0.01 *M* $AgClO_4$ couple is an excellent reference electrode for nonaqueous electrochemistry. When it is linked through a 0.1 *M* tetraethylammonium picrate salt bridge to other electrodes in various solvents, a host of electrochemical measurements, meaningful within the framework of the assumption, are possible.

We therefore recommend that the following extrathermodynamic assumption be considered. *There is a negligible liquid junction potential in a cell composed of silver wires in 0.01 M silver perchlorate solutions in two solvents connected by a bridge of 0.1 M tetraethylammonium picrate in that solvent of the pair which is the weaker solvator of silver cations.* We note that further work is required before this assumption can be accepted with confidence for aqueous solutions. Our interpretation of "negligible" is ±20 mV.[24]

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(24) NOTE ADDED IN PROOF Recent work by I. M. Kolthoff and M. K. Chantooni [*Anal. Chem.*, **44**, 194 (1972); *J. Amer. Chem. Soc.*, **93**, 7104 (1971)] has convinced us that the solubility product of $AgBPh_4$ is 14.4 in methanol and 17.2 in water, and of Ph_4AsBPh_4 is 17.3 in water. Thus values in Tables I, II, and VIII must be adjusted accordingly. Most important is the new value of 3.7 in Table VIII for transfer of Ag^+ from acetonitrile to water by the $Ph_4As^+ = Ph_4B^-$ assumption. This new value substantially changes our reservations about the assumptions of group I, insofar as they are applied to aqueous solutions. Our discussion should be read with the new values in mind. We are now confident that the all-important log γ_{Ag^+} for transfer from acetonitrile to water at 25° lies between 3 and 4 and that the value of 6.1 given by the ferrocene assumption is misleading. We thank Professor Kolthoff for communicating with us prior to publication of his papers.

A Quantitative Analysis of Cyclopropyl β Hyperfine Splittings[1]

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Abstract: The 4-(2-cyclopropyl-1-ethynyl)nitrobenzene anion radical and the (2-cyclopropyl-1-ethynyl)tropenyl radical, two π radicals having the cyclopropyl group attached to digonal carbon, have been synthesized and studied by esr spectroscopy. The corresponding methyl analogs were also synthesized and shown to have essentially equivalent spin distributions. The isopropyl analog was also prepared in the first, anion radical, series. Small, but appreciable, differences in spin densities (hfs) are observed for this anion radical in comparison to its methyl and cyclopropyl relatives. The esr data show that the cyclopropyl methine β hfs are smaller by factors of 0.83 and 0.77, in the anion radical and radical cases, respectively, than the methyl hfs even though the spin distributions are closely similar. These ratios are used, in conjunction with data previously collected, to calculate the explicit equation relating cyclopropyl β hfs to dihedral angle. This equation can be used to obtain cyclopropyl rotational barriers from a single esr measurement. A three-term equation for cyclopropyl β hfs involving (1) hyperconjugative, (2) cyclopropyl–cyclobutyl conjugative, and (3) σ electron spin transmission mechanisms has been further substantiated and the respective contributions of these various mechanisms calculated as a function of dihedral angle.

Esr hyperfine splittings (hfs) of the β type have found increasingly frequent use in the conformational analysis of radicals because of their pronounced orientation dependence.[3–7] Most analyses have used the simple form of eq 1 for the conformation dependence. According to this, the hfs (a_H) of a β proton is directly proportional to the spin density, ρ_α, at the α carbon and to $\langle\cos^2\theta\rangle_{av}$, where θ is the dihedral angle between the C_β–H bond and the relevant p orbital on C_α. However, eq 2 is more accurate.[8] It contains, in addition, a conformation-independent term $B_0\rho_\alpha$ representing, in part, spin transmission through the σ bonds. Evidence is available that the $B_0\rho_\alpha$ term is by no means negligible in general.[9]

$$a_H = B_2\langle\cos^2\theta\rangle_{av}\rho_\alpha \qquad (1)$$

$$a_H = [B_0 + B_2\langle\cos^2\theta\rangle_{av}]\rho_\alpha \qquad (2)$$

Availability of a methyl analog ($CH_3\dot{C}<$) to the pertinent system ($R\dot{C}<$) greatly facilitates the analysis, since $\langle\cos^2\theta\rangle_{av}$ is 0.500 for a rapidly rotating cylindrically symmetrical group and since ρ_α is often essentially identical for the two radicals. A conformational index C(R) has been defined as in the first segment of eq 3.[7] Application of eq 2 and cancellation of ρ_α lead to the right-hand side. If, instead, eq 1 is used the simplified relation of eq 4 results. The final form of eq 4 also requires the assumption of equal B_2's for R and CH_3. If one is willing to make all of these assumptions, the experimental C(R) values can be translated quite simply

$$C(R) = a_H(R)/a_H(CH_3) = [B_0(R) + B_2(R)\langle\cos^2\theta\rangle_{av}{}^R]/[B_0(CH_3) + B_2(CH_3)0.500] \qquad (3)$$

$$C(R) = a_H(R)/a_H(CH_3) = B_2(R)\langle\cos^2\theta\rangle_{av}{}^R/0.500B_2(CH_3) = 2\langle\cos^2\theta\rangle_{av}{}^R \qquad (4)$$

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(1) This research was supported by the Welch Foundation, Grant F-149.

