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Long-Range Proton Hyperfine Coupling

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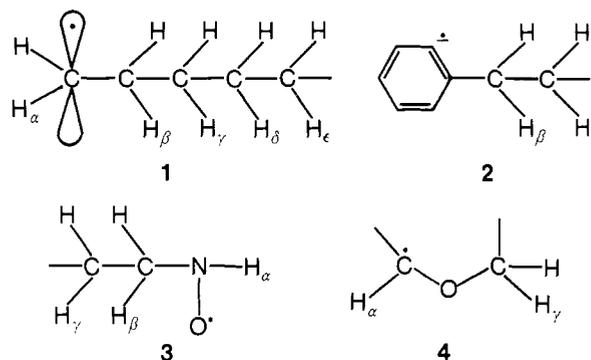
I. Introduction

Long-range coupling constants in electron spin resonance are those usually associated with hyperfine interactions which occur between nuclei separated by three or more σ bonds from some principal center containing a significant portion of the electron spin density. This statement is based on the intuitive classical description of radicals by means of localized bonds and localized spin distributions. The above definition in no way advocates the importance or unimportance of through-bond effects.

The present review attempts to correlate and evaluate the experimental results on long-range coupling from the period covering the first observations of large splittings to the time of submitting this article. Semiempirical theoretical methods which attempt to rationalize the multitude of data and other approaches which attempt a more detailed quantitative understanding of the origin of long-range coupling are examined. The conformational aspects and the stereospecificity of such couplings are a constantly recurring feature and comprise a central theme of this review. As the title suggests, proton

coupling constants are of primary concern, although a few paragraphs are devoted to the relatively sparse amount of information available for other nuclei for which long-range coupling constants have been reported.

There are various systems of nomenclature employed throughout the literature. The convention adopted here consists of labeling the proton bonded to the site which contains the orbital bearing the unpaired electron, or a portion of the spin density, as α . More distant protons are then designated β , γ , δ , etc. The nomenclature is exemplified by structures 1, 2, 3, and 4. This system is widely used by ESR spectroscop-



pists and will be adhered to throughout this review. All coupling constants are reported in gauss (G).

To date, no comprehensive discussion of long-range coupling has appeared. Russell and coworkers¹⁻⁴ have reviewed thoroughly the semidione radical anions, and this has involved discussion of some of the long-range coupled semidione radical anions. Russell⁵ has outlined an array of structures, predominantly semidiones, which exhibit long-range splittings and has also discussed briefly the mechanisms involved. Kaplan⁶ has cited some of the results on long-range coupling to explore the possibilities of bridged free radicals.

II. Survey of Long-Range Coupled Systems

A yardstick by which long-range coupling constants may be considered as large or anomalous is logically taken as the *n*-propyl radical for which $a_\gamma = 0.37$ G.⁷ Several workers have observed and, to varying degrees, stressed the somewhat larger than usual couplings observed in various aliphatic radicals.⁷⁻¹² However, the first observations of sizable long-range couplings were made by Russell, Chang, and Jef-

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TABLE I. Hyperfine Constants for the Bicyclo[2.2.1]heptane Derivatives^a

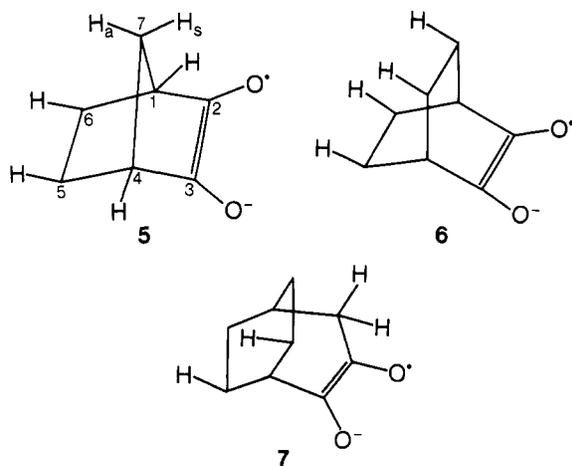
Semidione	Hyperfine constant, G	Assignment
8	2.90	exo C-5, C-6
	2.07	C-1, C-4
	0.26	endo C-5, C-6
	0.53	syn C-7
9	2.55	C-4, exo C-5, C-6
	3.05	anti C-7
	0.18	C-1 (CH ₃), syn C-7
10	3.01	exo C-5, C-6
	2.08	C-4
	0.55	syn C-7
	0.22	endo C-5
	0.15	Methyl
11	6.97	anti C-7
	0.4	syn C-7
	2.33	C-1, C-4
	1.84	exo C-5, C-6
	0.2	Methyl

^a Data from ref 3, 13, and 19.

ford^{13,14} for a series of bicyclic semidione radicals. The appearance of long-range coupling in the bicyclic semidiones was in marked contrast to the observations of Russell and co-workers on aliphatic semidiones^{15,16} and decalones^{17,18} for which no anomalous couplings were observed. In order to effectively present some representative data on long-range coupling, the approach taken is to categorize the data in terms of various spin labels. A spin label is any molecular fragment, most often a conjugated system, which can bind to the moiety of interest, and hence is capable of providing a source of spin density in the attached fragment.

A. Semidiones

The first members of the semidione family found to exhibit large long-range coupling constants were bicyclo[2.2.1]heptane (5), bicyclo[2.2.2]octane (6), and bicyclo[3.2.2]nonane

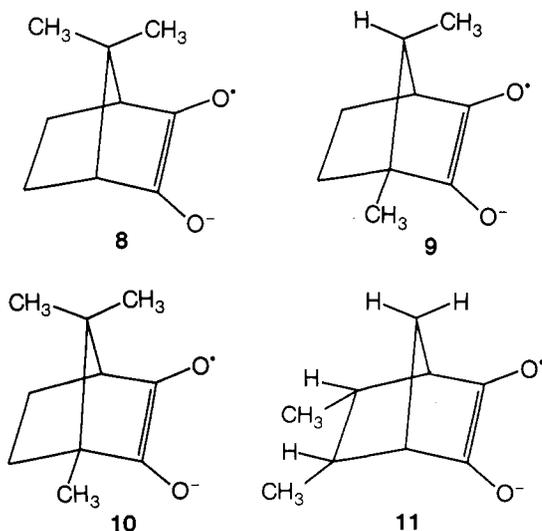


(7) semidione radical anions and some related compounds.^{13,14} The coupling constants for 5 were assigned as 6.54 G (doublet) to the 7-anti proton; 0.41 G (doublet) for the 7-syn proton, and 2.43 G to the accidentally equivalent protons at exo C-5, C-6 and the bridgehead protons C-1, C-4. This assignment was assisted by the results for the related derivatives 8, 9, 10, and 11, whose coupling constants are collected in Table I. The initial assignment of 5 based on deductions from methyl substitution studies has been verified by later work on labeled compounds. Russell and coworkers found that methyl substitution at the C-5 and C-6 positions of 5 en-

TABLE II. Hyperfine Constants for the Bicyclo[2.2.2]octane-2,3-semidione and Related Derivatives^a

Radical	Coupling constants, G
	$a(4) = 2.09$ (exo)
	$a_{7,8}(2) = 2.12$ $a_{5,6}(2) = 1.34$ (exo)
	$a_{6,7,8}(3) = 2.10$ $a_5(1) = 0.93$
	$a(4) = 2.14$
	$a(2) = 1.6, a(2) = 0.8$
	$a(4) = 2.21$

^a Data from ref 13, 19, 20, and 21.

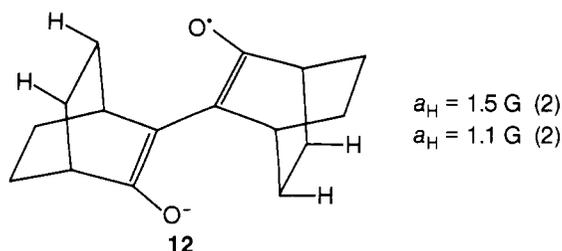


hanced the long-range coupling at C-7 anti; however, methyl substitution at the C-7 syn position greatly decreased the 7-anti coupling constant. There are a few particularly important features of the radical anion 5 which we emphasize at this point and will discuss in detail in a later section. These are the very large difference observed for the anti and syn splittings at C-7, the large bridgehead and exo proton couplings, and, of course, the very large magnitude of the 7-anti proton splitting.

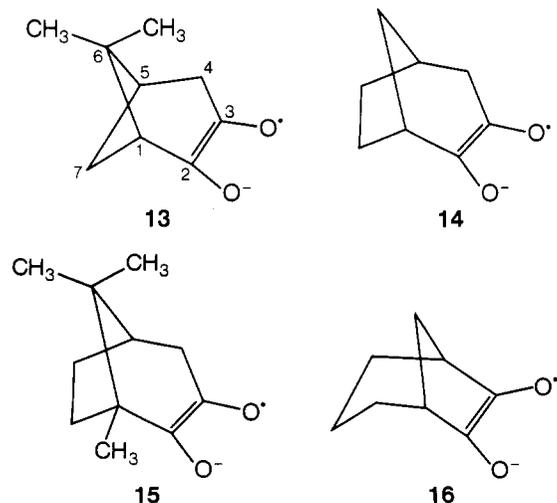
The bicyclo[2.2.2]octane-2,3-semidione radical anion (**6**) also exhibits sizable long-range coupling though not as large as **5**. A simple quintet spectra was observed for **6** with $a_H = 2.09$ G, and this was assigned to the exo protons at C-5, C-6, C-7, and C-8. The assignment has been supported by results from related derivatives,^{13,19-21} some of which are summarized in Table II. The careful assignment of coupling constants by Russell and associates for these radicals has been of considerable value to other workers who have made assignments by comparison with the above radicals. The relative ordering of the coupling constants for the anti and syn protons in **5** and the exo and endo protons of **5** and **6** is far from obvious and constitutes a somewhat subtle problem, which for some radicals has not been fully settled. This will be discussed in section IV. One result of note is that methyl substitution at endo C-5 and C-6 has a much smaller effect on the coupling constants at exo C-7 and C-8 (see Table II) than may have been anticipated based on the changes observed for **11**.

Having successfully assigned the basic radical anions **5**, **6**, and **7**, Russell and coworkers have since carried out an extensive investigation of the radicals based on the semidione spin label. In an effort to exemplify both the scope of this work and the variety of radicals studied, we intend to tabulate some of the results for representative systems and discuss some of the more interesting observations of the Iova group.

