $V_0 =$

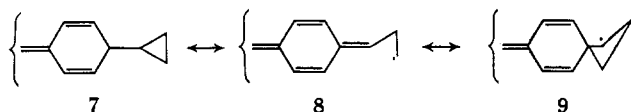
(32) J. Packer, J. Vaughan, and E. Wong, *J. Amer. Chem. Soc.*, **80**, 905 (1958).

2.22 kcal, which is not far from those of the unhindered, neutral radicals. This seems not unreasonable in view of the very small estimated q_i (-0.05) in this system. It should be noted that here and in the naphthalene anion radical case the twofold potential assumed in our calculations is lacking, and V_0 is merely an index of the over-all B or S preference and cannot be associated, accurately, with a particular B conformation.

These results establish a connection between V_0 and q_i , especially when appropriate consideration is given to steric effects and the ρ_i factor. It is of passing interest that a plot of q_i vs. V_0 for the unhindered radicals is roughly linear. No doubt a more complete plot will show curvature. It would be interesting to have some points in the vicinity of $q_i = +0.50$ and for large negative q_i . In the latter region it is, e.g., not clear whether the cyclopropylcarbinyl anion would simply have no conformational preference, or whether, as an extrapolation of our plot might suggest, it would have an S preference, in dramatic contrast to the corresponding cation. We have already mentioned the possibility that anionic cyclopropyl conjugation may preferentially occur through the internal (Walsh) cyclopropane orbitals, thus leading to an S bias, unlike cationic conjugation, which employs the peripheral Walsh orbitals and has a B preference.

Throughout this paper it has been assumed that B preferences are indicative of conjugative interactions. Although definite experimental proof is lacking, the following arguments rather strongly support this assumption. Steric effects can be discarded, it would appear, based upon the S proclivity engendered by *peri* steric interactions in the several examples discussed above. A conventional application of torsional considerations also predicts an S preference. No doubt the unorthodox nature of cyclopropane's bonding vitiates the accuracy of such a calculation, but it appears to be impossible to envision any reasonable calculation which would suggest a B preference based upon torsion. By elimination, conjugative effects are implicated.

γ Hfs. The temperature dependence of the γ hyperfine splittings of the cyclopropyl methylenes in the *p,p',p''*-tricyclopropyltrityl radical (Table I) sheds some further light on the problem. Unlike the β hfs, the γ hfs increase as the temperature is lowered and the bisected conformation becomes more highly populated. This is nicely consistent with the notion that conjugation is more efficient in the B conformation, which process increases the spin density on the γ carbon through cyclopropyl carbinyl \leftrightarrow allyl carbinyl radical resonance of the type shown in 7 and 8. Evidence for the contribution of cyclobutyl radical canonical forms is also



available in the negative B_0/B_2 value obtained for the tricyclopropyltrityl radical, which stands in contrast to the positive values mentioned for ordinary alkyl groups. Structure 9 "explains" the presence of positive spin density at the tertiary cyclopropyl carbon which, in the accustomed manner for α splittings, results in negative spin density at the attached proton.

These data indicate why we have assumed B_0 to be orientation dependent, but instead prefer to use B_0

$\langle \sin^2 \theta \rangle_{av}$ as the lead term in eq 1 when the cyclopropyl group is involved. Contributions from 9 should be maximized in the bisected form, which is presumed to be the most efficiently conjugating form of cyclopropyl. Ultimately, it appears likely that an even more complex expression, probably of the form $B_0' + B_0 \langle \sin^2 \theta \rangle_{av}$ will have to be used. This would allow for the σ - π polarization effect of a normal alkyl group (positive B_0'), as well as the special conjugative mechanism available to the cyclopropyl group as described above (negative B_0). Again, more reliable B_0 values for alkyl groups seem desirable.