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into a quantitative criterion of conformation, *viz.*, $\langle \cos^2 \theta \rangle_{av}^{R}$. For more quantitative work, *e.g.*, calculation of the barrier height, V_0, one has to calculate $\langle \cos^2\theta \rangle_{av}$ for various barriers until the experimental value of $\langle \cos^2\theta \rangle_{av}$ is matched. Calculations of essentially this kind, using eq 4 and approximated, *e.g.*, harmonic oscillator and/or rigid rotor, ψ's and E's have been reported.[3,6] As yet no wholly rigorous applications of eq 3 have been published, although an intermediate approximation has been employed by our group for cyclopropyl conformational analysis.[7] In that procedure, $B_0(CH_3)$ was neglected in comparison to $0.5B_2(CH_3)$, but $B_0(\Delta)$ was retained, since it is by no means small in comparison to $B_2\langle \cos^2\theta \rangle_{av}^{\Delta}$ for the small values of $\langle \cos^2\theta \rangle_{av}^{\Delta}$ usually found. Neglect of $B_0(CH_3)$ was not essential but was employed because it was felt that a reliable value of this quantity was not available. Additionally, the calculations used accurate torsional wave functions and energies, obtained by solving the Schrödinger equation for internal rotation. Since $B_0(CH_3)$ is now known fairly reliably,[9] the only arbitrary assumption remaining in the analysis is that of equal B_2's. As will be demonstrated in the present paper, the merits of this assumption can be examined and a value of $B_2(\Delta)/B_2(CH_3)$ derived by studying systems having cyclopropyl attached to *digonal* (*sp*) *carbon*, where $\langle \cos^2 \theta \rangle_{av}^{\Delta} = 0.500$. No such radicals have previously been synthesized or studied. This paper describes experiments involving two radicals of this type, their methyl analogs, and a single isopropyl analog.

Syntheses. The three *p*-alkynylnitrobenzene anion radicals **1a–c** were selected for study on the premise that, as radicals of the nitrobenzene family, they should have exceptional stability, over a range of temperatures. This circumstance would permit a check of the assumption of "free rotation" *via* the temperature dependence of the β hfs (nil for free rotation). The two neutral radicals **2a,b** and the dianion radicals **3a,b** were chosen partly because of our interest in the tropenyl series and partly because the same tropenyl dimer could serve as precursor for both series. The syntheses of the immediate precursors are outlined in Scheme I. Of particular interest is the reaction of tropenylium fluoroborate with cuprous acetylides in acetonitrile. The reaction requires bromide ion as catalyst. When this is provided, the reaction is much superior to the reaction of the acetylenic Grignard with tropenylium fluoroborate.

Results

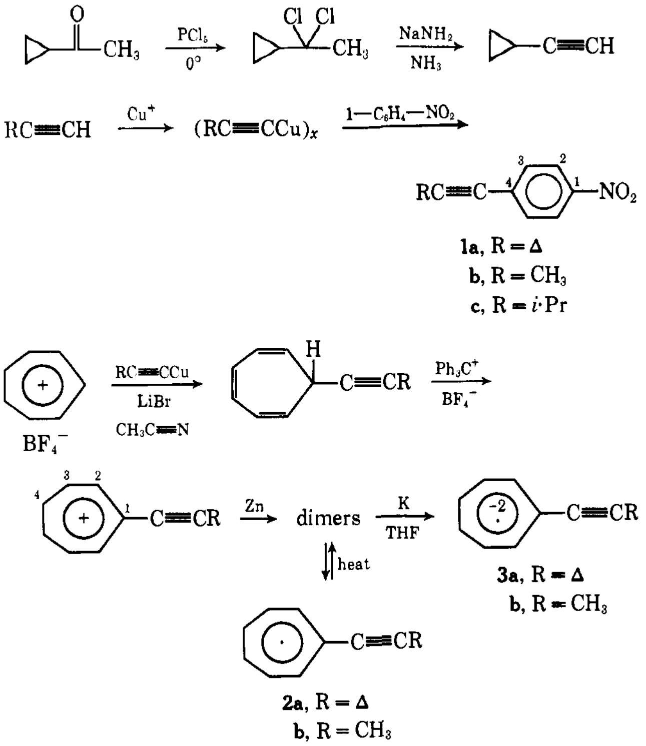
The anion radicals of **1a–c** were most satisfactorily generated by *intra muros* electrolytic reduction in DMF. Alkali metal–ether reductions gave spectra complicated by metal hfs. The hfs assignments are listed in Table I. In all cases the experimental spectra were satisfactorily matched by computer simulations using the assigned hfs. Since temperature control could not be achieved with the flat electrolysis cell employed, the temperature-dependence studies were performed on the anion radical of **1a** generated by Na–DME reduction. Although the spectrum of this radical resisted complete analysis, the spectrum length was identical at 0° and −50°. Moreover, the identifiable cyclopropyl methine doublet remained unchanged, to less than 0.1 G, as the temperature was varied. Apparently, any temperature dependence must be quite minute.

Table I. Esr Hfs of *p*-Alkynylnitrobenzene Anion Radicals (1a–c), Electrolytic in DMF

Substituent	LW[a]	a_N[b]	a_2	a_3	a_β
Cyclopropyl (**1a**)	0.27	8.02	3.16	1.04	1.76
Methyl (**1b**)	0.19	7.98	3.13	1.12	2.12
Isopropyl (**1c**)	0.20	8.37	3.53	1.12	2.02

[a] Indicates line width. [b] All figures are in gauss.

Scheme I



Neutral radicals **2a,b** were produced by thermolysis of their respective dimers (as the isomeric mixtures). The hfs are listed in Table II. Positional assignments are based on MO theory, but should be reliable. The β hfs were readily identifiable as the only hfs arising from odd numbers of protons. The intensities of the spectra were low and necessitated use of fairly high modulation amplitudes. As a result, the line widths are rather large. HMO calculated hfs are also listed in Table II. The agreement is only fair. In particular there is less spin density on the acetylene moiety than predicted. This point will be discussed below.