Russell, Holland, and Chang²⁰ observed that the oxidation of the monoketone precursor can in some cases produce dimeric 1,4-semidiones, e.g., **12**. Further exposure of **12** to

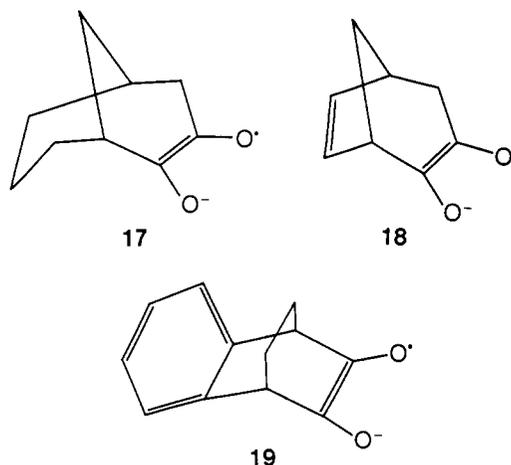


oxygen leads to the formation of **6**. The semidiones derived from bicyclo[3.2.2]nonane (**7**), bicyclo[3.1.1]heptane (**13**), bicyclo[3.2.1]octane (**14**, **15**, and **16**), bicyclo[3.3.1]nonane (**17**) and some representative unsaturated systems **18** and **19** are summarized in Table III. The spectra of many of the semidione radicals are relatively straightforward to analyze because of the limited number of observed lines. Added advantage has been taken of the labile nature of the α protons toward deuterium substitution in $\text{Me}_2\text{SO}-d_6$ as solvent. This deuterium exchange does not take place for the bridgehead

TABLE III. Hyperfine Splittings for the Semidiones^a

Semidione	Hyperfine constant, G	Assignment
13	9.46 (doublet)	C-4
	9.04 (doublet)	C-4
	3.88 (doublet)	anti C-7
	0.42 (sextet)	C-1, syn C-7, methyl
14	13.5 (doublet)	C-4
	8.69 (doublet)	C-4
	3.45 (doublet)	C-1, exo C-7 or anti C-8
	2.13 (doublet)	As above
15	1.42 (doublet)	As above
	0.28 (triplet)	endo C-7, syn C-8
	12.5 (doublet)	C-4
	8.4 (doublet)	C-4
16	4.1 (doublet)	exo C-7
	5.51 (triplet)	exo C-2, C-4
	4.03 (doublet)	anti C-8
7	0.53 (sextet)	C-1, C-4, endo C-2, C-4, syn C-8
	10.5 (triplet)	C-4
17	2.2 (triplet)	anti C-7, C-8
	12.74 (doublet)	C-4
18	6.93 (doublet)	C-4
	3.35 (doublet)	exo C-8 or anti C-9
	1.96 (doublet)	exo C-8 or anti C-9
	0.56 (doublet)	C-1
	8.74	C-4
19	7.70	C-4
	2.66	
	1.20	
	0.71	
	0.49	
	0.14	
	0.14	
	2.35 (triplet)	anti
	0.20 (triplet)	syn
	0.09 (quartet)	Aromatic

^aData from ref 14 and 20.

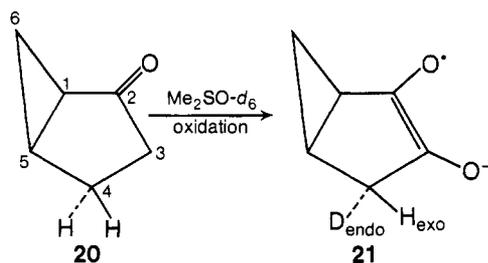


protons adjacent to the spin label. Semidiones derived from bicyclo[3.1.0]hexane have been investigated by Russell, McDonnell, and Whittle²²⁻²⁴ and the bicyclo derivatives of cyclopentane have been studied by Russell, Talaty, and Horrocks.²⁵ The bicyclo[3.1.0]hexane-2,3-semidione radical anion and some of its deuterated derivatives exhibited large anti-proton coupling constants.^{22,23} The stereoselectivity of deuterium exchange for the ketone precursor **20** after oxidation allowed assignment of the exo and endo protons at position 4 in **21**.²² Several alkyl-substituted derivatives were stud-

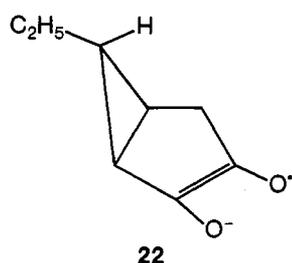
TABLE IV. Hyperfine Splitting Constants for Bicyclo[3.1.0]hexane-2,3-semidione and Some Alkyl Derivatives^a

Substituents	Coupling constant	Assignment
4-endo-Deuterio	7.9, 2.3, 0.8, 4.0	exo C-4, endo C-4, syn C-6 and C-5, anti C-6 and C-1
6-syn-Deuterio	14.9, 7.9, 4.0, 0.8	endo C-4, exo C-4, anti C-6 and C-1, C-5
4-endo, 4-exo-Dideuterio	2.3, 1.2, 4.0, 0.8	endo C-4, exo C-4, anti C-6 and C-1, syn C-6 and C-5
	14.9, 7.86, 4.0, 0.79	endo C-4, exo C-4, anti C-6 and C-1, syn C-6 and C-5
6,6-Dimethyl	14.59, 7.62, 5.08, 0.90, 0.45	endo C-4, exo C-4, C-1, C-5, anti CH ₃ , anti C-6
1-Isopropyl-4,4-dimethyl	4.83	
1-Isopropyl-exo-4-methyl	13.85, 4.90, 0.70, 0.58	endo C-4, anti C-6, C-5, C-6 syn
1-Isopropyl-endo-4-methyl	6.20, 4.80, 0.82, 0.58	exo C-4, anti C-6, C-5, syn C-6
6-anti-Methyl	14.6, 7.6, 4.3, 0.9, 0.4	endo C-4, exo C-4, C-1, C-5(?), CH ₃

^aData from ref 3 and 22.

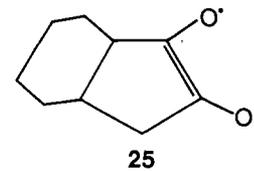
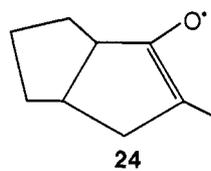
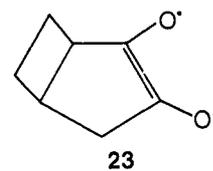


ied and the assignments are presented in Table IV. The absence of any splitting for the endo 4-methyl protons (see Table IV) is indicative of the rapid attenuation of the hyperfine coupling constants when preferred stereochemical environments do not occur. Also to be noted is the absence of any coupling for methyl protons at syn C-6, though anti C-6 methyl gives rise to a small coupling. An interesting feature of the preparative chemistry of these semidiones is the formation of **22** either by oxidation of the *syn*- or *anti*-6-ethylbicyclo[3.1.0]hexan-2-one precursor in basic Me₂SO.²³ A similar

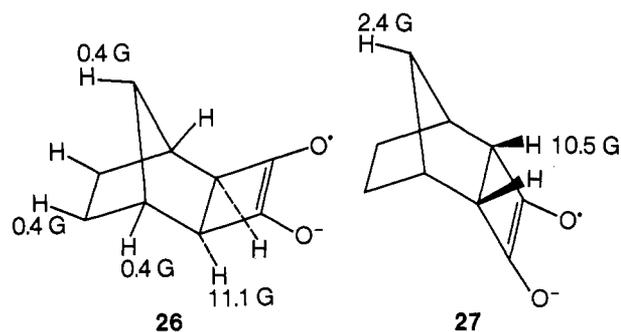


conversion was observed for the *syn*-6-methoxymethyl derivative with cesium *tert*-butoxide as base. Oxidation in the presence of the weaker base potassium *tert*-butoxide yielded a complex spectrum which converts to the same spectrum produced using CsOC(CH₃)₃ as base.

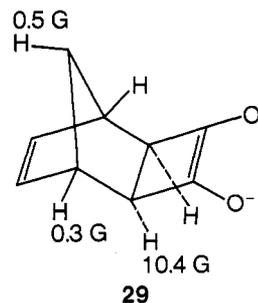
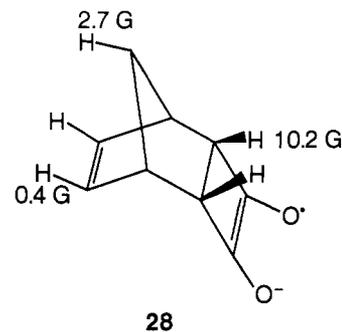
The bicyclo[3.2.0]heptane semidione **23** appears to lack a favorable stereochemistry since no long-range couplings have been detected.²⁵ The semidiones **24** and **25** also do not give to any long-range hyperfine couplings.



Russell and Whittle²⁶ investigated several semidiones derived from acyloin condensation reactions. The radical anions **26** and **27** showed interesting features. The long-range cou-

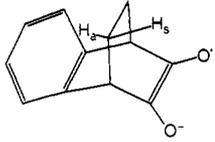
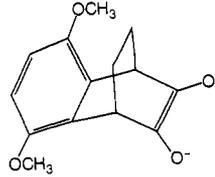
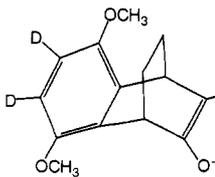
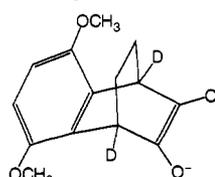
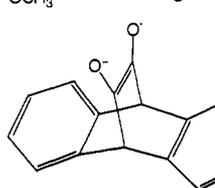


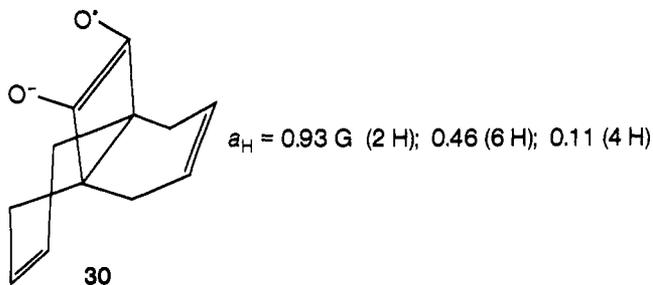
pling was considerably altered for the changes in conformation shown in structures **26** and **27**. A further interesting feature is the appearance of additional hyperfine structure on introducing unsaturated character as in **28**. The unsaturated analogue of **26** has also been investigated,²⁷ and it appears that no vinylic coupling takes place for this radical, **29**.