Summary. The time average values of $\cos^2 \theta$ can be calculated as a function of V_0 , the potential barrier to internal rotation. The calculation is quantum mechanically rigorous in that it does not assume idealized harmonic oscillator or rigid rotor states, but uses actual torsional states. However, the actual values of V_0 may be in error by as much as a few tenths of a kilocalorie because of uncertainties in the relationship between the calculated quantity $\langle \cos^2 \theta \rangle_{av}$ and the experimental quantity $C(R)$. These uncertainties derive mainly from the circumstance that $B_0^{CH_3}$ is not known with any certainty (in our opinion) and from the possibility of small solvent perturbations of V_0 . Nevertheless, several significant conclusions may be safely drawn (i) in sterically unencumbered situations the cyclopropyl group has a substantial preference for the bisected conformation, (ii) this preference is rather potently accentuated by positive and attenuated by negative charge, and (iii) *peri* and larger steric repulsions tend to cause an S preference, especially in anionic radicals where the inherent B preference is rather feeble. Further, we posit that reliable B_0 values can be obtained using our theoretical approach in conjunction with temperature dependence endor studies. Finally, evidence has been gathered that cyclopropylcarbinyl \leftrightarrow cyclobutyl \leftrightarrow allyl carbinyl radical resonance is real in terms of spin distribution and the orientation dependence thereof.

Experimental Section

Melting and boiling points are uncorrected. Elemental analyses were performed mainly by the Galbraith Laboratories, Knoxville, Tenn. Nmr spectra were obtained on a Varian A-60 spectrometer, and esr spectra on a Varian Model V-4502 X-band spectrometer. The endor unit was in the laboratories of Varian Associates, Analytical Instrument Division, Palo Alto, Calif. Calculations employed CDC 1604 and 6600 computers at the U.T. Computation Center. The radicals were generated using conventional vacuum line techniques.

***p*-Bromocyclopropylbenzene.** 3-*p*-Bromophenyl-2-pyrazoline (107.5 g)³³ was thoroughly admixed with 100 g of anhydrous, powdered K_2HPO_4 in a 500-ml 1-neck round-bottomed flask, which was then fitted with a microstill having a Vigreux fractionating column. Without stirring the reaction mixture, the flask was heated slowly in an oil bath, while N_2 was passed through the still. During a 20-min period, 61.5 g (71%) of *p*-bromocyclopropylbenzene distilled, bp 235–239°. Chromatography on alumina gave a colorless liquid: mp 14°; nmr (CCl_4) τ 2.73, 3.20 (AB quartet, 4 H, $J = 9$ Hz), 8.3 (m, 1 H, methine), 9.3 (m, 4 H, methylenes).

Tri(*p*-cyclopropylphenyl)methanol. To an ethereal solution of the Grignard reagent of *p*-bromophenylcyclopropane was added a 0.25 M quantity of diethylcarbonate. The reaction mixture was refluxed for 1.5 hr and then treated with saturated aqueous ammonium chloride. The usual work-up, followed by recrystallization from hexane, gave colorless crystals: mp 98° (92%); nmr (CCl_4) τ 3.05 (m, 12 H, aryl), 7.60 (s, 1 H, OH), 8.20 (m, 3 H, methines), and 9.25 (m, 12 H, CH_2); mass spectrum m/e 380 (P).

(33) J. Smejkal, J. Jonas, and J. Farkas, *Collect. Czech. Chem. Commun.*, **29**, 2950 (1964).

Anal. Calcd for $C_{23}H_{28}O$: C, 88.38; H, 7.42. Found: C, 88.18; H, 7.44.