Table II. Esr Hfs of Alkynyltropenyl Radicals, Thermolytic Generation[a]

Substituent	LW	a_2	a_3	a_4	a_β
Cyclopropyl	0.57	1.10	5.65	2.16	3.45
Methyl	0.30	0.92	5.72	2.26	4.48

[a] Temperatures were 160° for the cyclopropyl, 170° for the methyl derivative. [b] The HMO calculated hfs using the McConnell equation with $Q = -27$ are: −0.69 [2 H, 2 position), −4.10 (2 H, 3 position), −2.29 (2 H, 4 position).

It was originally intended that dianion radicals **3a,b** would also be studied. It was apparent that the substituents would be attached to nodal positions in these dianion radicals, but trial experiments nevertheless seemed worthwhile, based upon the hope that negative spin density might appear at the relevant positions. In addition, dianion radicals are still rather rare, and new members of their class are not devoid of inherent interest. Dianion radical **3b**, formed by Na–THF reduction, gave an esr spectrum consisting of 29 equidistant, broad lines, comprising a total length of 32.3 G. The length suggested appreciable metal hfs, as in the case of the parent tropenide ion,[10] but a secure analysis of the spectrum was difficult. Potassium reduction yielded a much better spectrum, the hfs of which are 6.99 (2 H, 2 position), 1.00 (2 H, 3 position), 4.53 (2 H, 4 position), 0.49 ($2K^+$). Note the appearance of double metal hfs as befits a dianion radical and as was found in disodium tropenide. The metal hfs of dipotassium tropenide was not resolved. The methyl hfs must be less than the line width (0.26 G). In retrospect, the absence of a methyl hfs appears reasonable, not only in view of the nodality of the substituent in the HMO approximation, but especially since the next *two* atoms in line are also nodal. This is a quite unusual structural feature and probably is responsible for the absence of even negative spin density on the methyl group. The HMO calculated hfs for **2b** are −6.80 (2 H, 2 position), −1.35 (2 H, 3 position), −4.24 (2 H, 4 position). The agreement is quite good, in contrast to the results for the neutral radical. No doubt the good agreement obtained for **3b** results from the nodality of the entire acetylenic side chain as described above. In view of the above results, the dianion radical of **3a** was not studied.

The nmr spectrum of the interesting intermediate propynyltropenylium fluoroborate merits brief mention: τ 7.75 (3 H, s), 1.04 (6 H, s). The average HMO calculated excess charge density is +0.132 for the six ring protons, compared to +0.143 for the parent cation, which absorbs at τ 0.76. The data for tropenylium lead to a predicted chemical shift of τ 0.86 for the propynyl derivative. HMO theory here badly *underestimates* the positive charge on the side chain. Both this result and that for the neutral radical must reflect the tendency of HMO theory to overestimate the relative stability of the tropenylium π system.

Discussion

The salient objective of this research was to obtain C(R) values for the cyclopropyl group, *i.e.*, $C(\Delta)$, in systems for which $\langle \cos^2\theta \rangle_{av}^{\Delta}$ is known. This appears to be possible only for $\langle \cos^2\theta \rangle_{av}^{\Delta} = 0.500$, which obtains for rapidly rotating, cylindrically symmetrical groups. Since the cyclopropyl group is not itself cylindrically symmetrical, it was attached to digonal carbon, which *is* a locally cylindrically symmetrical π system. Although the *p*-nitrophenyl and tropenyl groups disrupt the perfect cylindrical symmetry of the acetylenic moiety, they are remote from the cyclopropyl group and only to the extent that they interact with the latter conjugatively would the aforementioned symmetry be vitiated. Cyclopropyl is such a feeble conjugator with even a directly attached π system[7] that such an extended interaction should almost certainly be negligible for our purposes. The independence of $C(\Delta)$ on temperature over a 50° range provides experimental support for the foregoing claim. In the tropenyl radicals the additional factor of a relatively high temperature also acts to promote free rotation.

The data of Table I demonstrates that the cyclopropyl and methyl derivatives **1a,b** have virtually identical spin distributions. The assumption of equal ρ_α's is a very good one for these radicals. Somewhat surprisingly the isopropyl derivative **1c** exhibits larger perturbations, the ring protons and the nitro group having larger hfs than in either **1a** or **1b**. Accordingly, there must be less spin on the acetylenic moiety, and the assumption of equal ρ_α may not be valid here. The disparate behavior of isopropyl did not vanish when the anion radicals were generated with Na–DME. Whether the effect is caused by steric hindrance to solvation of the acetylene moiety or to a significantly greater electron-donating ability of isopropyl when attached to sp carbon is not yet known. Nevertheless, this result is a clear warning that assumptions of equality of ρ_α's are unjustified in the absence of direct experimental evidence.

Despite the demonstrable equality of ρ_α for **1a** and **b**, the cyclopropyl methine hfs (1.76) is appreciably smaller than the methyl hfs (2.12). The $C(\Delta)$ calculated from this ratio is 0.83. The $C(i\text{-Pr})$ value calculated from the data for **1a** and **1c** is 0.95, but is uncertain because of the shifted spin distribution in **1c**. Ordinarily, it would be assumed that $C(i\text{-Pr})$ would be essentially unity, since the B_0 and B_2 constants are assumed to be approximately equal for all simple alkyl groups.

In system **2**, also (see Table II), compounds **a** and **b** had quite similar spin distributions. In fact the total of the ring hfs is 17.82 G for **a** and 17.80 for **b**. Again, the assumption of equal ρ_α is valid. The value of $C(\Delta)$ determined here is 0.77, slightly lower than that for system 1.