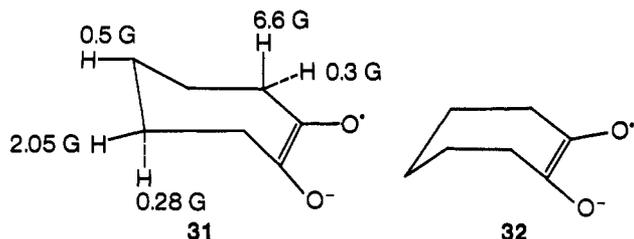
Fritsch and Bloomfield²⁸ have studied some interesting semidione systems. However, the only semidione which could be fully analyzed, though position assignments could not be made, was **30**. The radical anion can exist in conformations other than the one depicted by structure **30**. The one shown and its mirror image are likely of lowest energy. Russell et al.²⁷ have investigated an analogue of **30** in which the vinyl protons are replaced by methyl groups. They find $a_H = 0.87$ G (2 H), 0.35 G (2 H), 0.28 G (4 H) and $a_{CH_3} = 0.07$ G (2).

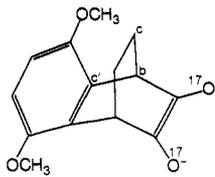
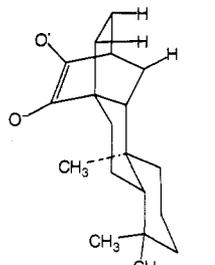
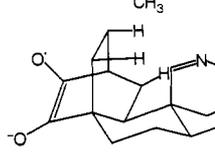
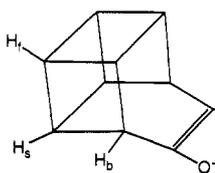
TABLE V. Hyperfine Constants for Some Unsaturated Bicyclo[2.2.2]octane Semidiones^a

Semidione	Coupling constants, G
	$a_a(2) = 2.35$, $a_s(2) = 0.20$, $a(4) = 0.09$
	$a_a(2) = 2.28$, $a_s(2) = 0.29$
	$a_a(2) = 2.32$, $a_s(2) = 0.28$
	$a_a(2) = 2.39$, $a_s(2) = 0.29$
	$a(8) = 0.15$

^a Data from ref 20.

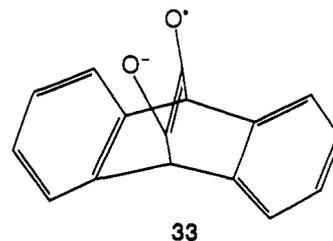
The monocyclic semidione derivatives were the subject of the investigations of Russell, Underwood, and Lini.²⁹ The radical anion which is of most interest is the cycloheptane semidione **31**, chair conformation, and **32**, boat conformation. These authors concluded that the conformation of the cycloheptane semidione could not be inferred from the observed long-range coupling constants. Further work by Russell and Keske³⁰ on **31** and its derivatives led these authors to conclude that only the chair conformation is populated at temperatures up to 70°C. These authors also investigated the conformations of some bridged semidione derivatives.³¹

TABLE VI. Hyperfine Constants for Some Semidione Derivatives^a

Semidione	Coupling constant, G
	$a(2) = 2.82$ (anti) $a(2) = 0.29$ (syn) $a = 6.15$ (¹³ C); b, c, c' $a(2) = 9.95$ (¹⁷ O)
	$a(3) = 2.3$
	$a(3) = 2.2$
	$a(4) = 0.53$ (H_s) $a(2) = 0.09$ (H_b or H_f)

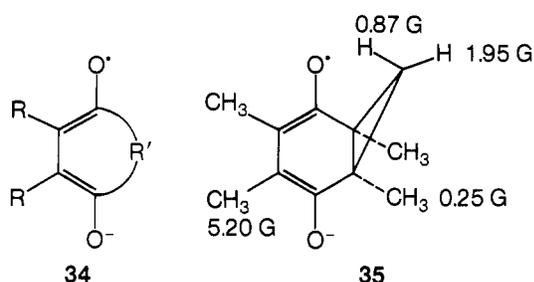
^a Data from ref 19, 20, and 270.

Several benzene analogues of the bicyclic radicals have been investigated.^{20,32} Some typical results are presented in Table V. A result of interest is the appearance of hyperfine interactions with all eight aromatic protons of **33**. This is to be contrasted with results for other spin labels discussed in following subsections. Table VI illustrates the results found for a few novel semidiones.



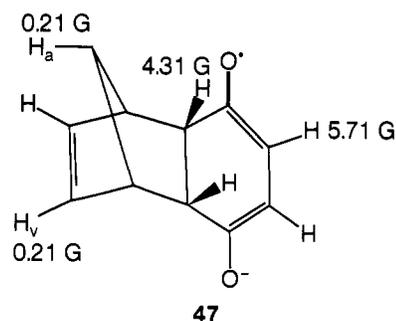
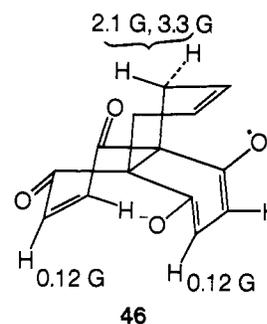
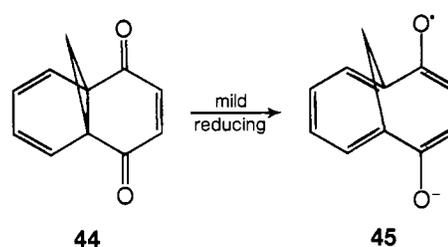
Russell and Holland³³ have examined the possibility of non-classical structures for the bicyclic radicals. This was carried out by studying the stereochemistry of the reaction of 7-*syn*- and 7-*anti*-bromonorbornene with tri-*n*-butyltin deuteride followed by subsequent conversion to the semidione radicals. These authors found that, although there is some stereospecificity in the reaction, it was concluded that it is not necessary to describe the results in terms of nonclassical structures. This work is a fine example of the possible applications that may be made, based on the stereospecific long-range couplings that are observed in such radicals.

Russell, Ku, and Lokensgard³⁴ have studied some bicyclic derivatives belonging to the 2,5-semidione spin label **34**. The semidione **35** was investigated^{34,35} and this was used to support the assignment of structure for the radicals produced from the reactions of **36**, **37**, **40**, and **41** to respectively **39** and **43**.³⁴ These reactions can be contrasted with the conversion of **44** to **45**. The 2,5-semidione spin label **34** exhibits