***p*-Cyclopropylphenyldiphenylmethanol.** A Grignard reagent was prepared from 0.025 mol of *p*-bromocyclopropylbenzene and 0.024 mol of Mg in 20 ml of ether. Over an interval of 10 min, 0.022 mol of benzophenone in 30 ml of benzene was added to the foregoing. After stirring *ca.* 20 min, the mixture was poured into a cold solution of 2 *N* H_2SO_4 and stirred 20 min more. The ether layer was worked up in the usual way and the solid residue chromatographed on alumina, using hexane, 30% benzene, 70% benzene, benzene, and 30% chloroform eluents. The first two solvents eluted 0.180 g of thin plates, which were identified as *p,p'*-dicyclopropylbiphenyl: mp 125–127° (lit.³⁴ 127.5–128°); ir, no carbonyl or hydroxyl stretch; nmr (CCl_4) λ 2.75 (AB quartet, 8 H, 9.0 Hz, aryls), 8.15 (m, 2 H, methines), 9.1 (m, 8 H, CH_2); mass spectrum *m/e* 234 (P). The benzene fraction yielded 3.2 g of the white solid carbinol: 71–73.5° (hexane); ir (CCl_4) free hydroxyl stretch; nmr ($CDCl_3$) τ 2.74 (s, 10 H, phenyls), 2.95 (m, 4 H, aryls), 7.26 (s, 1 H, OH), 8.2 (m, 1 H, methine), and 9.2 (m, 4 H, CH_2); mass spectrum *m/e* 300 (P).

Anal. Calcd for $C_{22}H_{28}O$: C, 87.96; H, 6.71. Found: C, 87.97; H, 6.74.

Tris(*p*-tolyl)methanol. This carbinol was prepared from the Grignard reagent of *p*-bromotoluene and diethylcarbonate by the same procedure followed in the preparation of tri(*p*-cyclopropylphenyl)methanol. The yield was 91%: mp 94–95° (lit.³⁵ 93–94°).

***p*-Tolyldiphenylmethanol.** A Grignard reagent was made from 0.60 g of Mg and 3.42 g of *p*-bromotoluene in 50 ml of ether. To this was added 2.7 g of benzophenone in ether. The usual work-up gave 3.6 g (86%) of the carbinol: mp 74–74.5° (hexane) (lit.³⁶ 73–74°).

Triarylmethyl Chlorides (3a–d). All of the chlorides were prepared according to reference 37. Acetyl chloride (2 ml) was added to 1 g of the carbinol in 1 ml of benzene. The solution was refluxed for 15 min in a 10-ml flask under a N_2 atmosphere. Two volumes of pentane was added, and the solution was cooled to *ca.* 6° to precipitate the chlorides. All gave satisfactory nmr spectra. The melting points were as follows: 3a, mp 149–151° dec; 3b, mp 181° dec (lit.³⁸ 181°); 3c, mp 78–80°; 3d, mp 98–99° (lit.³⁹ 98–99°).

Anal. (3a) Calcd for $C_{28}H_{27}Cl$: C, 84.28; H, 6.82. Found: C, 84.58; H, 6.76.

Anal. (3c) Calcd for $C_{22}H_{19}Cl$: C, 82.87; H, 6.01. Found: C, 82.87; H, 5.95.

Preparation of the Trityl Radicals. The appropriate substituted trityl chloride, zinc dust, and a stirring bar were placed in a reaction vessel on a vacuum line. Degassed toluene was then distilled into the reaction vessel and the resulting solutions allowed to warm to room temperature while being stirred. ESR samples were tipped into one of four 4-mm (o.d.) side-arm tubes, which was then melted off, sealed, and stored in liquid N_2 until time for the ESR measurements. Samples for the endor experiments were prepared similarly, except that quartz side-arm tubes were used instead of the usual Pyrex ones, and the toluene was stored over PbO_2 on the vacuum line after degassing.

1-Cyclopropylphenalan-1-ol. An ethereal solution of cyclopropyl-lithium was prepared by adding 2.4 g (20 mmol) of cyclopropyl bromide to 0.35 g (50 mmol) of cut lithium wire in 25 ml of anhydrous ether and refluxing for 1 hr. To this solution, maintained at 0°, was added an ethereal solution of 1.8 g (10 mmol) of phenalan-1-ol.⁴⁰ Aqueous work-up and ether extraction gave 1.7 g (75%) of the crude carbinol, which was not purified, but carried over directly to the next step.