The error involved in the latter determination is somewhat larger than in the first case because the line widths are greater in the neutral radicals. On the other hand, q_α, the excess charge density at the carbon α to the substituents, is probably more negative for the anion radical. This could cause a slight "symmetrical" conformational bias in the cyclopropyl group and lead to a slightly larger $C(\Delta)$ value than that for completely free rotation. It is now clear[7] that charge densities play a much larger role in determining cyclopropyl conformations than do spin densities. Evidence for this interesting possibility is being sought *via* endor experiments. In any case, the analysis presented in the following paper is not fundamentally nor substantially affected by the small discrepancy between the two values.

Finally, to be strictly accurate, our analysis requires that the ratio of B_2's and of B_0's for cyclopropyl and methyl be independent of the hybridization state (digonal or trigonal) of the α carbon. Since it is only the ratios which must be sensibly unchanged, the assumption appears a good one. Data have been presented which suggest that even the absolute magnitudes of these parameters are relatively insensitive to changes in hybridization from sp^2 to sp.[11]

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(10) N. L. Bauld and M. S. Brown, *J. Amer. Chem. Soc.*, **87**, 4390 1965).

(11) J. K. Kochi and P. J. Krusic, *ibid.*, **92**, 4110 (1970).

It is, then, quite clear that even for systems having equal ρ_α, cyclopropyl β hfs are generally smaller than those of methyl groups, and presumably of other simple alkyl groups. Different values of the B parameters are therefore required for cyclopropyl, as previously surmised.[7] A method for deriving the values of these parameters and thus completing the full application of eq 3 to cyclopropyl conformational analysis will be expounded in the following section.

Theoretical. Sufficient data are now available to permit explicit evaluation of the equation relating $C(\Delta)$ to $\langle\cos^2\theta\rangle_{av}^{\Delta}$, thus providing a simple and accurate means of obtaining torsional barriers of radicals in solution from β hfs.

The derivation commences with eq 3. The value $C(\Delta) = 0.83$ will be employed initially, but the comparable results for $C(\Delta) = 0.77$ will subsequently be discussed. Substituting R = Δ, $C(\Delta) = 0.83$, and $\langle\cos^2\theta\rangle_{av}^{\Delta} = 0.500$ into eq 3 and then subtracting from this eq 3 with R = Δ, there results eq 5. Rearrangement of the latter gives eq 6. Using the accurate

$$0.83 - C(\Delta) = B_2(\Delta)[0.500 - \langle\cos^2\theta\rangle_{av}^{\Delta}]/[B_0(CH_3) + 0.500B_2(CH_3)] \quad (5)$$

$$B_2(\Delta)/B_2(CH_3) = \{0.83 - C(\Delta)\} \times \{[2B_0(CH_3)/B_2(CH_3)] + 1\}/\{1 - 2\langle\cos^2\theta\rangle_{av}^{\Delta}\} \quad (6)$$

endor data for the $p,p'p''$-tricyclopropyltrityl radical,[7] values of V_0 and $B_2(\Delta)/B_2(CH_3)$ were calculated as follows. Values of $\langle\cos^2\theta\rangle_{av}^{\Delta}$ were calculated for several different barrier heights at the nine temperatures (−10 to −90°) at which $C(\Delta)$ had been measured, using the quantum mechanical method previously described.[7] These values of $\langle\cos^2\theta\rangle_{av}^{\Delta}$, $C(\Delta)$, and upper and lower extremes for $B_0(CH_3)/B_2(CH_3)$[9] were substituted into eq 6. The values of the ratio $B_2(\Delta)/B_2(CH_3)$ thus obtained were observed to drift with temperature except for a barrier height V_0 = 1.70–1.71 kcal, which is therefore accepted as the correct barrier. The value of the B_2 ratio corresponding to this value of V_0 was adopted as correct (Table III).

Table III

$\frac{B_0(CH_3)}{B_2(CH_3)}$	V_0, kcal	$\frac{B_2(\Delta)}{B_2(CH_3)}$	$\sigma^a \times 10^3$	$\frac{B_0(\Delta)}{B_2(CH_3)}$	$\sigma^a \times 10^3$
0.0985	1.70–1.71	1.11	2.9	−0.059	1.0
0.119	1.70–1.71	1.15	3.0	−0.061	1.0

[a] σ is the standard deviation.

Another necessary quantity, $B_0(\Delta)/B_2(CH_3)$, can be calculated from eq 7, which follows upon dividing numerator and denominator of the right-hand side of eq 3 with R = Δ by $B_2(CH_3)$ and rearranging terms. This ratio was calculated for all nine temperatures and the average value adopted (Table III).

$$B_0(\Delta)/B_2(CH_3) = [B_0(CH_3)/B_2(CH_3) + 0.500]C(\Delta) - [B_2(\Delta)\langle\cos^2\theta\rangle_{av}^{\Delta}/B_2(CH_3)] \quad (7)$$