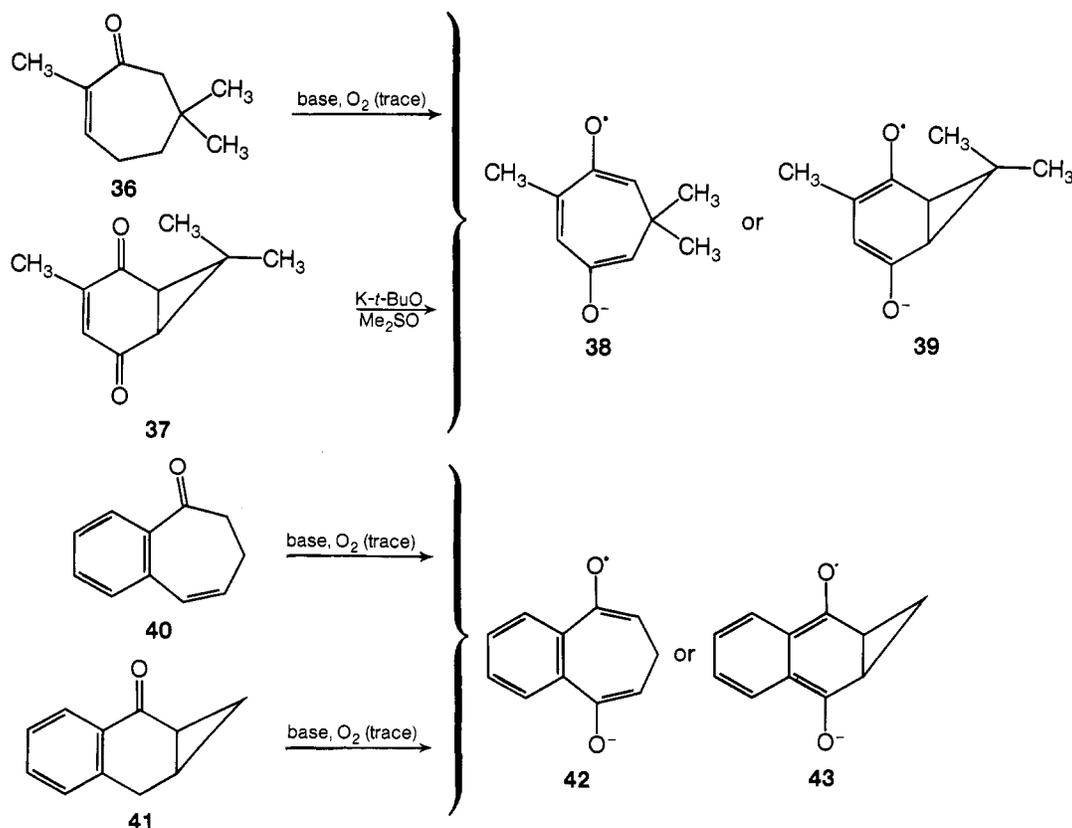


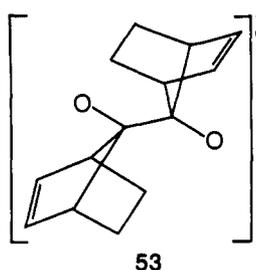
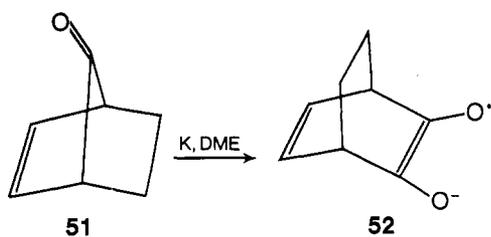
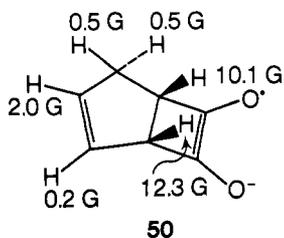
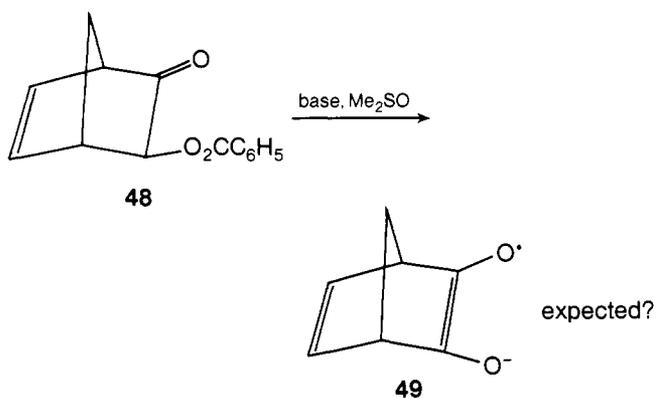
somewhat smaller long-range hyperfine couplings than those obtained for the related 2,3-semidiones. This has in part been rationalized by the particular differences in the symmetry of the highest occupied π molecular orbitals of the two spin labels. A 2,5-semidione propellane free radical has been prepared and tentatively assigned the conformation **46**.³⁶ The two major coupling constants are not as sensitive to the stereochemistry as may have been expected. Radical **35** exhibits a similar lack of sensitivity to stereochemistry for the long-range couplings. This is to be contrasted with radicals such as **5** and **6**. This lack of sensitivity arises in numerous radicals when the highest occupied π molecular orbital is of opposite symmetry (with respect to the appropriate symmetry planes, discussed in detail in section IV.B) to that of the 2,3-semidione spin label. Nelson and Trost³⁷ have examined the radical **47** and found small stereoselective long-range coupling. Russell and Whittle²⁶ have commented on the apparent anomaly for the splittings a_{H_v} , a_{H_a} compared with the corresponding 2,3-semidione radical. a_{H_v} in **47** is approximately half the value found in **28**, while the a_{H_a} value is different by a factor of about 13. These observations cannot be rationalized on the basis of symmetry arguments alone.

Russell and Schmitt³⁸ found that the product from the reaction of **48** with base did not yield the long-range couplings expected of **49**; instead the ESR spectra suggested assignment to the radical **50**. Another interesting chemical rearrangement which has been inferred from a study of the long-

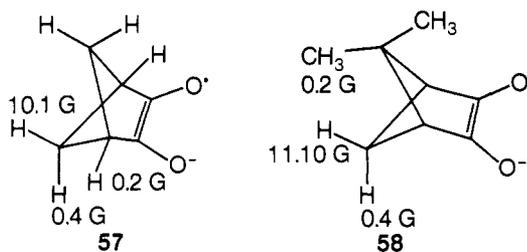
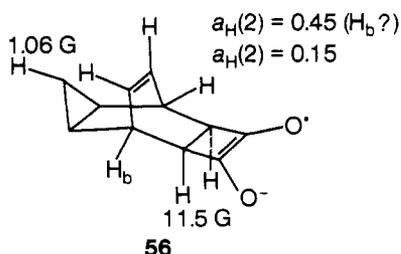
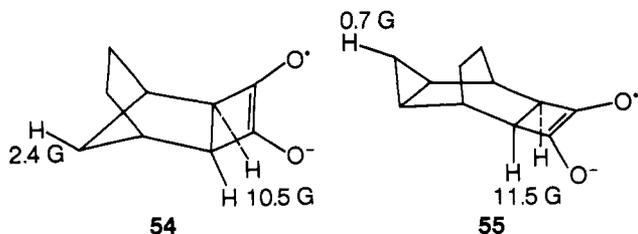


range couplings is the conversion of **51** to **52**.³⁹ Though the mechanism has not been elucidated, the dimeric species **53** has been suggested as a possible intermediate in the rearrangement.





Fairly substantial long-range couplings have been observed for some polycyclic cyclobutane semidione radicals. Structures **54**, **55**, and **56** are representative.²⁷ The largest long-range proton hyperfine couplings observed to date for the semidione spin label are those obtained from bicyclo-[2.1.1]hexane and its derivatives. Radicals **57** and **58** are examples.⁴⁰



B. Semiquinones

All the other spin labels that have been employed have not been so exhaustively studied, compared with the work of Russell and associates on the semidione systems. The semiquinone spin label **59** has been extensively investigated. Generally, the observed long-range couplings for the semiquinone derivatives are a good deal smaller than their counterparts in the semidione series. This can be rationalized to a fair degree, though not exclusively, by the symmetry properties of the highest occupied molecular orbital of the semiquinone label and by the more extended skeleton over which the π -electron delocalization may occur.

Stock and Suzuki⁴¹ carried out an investigation of some dibenzobicyclo derivatives of the semiquinone spin label, for example, **60**; however, they found no evidence for the delocalization of spin density in the neighboring phenyl groups. Kosman and Stock⁴² observed that several unsaturated bicyclic semiquinone derivatives related to **61** did reveal long-range hyperfine couplings. The initial assignment of protons H_a and H_b was based on comparison with the work of Russell and Chang.¹³ Since then, a sufficient number of derivatives have been prepared by Stock and coworkers⁴³⁻⁴⁶ and Russell et al.²⁰ which have substantiated this assignment. Nelson and Trost³⁷ have examined the saturated analogue of **61** and found a sizable reduction in the long-range couplings. Kosman and Stock⁴³⁻⁴⁵ have attempted to provide a conceptual

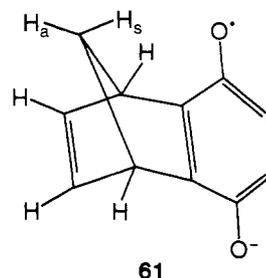
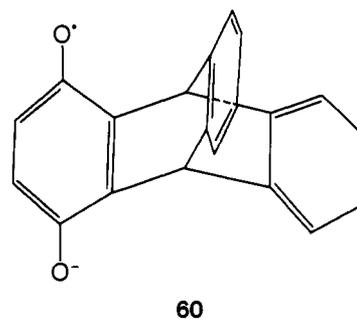
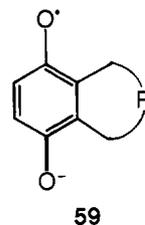


TABLE VII. Coupling Constants for Some Semiquinone Derivatives^a

Semiquinone	Coupling constant, G	Semiquinone	Coupling constant, G
	$a_1(2) = 2.36$ $a_a(1) = 0.80$ $a_{s,v}(3) = 0.40$		$a_1(2) = 2.55$ $a_a(1) = 0.47$ $a_v(1) = 0.47$
	$a_1(2) = 2.38$ $a_v(2) = 0.52$		$a_1(2) = 2.37$ $a_1(2) = 2.40$ $a_{F_B} = 0.15$
	$a_1(2) = 2.34$ $a_v(1) = 0.52$		$a_1(2) = 2.42$ $a(4) = 0.22$ (H_{en}, H_s, H_{sen} or H_{en}, H_s, H_{sex}) $a_a(1) = 0.65$ $a_b(2) = 0.10$
	$a_1(2) = 2.05$ $a_v(1) = 0.86$ $a_v(1) = 0.46$		$a_1(2) = 2.78$ $a_a(4) = 0.45$
	$a_1(2) = 2.72$ $a_{v,a}(4) = 0.54$ $a_s(2) = 0.13$		$a_1(2) = 2.70$ $a_a(2) = 0.49$
	$a_1(1) = 2.51, a_v(1) = 0.54$ $a_1(1) = 2.18, a_s(1) = 0.34$ $a_a(1) = 0.81$		$a_1(2) = 2.68$ $a_a(2) = 0.54$ $a_s(2) = 0.09$

^a Data from ref 42, 44-46.

understanding of the mechanistic pathways by which large long-range hyperfine couplings may be deduced. These mechanisms are best elucidated in comparison with other spin labels, and this is discussed in sections III and IV.B. To exemplify the diversity of compounds studied, we present a cross section of the observed results for the semiquinone spin label in Table VII.

There are a few qualitative features worthy of mention at this point. The introduction of further unsaturation is often observed to produce an additional coupling due to the syn protons of the bridging group. For example, the saturated analogue of **61** gives rise to no detectable syn proton coupling. Similar results are noticed for other radicals; see Table VII.

Although Stock and Suzuki⁴¹ found no evidence for long-range couplings in **60**, Anderson et al.⁴⁶ were able to detect fluorine hyperfine coupling in **62**, though not for **63**. Brodskii et al.⁴⁷ found no detectable long-range couplings from a variety of triptycene semiquinone derivatives. The triptycene-like semiquinone systems appear to have a far too extensive skeleton for any long-range couplings comparable to **61** to be observed by ESR.

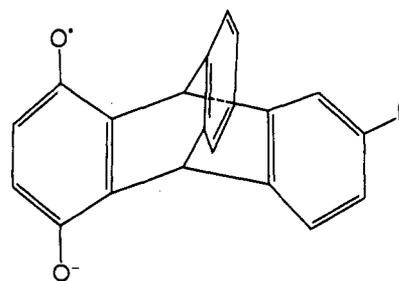
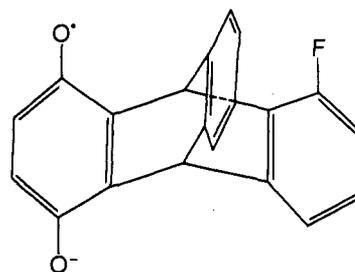
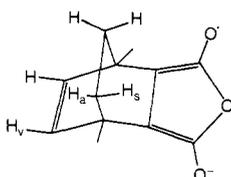
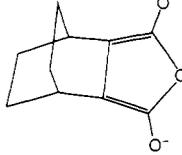
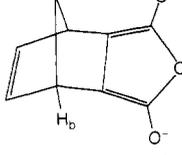
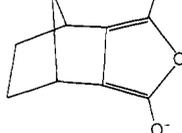
**62****63**

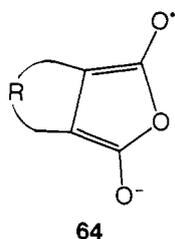
TABLE VIII. Hyperfine Coupling Constants for Some Semifuraquinone Systems^a

Semifuraquinone	Coupling constant, G
	$a_a = 1.55$ $a_v = 1.18$ $a_s = 0.33$
	$a_a = 1.36$ $a_s = 0.27$
	$a_a = 1.41$ $a_{v,s} = 0.79$ $a_b = 0.40$
	$a_a = 1.03$ $a = 2.04$ (exo) $a_b = 0.37$ $a = 0.27$ (endo) $a_s = 0.47$

^a Data from ref 48.