Cyclopropylphenalene Isomers. The crude carbinol (2.0 g) was dissolved in 6 ml of pyridine in a 25-ml 1-neck round-bottomed flask, the solution was cooled to 0°, and 0.75 g of $POCl_3$ in 3 ml of pyridine was slowly added to it. The mixture was stirred at 0° for 3 hr, let in the freezer 16 hr, and finally refluxed for 1.5 hr. Ether was then added, and the organic phase was washed several times. Evaporation of the solvent to dryness, followed by florisil chromatography (hexane elution), yielded 1.0 g (70%) of the isomeric

cyclopropylphenalenes. The nmr spectrum indicated the presence of at least two position isomers: mass spectrum *m/e* 206 (P), 205 (P–H), and 165 (P-cyclopropyl).

Anal. Calcd for $C_{16}H_{14}$: C, 93.11; H, 6.89. Found: C, 92.91; H, 6.83.

1-Methylphenalan-1-ol. Arapahoe 3 *M* ethereal methylmagnesium bromide (66 mmol, 22 ml) was placed in a 250-ml 3-necked flask and cooled to 0°. A solution of 6.0 g of phenalanone (33 mmol) in 80 ml of ether was added dropwise to this. Aqueous work-up yielded a yellow oil, which was recrystallized from hexane to give 5.0 g (75%) of the carbinol as pale yellow crystals: mp 74–76° (lit.⁴⁰ 74.6–76.1°); nmr (CCl_4) τ 2.7 (m, 6 H, aryl), 6.95 (t, 2 H, $J = 6.5$ Hz, 3- CH_2), 7.69 (s, 1 H, OH), 8.09 (t, 2 H, $J = 6.5$ Hz, 2- CH_2), and 8.59 (s, 3 H, CH_3).

Methylphenalene. Two grams of the above carbinol was dehydrated exactly as in the cyclopropylphenalene case. Florisil chromatography yielded 1.5 g (64%) of nearly colorless plates: mp 52–56°; nmr showed a mixture of position isomers; mass spectrum *m/e* 180 (P), 179 (P–H), and 165 (P- CH_3).

Anal. Calcd for $C_{14}H_{12}$: C, 93.23; H, 6.77. Found: C, 93.14; H, 6.80.

Preparation of Phenalenyl Radicals. The following method was shown to work well for the parent phenalenyl radical and was used both substituted phenalenyl radicals. The appropriate phenalene, excess sodium methoxide, and a stirring bar were placed in the usual reaction vessel on a vacuum line, and sufficient solvent was distilled into the vessel to form a 10^{-3} *M* solution. After stirring the mixture for a few minutes at room temperature, a small amount of air was admitted to the line. The blue-green solutions of the radical thus formed were tipped into ESR tubes and sealed off as described before.

7-Cyclopropylcycloheptatriene. Finely cut lithium metal (3.1 g) was suspended in 300 ml of anhydrous ether. To this, 18 g of cyclopropyl bromide in 20 ml of ether was added by dropping funnel. Refluxing was continued for 20 min after the exotherm was complete. Tropenylm fluoroborate (17.8 g, 0.10 mol) was then added during a 20-min period, followed by another reflux period, this time of 10 hr. After that, the mixture was filtered, the filtrate was poured into 300 ml of water, and the ether layer worked up as usual. Distillation gave 9 g (70%) of a clear, colorless liquid: bp 38–40° (0.1 mm); nmr (CCl_4) τ 3.4–4.7 (m, 6 H, tropanyl ring protons), 8.9 (m, 2 H, methines), 9.7 (m, 4 H, CH_2); mass spectrum *m/e* 132 (P).