$B_0(\Delta)/B_2(CH_3)$, and therefore $B_0(\Delta)$, was found to be negative, in accord with an interpretation in terms of a cyclopropyl ↔ cyclobutyl resonance interaction. More unexpectedly, the ratio $B_2(\Delta)/B_2(CH_3)$ is greater than unity. Using the preferred value $B_0(CH_3)/B_2(CH_3) = 0.11$,[9] the B_2 ratio is 1.13. Since B_2 is related to the efficiency of CH hyperconjugation, one would naively expect the shorter and stronger cyclopropyl C_β-H bond to hyperconjugate less, rather than more, efficiently than an sp^3 C_β–H bond. Equation 8 has been derived for B_2,[12,13] where J_{CC}^{π} is the exchange in-

$$B_2 = 502J_{CC}^{\pi}/2J_{CH} \quad (8)$$

tegral for π overlap of the carbon hybrid orbital of the C_β–H bond with the p orbital on C_α (*i.e.*, for hyperconjugation) and J_{CH} is the exchange integral for the C_β–H σ bond. Based on the qualitative argument given above, J_{CH} should be larger for the stronger cyclopropyl C_β–H bond. Also, J_{CC}^{π} should, if anything, be smaller in the cyclopropyl case, since the C_β hybrid orbital has less p character than does the sp^3 carbon of an ordinary alkyl group. These factors reinforce each other in the conclusion that $B_2(\Delta) < B_2(CH_3)$. It appears that the measured B_2 ratio is not extraordinarily sensitive to the experimental quantities used to determine it. For example, a 100% error in $B_0(CH_3)/B_2(CH_3)$ would be required to reduce the B_2 ratio to unity. Adoption of $C(\Delta) = 0.77$ also does not alter the basic point, though the B_2 ratio is reduced to 1.07. Apparently, $B_2(\Delta)$ is indeed larger than $B_2(CH_3)$, the previous theoretical arguments notwithstanding.

A plausible explanation can, however, be formulated, based upon arguments supplied previously.[7] As stated earlier, the negative value of $B_0(\Delta)$ apparently demands explanation in terms of cyclobutyl resonance interactions. The positive B_0's for ordinary alkyl groups are presumed to represent spin transmission *via* the σ electron system. Such a mechanism must also operate in the cyclopropyl case and, very likely, to about the same extent. This effect is, however, dominated by the resonance effect, leaving a net negative value of $B_0(\Delta)$. As was also mentioned previously,[7] the cyclobutyl resonance interactions are conformation dependent, being optimized in the bisected form, for which $\theta = 90°$. A revised, three-term equation (9) was therefore pro-

$$a_H(\Delta) = [B_0'(\Delta) + B_0''(\Delta)\langle\sin^2\theta\rangle_{av}^{\Delta} + B_2'(\Delta)\langle\cos^2\theta\rangle_{av}^{\Delta}]\rho_\alpha = \{B_0'(\Delta) + B_0''(\Delta)[\langle\sin^2\theta\rangle_{av}^{\Delta} + \langle\cos^2\theta\rangle_{av}^{\Delta}] + [B_2'(\Delta) - B_0''(\Delta)]\langle\cos^2\theta\rangle_{av}^{\Delta}\}\,\rho_\alpha \quad (9)$$

$$a_H(\Delta) = \{[B_0'(\Delta) + B_0''(\Delta)] + [B_2'(\Delta) - B_0''(\Delta)]\langle\cos^2\theta\rangle_{av}^{\Delta}\}\rho_\alpha \quad (10)$$

posed for the cyclopropyl group, where $B_0'(\Delta)$ reflects σ transmission, $B_0''(\Delta)\langle\sin^2\theta\rangle_{av}^{\Delta}$ the cyclobutyl interaction, and $B_2'\langle\cos^2\theta\rangle_{av}^{\Delta}$ the hyperconjugative interaction. Rearrangement affords eq 10, in which it is apparent that the conformation-independent term B_0 in the two-term equation for a_H actually corresponds to $B_0'(\Delta) + B_0''(\Delta)$. Since $B_0(\Delta)$ is observed to be negative and $B_0'(\Delta)$ is presumably positive, $B_0''(\Delta)$ must be even more negative than the net $B_0(\Delta)$. Now, since $B_2(\Delta) = B_2'(\Delta) - B_0''(\Delta)$, with $B_0''(\Delta)$ negative, $B_2(\Delta)$ is a larger

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(12) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

(13) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Amer. Chem. Soc.*, **91**, 1877 (1969).

positive number than $B_2'(\Delta)$. Assuming $B_2(\mathrm{CH_3}) \cong B_2'(\Delta)$, *i.e.*, comparable hyperconjugative terms, it follows that $B_2(\Delta)/B_2(\mathrm{CH_3}) > 1$. More quantitatively, if one assumes $B_0(\mathrm{CH_3}) = B_0'(\Delta)$, *i.e.*, equivalent spin transmission terms, the agreeable result ensues that $B_2'(\Delta)/B_2(\mathrm{CH_3}) = 0.96$–$0.97$, *i.e.*, that hyperconjugation with a C_β–H cyclopropyl bond is indeed a little less efficient than for ordinary alkyl groups. Also, $B_0''(\Delta)/B_2(\mathrm{CH_3}) = -0.15$ to 0.18, *i.e.*, the cyclobutyl interaction is about 15% as effective at inducing spin on the β hydrogen as is hyperconjugation with an ideally placed methyl C–H bond (30% as effective as a freely rotating methyl hydrogen).

The explicit form of the relationship between $C(\Delta)$ and $\langle\cos^2\theta\rangle_{\mathrm{av}}{}^{\Delta}$ is now attainable. Dividing eq 3 by $B_2(\mathrm{CH_3})$ and substituting the values $B_0(\Delta)/B_2(\mathrm{CH_3}) = -0.06$, $B_2(\Delta)/B_2(\mathrm{CH_3}) = 1.13$, and $B_0(\mathrm{CH_3})/B_2(\mathrm{CH_3}) = 0.11$ one obtains eq 11.

$$C(\Delta) = 1.85\langle\cos^2\theta\rangle_{\mathrm{av}}{}^{\Delta} - 0.10 \qquad (11)$$