C. Semifuraquinones

Nelson and Seppanen⁴⁸ were the first workers to employ the semifuraquinone spin label **64** for the detection of long-



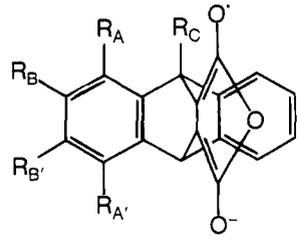
range couplings. Additional studies with this label have been carried out by Nelson et al.^{49,50} and Stock et al.^{46,51} In Table VIII, the results for representative long-range coupled semifuraquinone derivatives are presented. Generally, the observed long-range coupling constants for the semifuraquinone radicals are slightly larger than the corresponding semiquinone derivatives. Both these spin labels have the same symmetry properties for the highest occupied molecular orbital, so similarities are to be expected.

The introduction of additional unsaturated character for the semifuraquinone radicals leads to slightly enhanced long-range couplings. This behavior parallels that found in the semidione and semiquinone series. Stock and coworkers^{46,51} have investigated a number of semifuraquinone derivatives of the substituted bridged anthracene moiety. For some fluoro derivatives, small long-range proton couplings are observed, which are not resolved with the corresponding semiquinone spin label. These results are tabulated in Table IX.

D. Nitroxide and Iminoxy Radicals

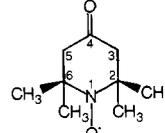
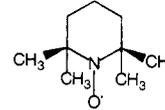
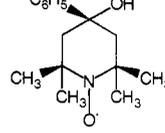
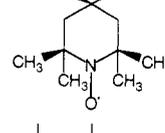
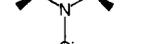
The available data on the nitroxide and iminoxy radicals which exhibit long-range coupling is extensive. The nitroxide spin label affords one advantage over the other spin labels

TABLE IX. Hyperfine Coupling Constants for Bridged Anthracene Derivatives of the Semifuraquinone Spin Label^a

				
R _A (R _{A'} = H)	R _B	R _B	R _C	Assignment
H	H	H	H	$a_{H_B}(4) = 0.12$
F	H	H	H	$a_{H_B}(4) = 0.12$ $a_F = 0.12$
H	F	H	H	$a_{H_B}(3) = 0.12$ $a_F = 0.62$
H	CH ₃	CH ₃	H	$a_{H_B}(2) = 0.11$
H	H	H	F	$a_{H_B}(4) = 0.13$ $a_F = 1.26$

^a Data from ref 46 and 51.

TABLE X. Proton Isotropic Coupling Constants for Nitroxide Derivatives Determined from NMR Shifts

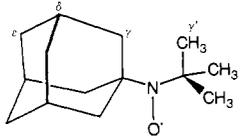
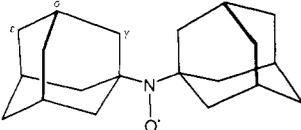
	Coupling constant, G	Assignment
	-0.11 ^a -0.01	Methyl Methylene
	-0.22 ^a -0.39 +0.18	Methyl Methylene (3,5) Methylene (4)
	-0.44 ^b -0.08 -0.31 -0.50 0	Methyl (ax) Methyl (eq) Methylene (ax) Methylene (eq) Phenyl
	-0.45 ^b -0.02 -0.31 -0.48 +0.07	Methyl (ax) Methyl (eq) Methylene (ax) Methylene (eq) H ₄
	-0.107 ^c	Methyl

^a Data from ref 61. ^b Data from ref 64. ^c Data from ref 66.

discussed thus far. This concerns the fact that certain nitroxide radicals have been investigated by NMR, which has provided valuable information as to the sign of the long-range coupling constants. Rassat⁵² and Janzen⁵³ have summarized some of the conformational aspects of nitroxide radicals as determined by ESR.

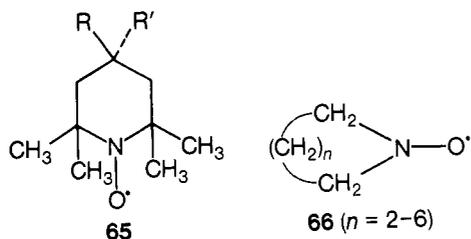
The early studies of monocyclic nitroxides⁵⁴⁻⁵⁹ of the basic form **65**, gave no indication of any long-range proton hyperfine coupling. Several groups have examined the NMR of nitroxides related to **65**.⁶⁰⁻⁶⁴ In Table X, some typical results are presented. These studies are important because they illustrate that the methyl coupling constant is negative and that long-range splittings are not all of the same sign. Watanabe

TABLE XI. Isotropic Hyperfine Coupling Constants for Adamantane Nitroxide Derivatives from NMR Shifts^a

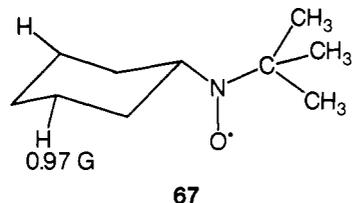
	Coupling constant, G	Assignment
	-0.42	γ
	+0.54	δ
	-0.04	ϵ
	-0.02	ϵ
	-0.04	γ'
	-0.41	γ
	+0.54	δ
	-0.04	ϵ
	-0.02	ϵ
	-0.02	ϵ

^aData from ref 86.

et al.⁶⁵ have obtained ESR spectra for some 4-derivatives of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl, i.e., **65** with R = OH, R' = CH₃, C₂H₅, etc., in which the adjacent methyl hyperfine coupling has been resolved. The values obtained are all in the range -0.34 to -0.43 G (negative couplings by comparison with Table X).



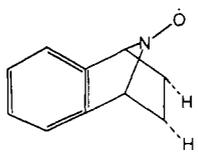
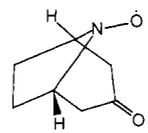
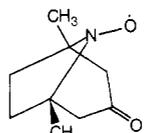
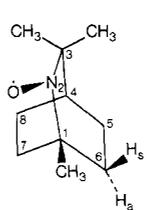
Long-range proton hyperfine splittings observed for the dialkyl nitroxide radicals are usually fairly small or nonexistent.⁶⁶⁻⁷⁴ Typically, values for $|a_{H\gamma}|$ are approximately 0.4 G or less. Hudson and Hussain⁷⁵⁻⁷⁷ have examined the conformational preference for a series of monocyclic nitroxides **66**, and related systems. For $n = 2$, $a_{H\gamma} = 0.47$ G, and for $n = 3$, $a_{H\delta} = 0.75$ G, with no other γ or δ couplings being recorded. A number of groups have examined a variety of monocyclic nitroxide derivatives.⁷⁸⁻⁸⁵ Windle et al.⁷⁹ found for **66**, with $n = 3$, that $a_{H\gamma} = 0.65$ G and this splitting is accidentally equivalent with the splitting constant of the equatorial δ proton. The measurement of these coupling constants is indicative of the stereospecificity that occurs for various conformations. Wajer et al.⁷⁸ noted similar effects in **67**. The appearance of couplings such that $a_{H\delta} > a_{H\gamma}$ is highly suggestive of a cer-

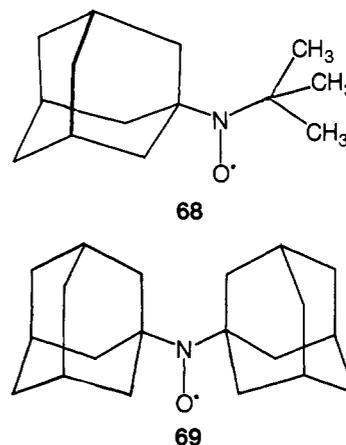


tain conformational preference for this radical. Morat and Rassat⁸⁶ have examined the NMR of some adamantane nitroxide derivatives (**68** and **69**) and were able to make assignments shown in Table XI. Once again, $|a_{H\delta}| > |a_{H\gamma}|$, and, secondly, there is an alternation in sign for $a_{H\gamma}$, $a_{H\delta}$, and $a_{H\epsilon}$. A variety of bicyclic nitroxide derivatives have been examined by several groups.⁸⁷⁻⁹³ As would be expected, some moderately large and stereoselective long-range hyperfine couplings are recorded. Table XII illustrates some of the variations in sign which have been recorded.

The iminoxy label has been employed to examine a number of alkyl, monocyclic, and bicyclic radicals.⁹⁴⁻¹⁰⁴ There are two possible conformational isomers for each of the un-

TABLE XII. Hyperfine Coupling Constants for Representative Bicyclic Nitroxides from ESR and NMR Studies

	Coupling constant, G	Assignment
	$a_N = 22.7^a$	endo Aromatic
	$a_H = 1.44(2)$	
	$a_H = 0.77(4)$	
	$a_N = 20^b$	C-1, C-5 C-2, C-4 (ax) C-2, C-4 (eq) C-6, C-7 (exo) C-6, C-7 (endo)
	$a_H = 5.75$	
	$a_H = 1.25$	
	$a_H = 2.5$	
	$a_H = 0.1$	
	$a_H = 0.2$	
	$a_N = 19.5^b$	Methyl C-1, C-5 C-2, C-4 (ax) C-2, C-4 (eq) C-6, C-7 (exo) C-6, C-7 (endo)
	$a_H = -0.44$	
	$a_H = -1.3$	
	$a_H = 2.3$	
	$a_H = -0.15$	
	$a_H = -0.3$	
	$a_N = 17.4^c$	C-6, C-7 (anti) C-6, C-7 (syn) CH ₃ (C-1) CH ₃ (C-3) C-4 C-5, C-8 (syn) C-5, C-8 (anti)
	$a_H = 3.5$	
	$a_H = -0.63$	
	$a_H = -0.21$	
	$a_H = -0.34$	
	$a_H = -0.28$	
	$a_H = 0.21$	
	$a_H = 0$	
	$a_H = 0$	
	$a_H = 0$	
$a_H = 0$		

^aData from ref 91. ^bData from ref 90. ^cData from ref 88.

symmetric iminoxy radicals. From a knowledge of the stereoselective long-range proton couplings, the conformation of a particular isomer can often be deciphered. The range of coupling constants is more or less similar to the nitroxide derivatives, though most likely the various mechanistic contributions for the two groups are somewhat different. There appears to be sufficient data available to make the iminoxy label an excellent probe for conformational studies. A cross section of some typical results is given in Table XIII.