Cyclopropyltropenylm Fluoroborate. To 17 g (50 mmol) of trityl fluoroborate dissolved in 30 ml of dry acetonitrile was added 6.6 g (50 mmol) of 7-cyclopropylcycloheptatriene in 10 ml of acetonitrile, the addition being made *via* dropping funnel, over a 15 min period. After the addition was complete (mild exotherm), the reaction mixture was stirred 2 more hr at room temperature. The solvent was then evaporated, and the residue was extracted with two 200-ml portions of dry ether. The ether-insoluble, pale orange solid was recrystallized from acetonitrile–ethyl acetate (1:4), giving 4.5 g (45%) of fairly pure (nmr) crystals. For purposes of characterization, purer samples were prepared by two further recrystallizations. The pale yellow crystals rather rapidly acquired a greenish cast while standing exposed to air: nmr (D_2O) τ 1.12 (m, 6 H), 7.2 (m, 1 H, methine), and 7.9–8.6 (m, 4 H, CH_2).

Anal. Calcd for $C_{10}H_{11}BF_4$: C, 55.10; H, 5.10; B, 5.10. Found: C, 55.20; H, 5.10; B, 4.34.

Cyclopropyltropenyl Dimers. Cyclopropyltropenylm fluoroborate (4.4 g, 20 mmol) was dissolved in 80 ml of water. Zinc dust (1.2 g, excess) was added, and the mixture was stirred vigorously for 0.5 hr (exotherm). Thereupon, 100 ml of pentane was added and the mixture was stirred 0.3 hr more. Work-up of the pentane layer in the usual way, followed by alumina chromatography (hexane eluent) yielded 2.2 g (80%) of a colorless oil, which could not be induced to crystallize: nmr (CCl_4) was consistent with a mixture of the desired position isomers; mass spectrum *m/e* 262 (P) and 131 (monomer).

Anal. Calcd for $C_{20}H_{22}$: C, 91.60; H, 8.40. Found: C, 91.68; H, 8.35.

Methyltropenyl Dimers. The mixture of position isomers of this dimer was prepared exactly as in the cyclopropyltropenyl instance. Once more, the nmr spectrum indicated a mixture of isomers; mass spectrum *m/e* 210 (P), 105 (monomer).

Anal. Calcd for $C_{18}H_{18}$: C, 91.43; H, 8.57. Found: C, 90.86; H, 7.95.

Preparation of Samples and Generation of the Substituted Tropanyl Radicals. The neat, oily dimer was warmed to *ca.* 60° and poured into a 4-mm (i.d.) Pyrex tube joined to a vacuum stopcock with ground glass joint to form a *ca.* 2-in. column of dimer. The

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"reaction vessel" was then attached to the vacuum line and degassed (freeze-thaw) several times. Finally, the vacuum line was filled with dry N₂ and the esr tube melted off and sealed.

Isomeric Cyclopropyltropylenyl Methyl Ethers. To the crude cyclopropyltropylenium fluoroborate salt from 6.6 g of cyclopropylcycloheptatriene dissolved in dry methanol and cooled to -70° was added a solution of 5.0 g (excess) of sodium methoxide in methanol. The solution was allowed to warm to room temperature and then stirred an additional 0.5 hr, whereupon the product was watered out and taken up in ether. Work-up and vacuum distillation gave a colorless oil: bp 50–53° (0.5 mm); nmr (CCl₄) τ 3.4–4.6 (m, 5 H), 6.65 (s, 3 H, CH₃), 6.8 (m, *ca.* 1 H, CHOMe), 8.3 (m, 1 H, cyclopropyl methine), and 9.2 (m, 4 H, CH₂); mass spectrum *m/e* 162 (P), 161 (P-H), 147 (P-CH₃), and 131 (P-OCH₃).

Cyclopropyltropylenide Dianion Radical. This radical proved unstable above *ca.* -100° and could not be prepared in THF or DME. Use of dimethyl ether as the solvent, which allowed the radical to be generated at or below -130°, did lead to the desired species. Both the disodium and dipotassium salts were made and each dianion radical showed the expected splittings from two metal ions. Aside from the solvent and temperature changes, the procedure was as described for the parent tropylenide dianion radical, using the isomeric mixture of methyl ethers as the dianion radical precursor.¹⁷

Methyltropylenide Dianion Radical. This dianion radical was not so unstable as the cyclopropyl derivative and so was prepared in the more orthodox manner, using THF and Na.