Note that the bisected conformation is predicted to have $C(\Delta) = -0.10$, *i.e.*, the cyclopropyl β hfs should be 0.1 the methyl hfs and *negative*. Negative cyclopropyl β hfs have not yet been established, and are not likely in most cases, but in an instance such as the cyclopropylcarbinyl radical ($-150°$) where the bisected preference might be rather strong, the definite possibility exists. The $C(\Delta)$ value (± 0.095) for this radical[2] is consistent with $\langle\cos^2\theta\rangle_{\mathrm{av}}{}^{\Delta} = 0.003$ (if the hfs is negative) or $\langle\cos^2\theta\rangle_{\mathrm{av}}{}^{\Delta} = 0.105$ (if the hfs is positive). The question is particularly interesting because, though $C(\Delta)$ appears to be acutely dependent on charge density, a pronounced dependence on spin density has not been observed. The value of 0.105 for $\langle\cos^2\theta\rangle_{\mathrm{av}}{}^{\Delta}$ would be rather close to that, *e.g.*, of the *p,p'p''* -tricyclopropyltrityl radical. If the β hfs of the cyclopropylcarbinyl radical is positive, therefore, the barrier in the latter radical would be quite close to that in the former, despite the much higher value of ρ_α in the cyclopropylcarbinyl radical. This in turn would suggest that cyclopropyl conjugates about equally well (or poorly) with a double bond as with a free radical site.

The symmetrical conformation, according to eq 11, should have $C(\Delta) = 1.75$. The free rotation value is, of course, 0.83. For comparison, the one-term equation (neglect of all B_0's) requires values of 0, 2.00, and 1.00, respectively, for the bisected, symmetrical, and free rotation cases. The equation resulting from the use of 0.77 as the free rotation value of $C(\Delta)$ is $C(\Delta) = 1.75\langle\cos^2\theta\rangle_{\mathrm{av}}{}^{\Delta} - 0.10$, only slightly different from eq 11. Some further work is in progress to settle the issue of the correct value of $C(\Delta)$ for free rotation.

Using eq 11 revised barriers have been calculated for several of the radicals reported previously[7] (Table IV).

Summary. Equation 11 provides a direct qualitative index to symmetrical or bisected conformational preferences from esr measurements on two radicals (the cyclopropyl compound and its methyl analog) at a single temperature, providing only that ρ_α is verifiably essentially identical for both radicals. In addition, the barrier height, V_0, can be obtained by calculating $\langle\cos^2\theta\rangle_{\mathrm{av}}{}^{\Delta}$ for various barrier heights by either of the two methods presented previously.[7] Although the quantum mechanical method is more rigorous, the statistical method is operationally much simpler and as far as we can tell, gives essentially identical results.

Table IV

Radical	V_0, kcal
4,4'-Dicyclopropylbiphenyl anion radical	0.46
Cyclopropyltropenide dianion radical	0.52
9-Cyclopropylanthracene cation radical	0.85
p-Cyclopropylnitrobenzene anion radical	1.21
p,p',p''-Tricyclopropyltrityl radical	1.71
1-Cyclopropylphenalenyl radical	~0

The B_2 value (coefficient of the conformation dependent, *i.e.*, π electron term of the β hfs) of cyclopropyl is, surprisingly, greater than that for the methyl group. Hyperconjugation with a cyclopropyl C–H bond is expected to be less efficient than with a methyl C–H bond. The previously proposed three-term equation for cyclopropyl β hfs provides a plausible explanation. In this it is recognized that the conformation-dependent term is comprised not only of the hyperconjugative effect but also of a cyclopropyl–cyclobutyl conjugative effect. This interaction engenders negative spin density on the β hydrogens, opposite to the positive density caused by the hyperconjugative effect, but with an opposite $[\langle\sin^2\theta\rangle_{\mathrm{av}}]$ conformation dependence. The net effect is to increase the $\langle\cos^2\theta\rangle_{\mathrm{av}}$ dependence (*i.e.*, B_2). The various terms are separated and their respective magnitudes evaluated.

Experimental Section

Elemental analyses were performed by the Galbraith Laboratories, Knoxville, Tenn. Esr spectra were measured on a Varian V-4502 X-band spectrometer and nmr spectra on a Varian A-60 spectrometer.

Purification of Esr Solvents. *N,N*-Dimethylformamide (DMF) was distilled from CaH and anhydrous $\mathrm{CuSO_4}$ through a 15-in. Vigreaux column. Only a center cut was retained. DME and THF were refluxed over LAH and K before distillation through a Vigreaux. A center cut was stored over metallic potassium.

Generation of Radical Ion. A. *In situ* Method. To the freshly distilled solvent was added enough supporting electrolyte (tetra-*n*-butylammonium perchlorate or iodide) and substrate to make their concentrations about 0.2 and 0.001 *M*, respectively. This solution was poured into the flat Varian electrolytic cell and the solution degassed for 0.5 hr with dry nitrogen. A mercury cathode and silver anode were used in the cell, which was placed in the esr cavity, and sufficient voltage was applied across the terminals to produce a current of *ca.* 20 μA.

B. Alkali Metal Method. This method is conventional and has already been described in detail in many references.[8]

(1,1-Dichloroethyl)cyclopropane. To 40 g (0.476 mol) of cyclopropyl methyl ketone cooled in an ice–salt bath was added, in ~2 g portions over a 1-hr period, 110 g (0.48 mol) of $\mathrm{PCl_5}$. The reaction was stirred 3 hr more at this temperature and then poured onto ice (800 g)–pentane (400 ml). Distillation of the oil obtained after the usual work-up gave 39 g (59%) of semipure product: bp 57–67° (60 min); nmr ($\mathrm{CCl_4}$) 9.3 (4 H, m), 8.4 (1 H, m), 7.88 (3 H, s); ir ($\mathrm{CCl_4}$) had a very weak 1700 $\mathrm{cm^{-1}}$ peak corresponding to starting ketone.