E. Aliphatic and Alicyclic Radicals

While considerable attention has been directed toward studying monocyclic and, in particular, polycyclic derivatives which exhibit long-range coupling, a wealth of information on aliphatic and alicyclic radicals is also available. As pointed out at the onset of this section, various members of the aliphatic series serve as a guide as to what constitutes a large splitting, e.g., the *n*-propyl radical. A number of substituted aliphatic derivatives exhibit enhanced long-range coupling,

TABLE XIII. Hyperfine Coupling Constants for Some Bicyclic Iminoxy Radicals

	Coupling constants, G	Assignment
	$a = 1.95(4)^a$ $a = 0.88(1)$	$H_a, H_b, H_c,$ and H_d H_e
	$a = 4.4(1)^a$ $a = 2.0(2)$	H_a and H_b H_c
	$a = 2.35(3)^b$	$H_a, H_b,$ and H_c ($R = H, CH_3$)
	$a = 2.3(1)^b$ $a = 1.15(6)$	H_a Methyl (a, b)
	$a = 1.75(1)^b$	H_a

^a Data from ref 96. ^b Data from ref 98.

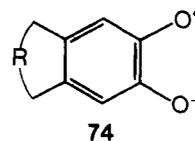
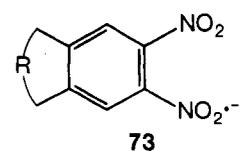
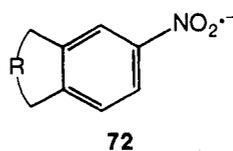
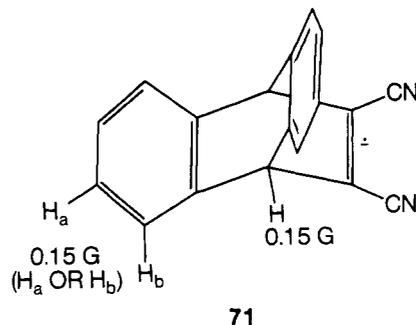
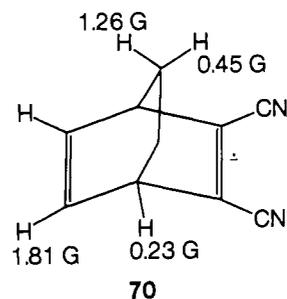
and this can probably be taken as a reliable guide to the possible stereochemical preferences of these radicals. All radical types except those which fit into sections II.A–II.D are incorporated within section II.E. Some order can be established by organizing the conglomerate of data according to the following classifications: (i) less extensively employed spin labels; (ii) bicyclic radicals produced by irradiation, uv, γ , etc.; (iii) cyclopropyl derivatives; (iv) adamantane derivatives; (v) aliphatic radicals (alkyl, oxygen derivatives, sulfur derivatives); (vi) alicyclic systems; and (vii) fluorine derivatives.

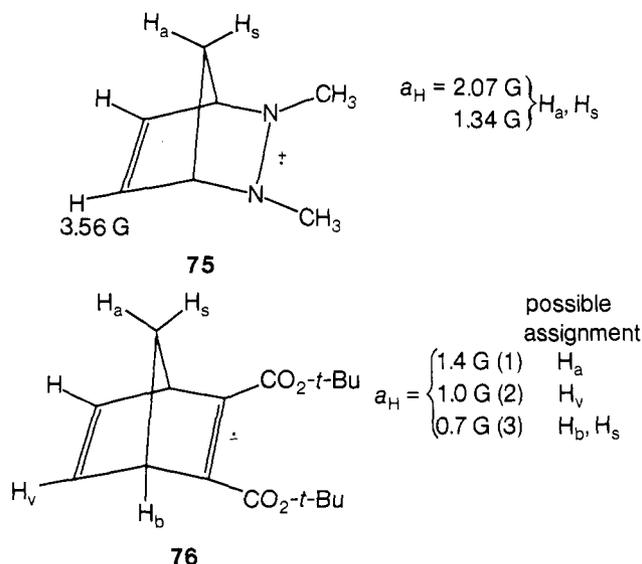
McKinney¹⁰⁵ utilized the dicyanoethylene group as a spin label in a study of two bicyclic derivatives **70** and **71**. The dicyanoethylene anion moiety has the same symmetry properties for the highest occupied molecular orbital as the semiquinone and semifuraquinone spin labels. The splitting constants for **70** are similar to those found for the semifuraquinone derivative (Table VIII); however, the splittings for the semiquinone analogue (Table VII) are a good deal smaller. Terabe and Konaka^{106,107} have employed the nitrobenzene (**72**), dinitrobenzene (**73**), and the *o*-semiquinone (**74**) spin labels to examine long-range coupling in a variety of bicyclic derivatives. Label **74** has a highest occupied molecular orbital (HOMO) whose symmetry is the same as the semidione radical anion label, while label **73** is the same as the semifuraquinone radical anion. Following a pattern of consistency, derivatives of **74** give rise to substantial hyperfine couplings, whereas the splitting constants observed for derivatives of **73** are comparable to results obtained for the semiquinone spin label. The correlation of the size of long-range couplings with HOMO symmetry is followed by the exo and anti protons; however, the syn couplings do not follow a completely systematic trend. Table XIV outlines some of the typical values found by Terabe and Konaka for the labels **72**, **73**, and **74**. Nelsen and coworkers have prepared several bicyclic cationic hydrazine derivatives,^{108–111} e.g., **75** and the diester deriv-

TABLE XIV. Coupling Constants for Some Bicyclic Derivatives of the Nitrobenzene, Dinitrobenzene, and *o*-Semiquinone Spin Labels^a

	Coupling constants, G
	$a = 3.10$ (anti) $a = 1.09(2)$ $a = 0.96(4)$ } H_b, H_1, H_{exo}
	$a = 1.46(1)$ H_{2exo} $a = 0.63(1)$ H_{b1} $a = 0.37(1)$ } H_{anti} $a = 0.24(1)$ } H_{b2} or H_{syn} $a = 0.24(1)$ H_{1exo}
	$a = 1.04(2)$ H_1, H_2 exo
	$a = 0.44(1)$ H_{b1} $a = 0.44(1)$ } H_{anti} $a = 0.26(1)$ } H_{syn} $a = 0.19(2)$ } H_{b2}, H_{v2}
	$a = 0.74(2)$ H_{exo}

^a Data from ref 107. See also Table XVI for further data on dinitrobenzene spin label.





ative **76**.¹¹² The hydrazine radical **75** (and others) are the first bicyclic cationic long-range coupled systems to be studied. No other radical cations for the other spin-labeled bicyclic radicals have yet been prepared.

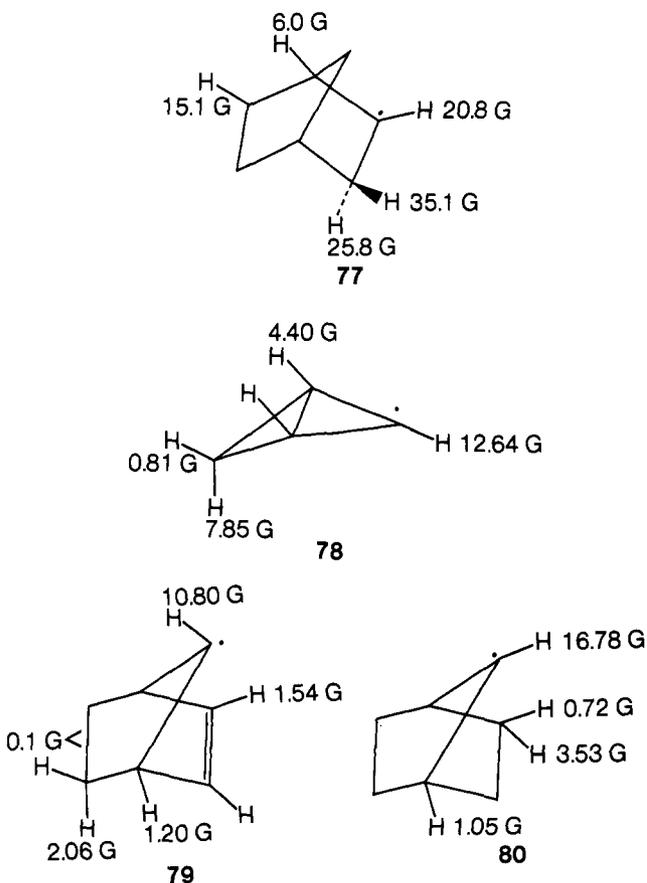
A number of bicyclic radicals exhibiting long-range coupling have been produced by γ irradiation of the parent hydrocarbon,¹¹³⁻¹¹⁷ photolysis of the perester precursors,¹¹⁸⁻¹²⁰ generation by rapid flow techniques from various saturated derivatives,^{121,122} and alkali metal reduction.¹²³ Gloux et al.¹¹⁵ and Marx and Bonazzola¹¹⁴ present fairly complete tabulations of hyperfine coupling constants for bicyclic radicals produced by γ irradiation. Some quite large long-range proton couplings have been assigned for some of these systems. Radical **77** gives rise to the largest long-range coupling yet reported. Surprisingly, no 6-endo splitting is observed, although line width factors may preclude such observations. Extensive deuterium substitution has not been carried out to corroborate these results. However, other related systems also appear to give rise to large γ -proton couplings.¹¹⁵ The splitting constants are found to be sensitive to methyl substitution at various sites. The bicyclobutyl radical (**78**) is an interesting system because of the observation of a quite large γ coupling. Krusic et al.¹²⁰ have assigned the splittings based on the results of INDO calculations to be $a_{endo} > a_{exo}$, contrary to what might be expected. Deuterium substitution work is certainly needed to confirm this assignment. The 7-norbornenyl radical (**79**) and the 7-norbornyl radical (**80**) give rise to long-range couplings which are substantial, but not excessively so, by comparison with **77** and its derivatives. For **79**, the order $|a_{endo}| > |a_{exo}|$ has been established by deuterium substitution studies.^{118,124}