1,4-Dicyclopropyl-naphthalene. Cyclopropyllithium (88 mmol) in diethyl ether was added to *cis*-2,3,5,8,9,10-hexahydro-1,4-naphthoquinone (5.8 g, 35 mmol) in 20 ml of dry THF. After stirring 3 hr, 50 ml of ice-water was cautiously added. Work-up gave an oil which was then chromatographed on alumina. The fraction eluted with benzene-Skellysolve B (1:4) was a yellow solid: ir (CHCl₃) no carbonyl stretch, strong OH stretch; nmr (CDCl₃) τ 3.8 (m, 2 H), 7.0–8.5 (m, *ca.* 10 H), 8.7 (m, *ca.* 2 H, cyclopropyl methines), and 9.3 (m, 8 H, cyclopropyl CH₂). A mixture of the *cis* and *trans* diols was indicated.

The crude diol (1.9 g, 7.7 mmol) was treated with POCl₃ (1.4 g, 9.1 mmol) in 10 ml of pyridine and allowed to react for 3 hr at 0°. The solution was then refluxed 0.3 hr and cooled and poured into ice-dilute HCl. Ether extraction and work-up gave 0.90 g of a colorless oil having no ir hydroxyl stretch.

The crude triene (600 mg, 2.9 mmol) was dehydrogenated without further purification by refluxing it for 12 hr with DDQ in 20 ml of

benzene. Evaporation of the solvent, extraction of the residue with Skellysolve B, and evaporation of the latter solvent left an oil, alumina chromatography of which yielded 500 mg of 1,4-dicyclopropyl-naphthalene in the Skellysolve B eluate: nmr (CCl₄) τ 2.1 (A₂B₂, 4 H), 2.94 (s, 2 H), 7.8 (m, 2 H, methines), and 9.1 (m, 8 H, CH₂); mass spectrum *m/e* 208 (P).

9-Cyclopropylanthracene. An ethereal solution of a cyclopropyl Grignard reagent was prepared from 4.9 g (40 mmol) of cyclopropyl bromide and 1.5 g (63 mg-atom) of Mg in 50 ml of ether. A solution of 7.0 g (36 mmol) of anthrone in 60 ml of benzene was slowly added to the Grignard solution. After the exotherm subsided, the mixture was heated under reflux for about 1 hr. It was then cooled, poured into an ice-dilute HCl slurry and stirred 0.5 hr to dissolve the salts. The usual work-up gave 4 g of a yellow residue, which was chromatographed on alumina. Elution with Skellysolve B yielded 1.6 g (22%) of pale yellow 9-cyclopropylanthracene. Two recrystallizations from methanol gave 0.75 g of colorless prisms: mp 133–134.7°; nmr (CDCl₃) τ 1.3 (m, 2 H, 1 and 8 protons), 1.75 (s, 1 H, 10 H), 2.1 (m, 2 H, 4 and 5 H), 2.55 (m, 4 H), 7.6 (m, 1 H, cyclopropyl methine), 9.1 (m, 2 H, CH₂); mass spectrum *m/e* 218 (P).

Phenylcyclopropyl Ketone- α -d. Ten millimoles of the commercially available (Aldrich) ketone was mixed with 6.5 ml of D₂O, 1.0 g of potassium *t*-butoxide, and 10 ml of DME and heated under reflux in a N₂ atmosphere for 7 days. Ether and water were then added and the product worked up in the usual way. Nmr spectra indicated exchange to be 95% complete. The process is much slower than with, *e.g.*, phenyl isopropyl ketone, in which case exchange was essentially complete in less than 1 day.

***p*-Cyclopropylnitrobenzene.** Preparation was by nitration of phenylcyclopropane.⁴¹ The *o* and *p* isomers were separated on a 20-ft vpc column (silicone on Chromosorb W) at 180°.

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