Cyclopropylacetylene. A solution of sodium amide in liquid ammonia was prepared, in a hood, by dissolving 25 g (1.1 g-atom) of sodium in 750 ml of ammonia at $-78°$ and then adding a small amount of ferric nitrate. To this grey solution was added 27.8 g (0.20 mol) of (1,1-dichloroethyl)cyclopropane. After stirring the mixture at $-78°$ for 1 hr, the $-78°$ bath was removed and stirring continued another hour. The ammonia was permitted to evaporate overnight, the flask was recooled to $-78°$, 200 ml of triethylene glcyol was added, and the flask was connected to a vacuum pump *via* a N_2(l) trap. Gentle heating of the flask under vacuum for 5 hr and subsequent warming of the trap to 0° to remove ammonia gave a two-phase liquid system. The upper phase was separated and distilled (care should be taken to remove all of the lower phase (water), since the product forms an azeotrope with it, bp 47°), giving 5.5 g (42%) of product: bp 54–57°; nmr (CCl_4) τ 9.3 (4 H, m), 8.8 (1 H, m), 8.30 (1 H, d, J = 2 Hz); ir (CCl_4) 3320, 3110, 3010, and 2120 cm^{-1}. The structure has also been studied by microwave spectroscopy (Drs. Boggs and M. Collins).

Cuprous Cyclopropylacetylide. An ammoniacal solution of cuprous chloride was prepared by adding 20 g of 90% cuprous chloride (0.24 mol) to 100 ml of 28% ammonium hydroxide and, after stirring for a short time, further adding 350 ml of distilled water, and finally enough solid ammonium chloride to bring all of the solids into solution. Neat cyclopropylacetylene (6.6 g, 0.10 mol) was then added. A yellow precipitate slowly began to form, and after 0.5 hr stirring, this was filtered and washed twice with 100 ml of water (each), 100 ml of 95% ethanol, and 100 ml of ether. Drying overnight in a vacuum oven (room temperature) gave 5.3 g (41%) of product. Repeated attempts to prepare the acetylide by the method used for propyne (*vide infra*) failed completely.

4-Nitrophenylcyclopropylacetylene (1a). Cuprous cyclopropylacetylide (5.2 g, 0.04 mol) was added to 125 ml of pyridine and the system flushed by nitrogen flow. Addition of 9.7 g (0.039 mol) of 4-iodonitrobenzene followed, and the mixture was heated at 85° for 12 hr with continuous stirring. The reaction flask was allowed to cool, poured into 500 ml of water and 300 ml of ether, and stirred several minutes to dissolve the product in the ether phase. The mixture was then filtered, the layers were separated, and the usual work-up procedure was followed, except that the ether layer was additionally washed five times with dilute HCl and then twice more with water. The ether layer was filtered again to remove solids which had appeared during the extractions, dried, and evaporated. Chromatography of the yellow oil on alumina using 90% Skellysolve B–10% benzene eluent gave the product in the early fractions. This was dissolved in a small amount of Skelly B, at room temperature, filtered, and cooled in the refrigerator, giving 2.4 g of pure, crystalline product. Later chromatographic fractions yielded more product, but this was less pure and was not purified. The yield of purified product was 33%: mp 53–54°; nmr (CCl_4) 9.1 (4 H, m), 8.6 (1 H, m), 2.58 (2 H, m, meta to nitro), 1.92 (2 H, m, ortho to nitro); ir (CCl_4) 2240, CC≡(—) 1600, 1525, and 1340 (NO_2); mass spectrum (70 eV) *m/e* 187 (M).

Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.63; H, 4.91; N, 7.36. This compound is unstable to air and light, gradually turning yellow, and then orange on exposure to either. Storage in a vial wrapped with black tape, under nitrogen, in a refrigerator is recommended.

4-(1-Propynyl)nitrobenzene (1b). The cuprous acetylide of propyne was prepared *via* the method of Quin and Montgomery.[14]

Ten grams of this acetylide (0.098 mol) and 24.0 g (0.096 mol) of 4-iodonitrobenzene were heated in 250 ml of pyridine for 10 hr at 80° under nitrogen. The solution was cooled, filtered, and poured into ether (200 ml) and water (300 ml). Work-up of the ether phase, with removal of pyridine by repetitive extractions with 15% HCl, gave a brown solid. Recrystallization from Skelly B and then Skelly B–CCl_4 gave yellow crystals, mp 95–102°. Chromatography on alumina gave the product in the 30% benzene in Skelly B eluate. Recrystallization from Skelly B–50% CCl_4 raised the mp to 97–102°. Sublimation and recrystallization from Skelly B–30% ethyl acetate gave a product with mp 107–109°. A final recrystallization from the same solvent mixture did not change the melting point, nor did a second sublimation. The literature mp[15] is 108°. The overall yield of purified product was <1%: nmr ($CDCl_3$) τ 7.93 (3 H, s), 2.55 (2 H, m), 1.70 (2 H, m); mass spectrum, *m/e* 161 (M).

4-(3-Methyl-1-butynyl)nitrobenzene (1c). The curpous acetylide was prepared in the same manner as for cyclopropylacetylene.