Cyclopropyl derivatives have been studied extensively in connection with their conformational preferences.¹²⁵⁻¹³⁶ The likelihood that a strong conformational preference occurs for some cyclopropyl radical derivatives has been noted by Russell and Malkus.¹²⁶ The cyclopropylcarbinyl radical is one of the simplest radicals which shows long-range coupling. In Table XV are presented some results for this radical and its derivatives. The assignment for the ordering of the exo and endo proton coupling constants in Table XV was made on the basis of comparison with the work of Russell and coworkers¹³ and on the basis of an extended Hückel spin density calculation by Hoffmann.¹²⁸ The comparison with Russell and coworker's results may not be that meaningful, particularly in view of the results found for radical **79**. The extended Hückel calculations are not a sufficiently reliable guide, since the calculations for the endo proton are out by almost an order of magnitude. It is of some interest to note that the exo and

TABLE XV. Hyperfine Constants for the Cyclopropylcarbinyl Radicals^a

Radical	Coupling constants, G
	$a_\alpha = 20.74; a_\beta = 2.55; a_\gamma = 2.98$ (exo); $a_\gamma = 2.01$ (endo) ^b
	$CH_3 = 22.3; a_\alpha = 22.3; a_\beta = 2.9;$ $a_{\gamma_{1,2}} = 1.9; a_{\gamma_{3,4}} = 1.1$
	$CH_3 = 21.76; a_\beta = 2.27; a_{\gamma_{1,2}} =$ $1.69; a_{\gamma_{3,4}} = 1.27$
	$a_\alpha = 19.50; a_\beta = 4.04; a_{\gamma_{1,2}} =$ $2.27; a_{\gamma_{3,4}} = 1.75$
	$a_\alpha = 20.60; a = 0.78$ (CH_3), $a_{\gamma_{1,2}} =$ $3.51; a_{\gamma_{3,4}} = 1.95$
	$a_\alpha = 22.06; a_\beta = 28.37; a_\gamma = 0.63$ (for the trans radical)
	$a_\alpha = 22.06; a_\beta = 28.37; a_\gamma = 0.61;$ $a_\delta = 0.61$ (cis radical)

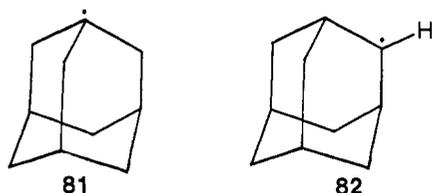
^a Data from ref 128 and 129. ^b The endo coupling is probably negative based on the results of INDO calculations.



endo proton couplings are fairly similar in magnitude, and this is indicative of the fact that the preferred conformation of the cyclopropylcarbinyl radical is not highly favorable for stereoselective couplings, though the γ couplings are still sizable. The proton contact shift method, which has become widely used to monitor long-range coupling constants,¹³⁷⁻¹⁴⁵ has been employed by Stock and Wasielewski¹³⁴ to determine the sign of the exo and endo proton coupling constants for some cyclopropyl radicals. They found that a_{exo} and a_{endo} dif-

fer only slightly in magnitude; however, a_{endo} is negative whereas a_{exo} is positive. Similar sign alternations are found for a_{endo} , a_{exo} and a_{anti} , a_{syn} in some bicyclic derivatives.^{141,144,145} The radicals 1-aziridylcarbonyl,¹⁴⁶ cyclopropylbenzene,¹⁴⁷ and triphenylcyclopropylsilane¹⁴⁸ do not show any long-range coupling.

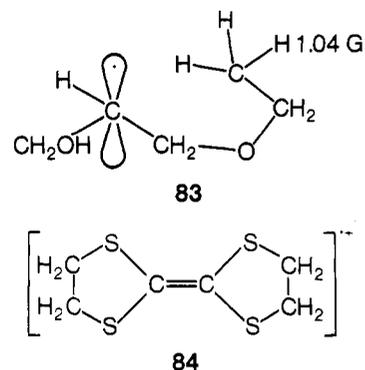
The adamantane system is the first bicyclic radical reported.¹⁴⁹ However, the observed spectrum was later identified by Jones¹⁵⁰ to be due to the benzene anion. γ irradiation of adamantane by different groups has produced conflicting results. Gee et al.¹⁵¹ reported that the 1-adamantyl radical **81** and the 2-adamantyl radical **82** were produced, with the latter



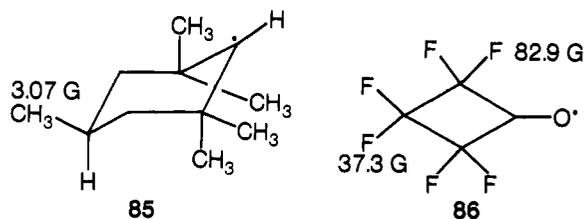
radical being assigned an extremely large γ -proton coupling of 23.6 G. Bonazzola and Marx¹⁵² obtained similar spectra but interpreted the results as arising from a substituted 1-methylcyclohexyl radical. Filby and Günther^{153,154} obtained results conflicting with the previous two studies. Ferrell et al.¹⁵⁵ have apparently observed the spectra of **82**; however, no γ couplings were resolved. Lloyd and Rogers¹⁵⁶ have investigated γ -irradiated adamantane by ENDOR. These authors argued that because the β proton is thought to be almost in the nodal plane of the "pi-orbital bearing the unpaired electron", the assignment by Ferrell et al.¹⁵⁵ of an approximately 5-G splitting to the β proton is incorrect. Instead these authors assumed, on the basis of INDO calculations, that the observed coupling of 3.55 G arises from two δ protons. The definitive work on adamantane is by Krusic et al.,¹⁵⁷ who have obtained the 1-adamantyl radical by photolysis of *tert*-butyl 1-peroxyadamantanecarboxylate. The splitting constants obtained were $a_{\text{H}_3} = 6.58$ G, $a_{\text{H}_\gamma} = 4.66$ G, $a_{\text{H}_\beta(\text{eq})} = 0.80$ G and $a_{\text{H}_\beta(\text{ax})} = 3.08$ G, the assignments based on INDO calculations. The large long-range δ coupling is to be noted, and this parallels the result of Lloyd and Rogers for the 2-adamantyl radical. Further studies on adamantane and derivatives have been carried out.^{86,158-161}

The aliphatic radicals,^{7,162} including oxygen and sulfur derivatives, give rise to γ and δ and even ϵ couplings which are surprisingly large in certain cases. The appearance of sizable γ couplings has been noted for some time as we pointed out at the start of section II. Dixon and Norman⁸ observed that the radical $\dot{\text{C}}\text{H}_2\text{C}(\text{CH}_3)_2\text{OH}$ gave rise to a γ hyperfine coupling of $a_{\text{H}_\gamma} = 1.3$ G which is substantial in comparison with a_{H_γ} for the *n*-propyl radical. Dixon and Norman¹⁶³ observed a coupling of $a_{\text{H}_\gamma} = 0.70$ G for the related radical $\dot{\text{C}}\text{H}_2\text{C}(\text{CH}_3)_2\text{COOH}$ and $a_{\text{H}_\gamma} = 1.4$ and 2.1 G for the radicals $\text{CH}_3\dot{\text{C}}\text{HOCH}_2\text{CH}_3$ and $\dot{\text{C}}\text{H}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$, respectively. The ether linkage substantially increases the possibilities for the observation of long-range coupling. Fisher⁹ and Smith et al.¹² noticed similar results for some ester derivatives.¹⁶⁴ A number of ether derivatives,¹⁶⁵⁻¹⁷¹ esters and related radicals,¹⁷²⁻¹⁷⁷ and sulfur derivatives¹⁷⁸⁻¹⁸³ have resulted in long-range couplings, usually less than 1 G. While it is possible to attribute γ proton couplings in the ether and ester series for which the heteroatom is adjacent to the "pi-orbital containing the unpaired electron", as arising from a simple delocalization scheme,¹⁶⁴ this will not be true for radicals in which the heteroatom is not adjacent. Smith et al.¹⁷⁰ have assigned a sizable coupling to the ϵ protons of **83**, which they interpret as suggestive of the conformation shown. Chambers et al.¹⁷⁸ have examined the radical **84** and have sug-

gested that even though the highest occupied molecular orbital may be partially delocalized over the sulfur 3p_z orbital, "alkyl protons linked to a π^+ system by a bivalent sulfur atom do not seem to arise predominantly from a hyperconjugation mechanism similar to that found for hydrocarbons".

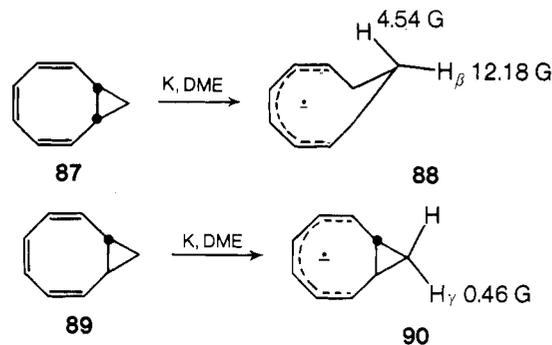


A number of alicyclic radicals and related systems have been examined.^{10,184-195} The most interesting long-range coupled system is **85**, for which Griller et al.¹⁹³ have observed an exceptionally large ϵ proton coupling $a_{\text{H}_\epsilon} = 3.07$ G. The only other large ϵ couplings are those reported by Smith et al.¹⁷⁰ and Russell et al.,⁴⁰ which are roughly one-third the value found for **85**. The similar species 4-methylcyclohexylketyl¹⁹⁵ does not give rise to any long-range coupling. Griller et al. have also noticed that conformationally similar nitroxide derivatives do not exhibit such long-range couplings.^{54,57,65,81}



γ and δ fluorine couplings have been observed in a number of radicals.¹⁹⁶⁻²⁰² The largest γ -fluorine couplings reported are those for the perfluorocyclobutanone ketyl **86**. A number of fluorine derivatives of the bridged anthracenes have been mentioned under the appropriate spin labels.