A mixture of 14.4 g (0.11 mol) of 1-(3-methylbutynyl)copper, 25 g (0.10 mol) of 4-iodonitrobenzene, and 250 ml of pyridine was heated by oil bath until, after 1.5 hr, the temperature had risen to 95° and the acetylide had dissolved. Heat was discontinued, but stirring was continued until the contents of the flask had cooled to 45°. The solution was poured into a mixture of cracked ice (400 g), 100 ml of 28% HCl, and 200 ml of ether. The precipitate was filtered and the usual pyridine-removing work-up applied. The resulting yellow solid was dissolved in 150 ml of boiling chloroform, precipitating 4-iodonitrobenzene, which was filtered off. The chloroform was evaporated from the filtrate and the resulting oil chromatographed on alumina using 80% Skelly B–20% benzene eluent. All of the 4-nitroiodobenzene was removed by this procedure. A second chromatography using Skellysolve B removed other impurities (nmr). The resulting material was dissolved in Skelly B at room temperature and recrystallized at −20°, decolorized with Norite in Skelly B (room temperature), and finally recrystallized from 9 ml of Skelly B–1 ml of CCl_4 at −20°, giving 0.8 g (4.1%) of faintly yellow plates. The yield could probably be improved with longer reaction times: mp 49–51°; nmr (CCl_4) 8.75 (6 H, d, 7 Hz), 7.20 (1 H, septet, 7 Hz), 2.40 (2 H, m), and 1.95 (2 H, m); ir (CCl_4) 2220 (C≡C stretch), 1525, and 1345 (NO_2) cm^{-1}.

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.73; H, 6.03; N, 7.26.

7-(1-Propynyl)cycloheptatriene. Two methods were used, the second giving considerably higher yields, but the product is more difficult to purify.

Grignard Method. A solution of ethylmagnesium bromide (0.10 mol) in THF was prepared freshly. Approximately 10 ml of propyne was allowed to bubble into this solution. More propyne was then bubbled in slowly during a 0.5-hr period. To this solution of propynylmagnesium bromide was added 20 g (0.11 mol) of tropenylium fluoroborate. The mixture was stirred under nitrogen for 35 hr. Saturated aqueous ammonium chloride (100 ml) was added and the mixture was poured into ether (300 ml). The oily product of the usual work-up was chromatographed (alumina, Skelly B), giving 2.5 g (19%) of the product.

Cuprous Acetylide Method. Cuprous methylacetylide (10.2 g, 0.10 mol) and LiBr (1 g) were added to 50 ml of dry (P_2O_5) acetonitrile and the flask was purged with nitrogen. A solution of 20 g (0.112 mol) of tropenylium fluoroborate in the minimum volume of acetonitrile (*ca.* 150 ml) was added dropwise to the previous suspension. Stirring was continued for 2 hr more before partitioning the products between pentane (300 ml) and water (300 ml) containing 50 g of $Na_2S \cdot 9H_2O$. The black precipitate of cuprous sulfide was filtered and the filtrate worked up as usual. Chromatography of the black oil gave 10.4 g of a clear oil. Distillation at 5 mm gave 8.7 g of product: nmr (neat) τ 8.22 (3 H, d, 2.4 Hz), 7.64 (1 H, m), 4.75 (2 H, m), 3.95 (2 H, m), 3.43 (2 H, m).

Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.08; H, 7.79.

(1-Propynyl)tropenylium Fluoroborate. To a solution of 33 g (0.010 mol) of triphenylmethyl fluoroborate in 50 ml of anhydrous acetonitrile was added dropwise 1.3 g (0.010 mol) of 7-(1-propynyl)-cycloheptatriene as the neat liquid. After stirring the mixture 4 hr, it was poured into 425 ml of anhydrous ether, precipitating the salt as a black viscous oil. Decantation of the ether, and washing of the oil twice with more ether did not induce crystallization, nor were attempts to crystallize this salt from water or acetonitrile successful: nmr ($CH_3C{\equiv}N$) τ 7.75 (3 H, s), 1.04 (6 H, s).

Mixture of Isomeric Dimers of the 1-Propynyltropenylium Radical. To a solution of the crude salt of the previous preparation in 50 ml of acetonitrile was added 6 g (excess) of zinc dust. After stirring for 0.5 hr, 100 ml of pentane was added and the stirring continued 0.5 hr more. Water (100 ml) and pentane (100 ml) were then added, the zinc was filtered off, and the pentane phase dried over sodium sulfate. Since the dimers were not indefinitely stable, this pentane solution was either worked up and used for the esr experiments immediately or else the solution was stored overnight at −20° and then worked up and used the following day. The pentane was evaporated without heating and the oil chromatographed on alumina (Skelly B eluent), giving a light yellow, viscous oil: nmr (CCl_4) τ 8.1 (6 H, several singlets), 4.7 (4 H, m), 3.9 (4 H, m), 3.4 (4 H, m).

1-Propynyltropenyl Radical. A portion of the preceding dimeric mixture was placed in a 4-mm glass tube. The latter was evacuated, sealed off with a torch, and inserted into the esr cavity. The spectra were observed at only a single temperature because signal intensity fell off rapidly above and below the optimum temperature of 170°.

7-(Cyclopropylethynyl)cycloheptatriene. This compound was prepared *via* the cuprous acetylide precisely as in the case of 7-(1-propynyl)cycloheptatriene. The yield was 57%: bp 53–54° (0.05 mm); nmr (neat) τ 9.35 (4 H, m), 8.8 (1 H, m), 7.62 (1 H, t of d's, J = 5.7, 1.9 Hz), 4.7 (2 H, m), 3.9 (2 H, m), 3.4 (2 H, m); mass spectrum *m/e* 156 (M), and 155 (M − 1).

Anal. Calcd for $C_{12}H_{12}$: C, 92.25; H, 7.74. Found: C, 92.13; H, 7.84.

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(14) L. D. Quin and R. E. Montgomery, *J. Org. Chem.*, **28**, 3313 (1963).

(15) A. Zaki and Y. Iskanda, *J. Chem. Soc.*, 68 (1943).