Observations of γ proton couplings have been recorded in a variety of partially hydrogenated aromatic systems,²⁰³⁻²⁰⁹ tryptcene derivatives,²¹⁰⁻²¹⁴ and alkyl aromatic derivatives.²¹⁵⁻²²⁰ The γ proton coupling constants have not been found to be excessively large, but their appearance makes possible deductions on structural conformations. There is a dearth of information available from ENDOR studies on these systems.^{215,216} Adams and Atherton²¹⁵ have made an interesting application for the 2,6-di-*tert*-butyl-4-cyclohexylphenoxy radical. The reaction of **87** and **89** to give **88** and **90**, in preference to other alternative products, has been partly ra-



tionalized in terms of the size of anticipated γ -proton couplings.²²¹⁻²²⁷

The intention of the above survey has been to exhibit the wide variety of structures and the appreciable range, $a_H \sim -2$ to $+15$ G, for which long-range coupled protons have been observed. This overview has proceeded according to various structural features, which in no way is intended to imply any special priorities to *this* division. However, certain rationalizations of long-range coupling based on HOMO symmetries, extent of delocalization of spin label, etc., may be made by classifying data more or less as has been done. Such general features which appear essential for the observation of large long-range couplings will be examined below in detail. In particular, can we predict a priori when to expect sizable long-range splittings in constrained and nonrigid structures? What conformations are favorable? Which substituents enhance or diminish such couplings?

III. Stereochemical Requirements

The early recognition of the general requirement of a frozen conformation on the time scale of an ESR measurement ($\sim 10^{-6}$ sec) as a prerequisite for the observation of sizable long-range couplings has been remarked upon at length. A radical in a constrained configuration may often position various nuclei in locations which are highly favorable for isotropic hyperfine interactions to occur, whereas for the case of a mobile species, in which many conformations are all in equilibrium, the observed hyperfine coupling is then a Boltzmann weighted average of the hyperfine splittings arising from each of the separate conformations. In this particular situation, the observed coupling constants tend to be smaller, since for only a small fraction of the time does the nuclei of interest reside in the most favorable position from the point of view of enhanced electron spin nuclear spin interactions. Also, it is well known that the sign of a long-range coupling constant is very sensitive to the conformation. Hence, the weighted Boltzmann average over possible conformations may in fact be small due to the cancellations of contributions which are equally large in magnitude, but are of opposite sign. These ideas seem to be supported by the results of Windle et al.⁷⁹ and others, who have observed that on warming solutions of various monocyclic radicals, the long-range couplings disappear when ring inversion becomes rapid. The idea of "rigidity" favoring enhanced long-range couplings does not automatically exclude aliphatic derivatives from exhibiting large long-range splittings. It appears necessary to conjecture that certain aliphatic radicals, for example, **83**, adopt highly preferred conformations in solution, in order to arrive at some rationale for the ESR observations. The difficulties here are that we are far less certain as to what the most preferred conformations of radicals such as **83** will be, while for the bicyclic radicals, *reasonable* estimates of the geometry can be made. There is a lack of evidence, both theoretical and experimental, to guide us sufficiently to accurately forecast the preferred conformations of aliphatic ether radicals such as **83**. Although the ESR results are indicative of various preferences, the conformations need to be known independently of the data which is to be rationalized. There are exceptions in which sizable long-range couplings are obtained which indicate that, even in the presence of free rotation, the stereochemical environment is particularly favorable as to allow the Boltzmann weighted average to be quite large. This is the case for radicals **83** and **85** in which the long-range couplings arise from freely rotating methyl groups.

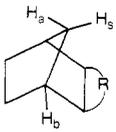
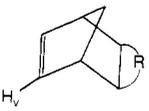
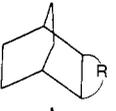
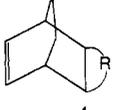
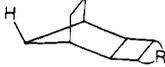
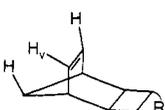
The polycyclic radicals typify the highly rigid structures that are most suitable candidates for the appearance of long-range coupling. Russell and coworkers in their first papers recognized the possibilities of an intimate connection be-

tween long-range coupling and the stereochemical environment, as exemplified by the bicyclic radicals. The bicyclic derivatives may be conveniently divided into two categories: (i) those whose σ moieties are saturated and (ii) unsaturated analogues. There are some comparisons between the two and some frequently occurring differences which can be noted. It has been suggested that the additional unsaturated character plays an important role in determining the size of various couplings. These changes have been discussed by invoking arguments pertaining to *orbital overlap* between the appropriate centers. While this line of thinking may be plausible to a certain extent, it is necessary to bear in mind that other factors which may be of greater importance need to be simultaneously considered, the simplest being the stereochemical perturbations which accompany the change from saturated to unsaturated σ moiety. Though such changes may be geometrically small, the effect for various long-range splittings may be significant. Secondly, the introduction of unsaturated character will lead to a redistribution of charge density in the vicinity of the particular C-H bonds of interest, and this will cause a reorganization of spin density around the same C-H bonds. Similar charge density reorganization can be induced by various substituents, for example, F and CH₃, which results in an appreciable modification of the long-range splittings in many instances. For example, the results for **8**, **9**, **10**, and **11** (see Table I) show the effects of methyl substitution on various long-range splittings. In Table XVI we present a comparison of the changes between saturated and unsaturated σ moieties for the different spin labels. It is apparent from Table XVI (see also **55** and **56**) that the introduction of unsaturation in the semidione derivatives enhances the long-range coupling constants at various locations. The same trend is followed by the semiquinone and semifurquinone derivatives. Evidently the symmetry properties of the HOMO of the spin label do not control this effect. The change for the dinitrobenzene spin label is interesting. The saturated system has no anti or syn proton coupling; however, the introduction of unsaturation causes the appearance of both couplings of approximately the same magnitude. The change in a_{anti} and a_{syn} on going from saturated to unsaturated derivative is usually an increment of approximately 0.1 to 1.6 G for both these couplings for the spin labels considered in Table XVI. Unfortunately, there is lacking a certain amount of data to examine these correlations further. Additional data for some of the missing entries of Table XVI would be valuable.

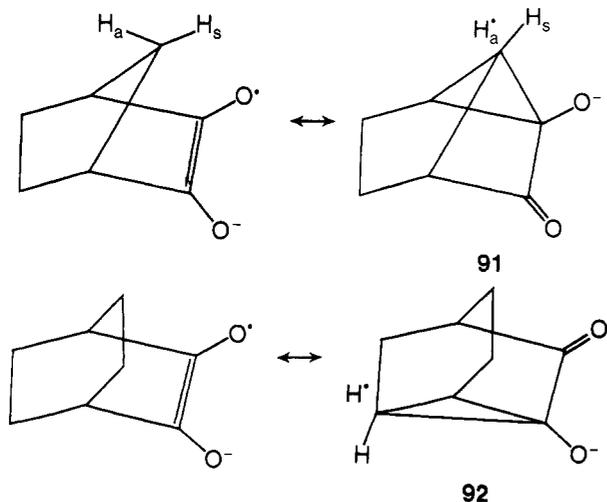
At this point it is perhaps appropriate to emphasize the lack of sign determinations for the hyperfine coupling constants listed in Table XVI. The importance of knowing the sign of the hyperfine coupling aids us in two ways. It allows a distinction to be made between two different presupposed mechanisms, whose estimated signs are different. Qualitative arguments are often sufficient for this purpose. Sign determinations have also been of assistance in laying to rest a number of calculations whose results have been in agreement with absolute experimental values, but of incorrect sign. For long-range coupling, the necessity of knowing both the magnitude and the sign are essential if an adequate theoretical basis for these results is to be established.

Intimately connected with the question of the importance of *orbital overlap* in discussing the effects of unsaturation on long-range coupling is the possibility of representing the bicyclic radicals by means of nonclassical structures. This concept was one of the early proposals advanced to rationalize the appearance of unpaired spin density in the σ -framework. Russell et al.^{19,20} proposed the following type of valence bond structures **91**, **92** for spin density to occur at the anti proton and the exo protons. These authors then compute the weights of such structures according to the observed hyperfine coupling. This procedure of calculating the weights of a

TABLE XVI. Comparison of Coupling Constants for Saturated and Unsaturated Analogues of Some Bicyclic Radicals

	2,3-Semidione	Semiquinone	Semifuraquinone	Dinitrobenzene ^g
	$a_a = 6.47^a$ $a_s = 0.41$ $a_b = 2.49$ $a_{\text{exo}} = 2.49$ a_{endo}	0.70 ^e	1.03 ^f 0.47 0.37 or 0.27 2.04	0.64
	$a_a = 8.08^b$ $a_s = 2.14$ $a_b = 1.04$ $a_v = 0.70$	0.80 ^e 0.40 0.40	1.41 ^f 0.79 0.79	0.35 0.23 or $\left. \begin{matrix} a_v \\ a_b \end{matrix} \right\} 0.10$
	$a_{\text{exo}} = 2.09^a$ a_{endo}	0.45 ^e	1.36 ^f 0.27	0.41 0.08
	$a_a = 2.60^c$ $a_s = 0.41$ $a_v = 0.41$	0.54 ^e 0.13 0.54	1.55 ^f 0.33 1.18	
	$a_H = 2.4^d$			
	$a_H = 2.7^d$ $a_v = 0.4$			

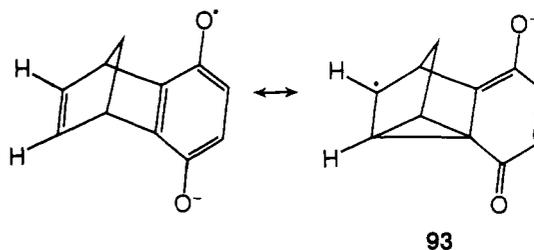
^aData from ref 19. ^bData from R. L. Blankespoor, *J. Am. Chem. Soc.*, **96**, 6196 (1974). ^cData from ref 20. ^dData from ref 27. ^eData from ref 45. ^fData from ref 48. ^gData from ref 107.



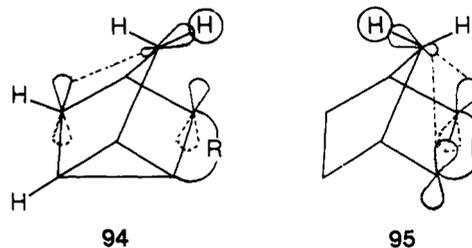
specific valence bond configuration by comparison with the observed hyperfine couplings is invalid. It excludes the possibility that spin density can occur at the appropriate protons by mechanisms other than that implied by structures such as **91** and **92**. Also a very important point which is usually overlooked is that several hybrid structures which *do not* themselves give rise to a hyperfine coupling contribution at the relevant proton, may markedly alter the weights of other valence bond representations which do produce a resultant spin density at the protons of interest. Another point which has not been given adequate explanation is why the anti proton representation **91** should be energetically more stable than the syn proton nonclassical analogue structure. Both structures would be anticipated to be of very similar energy and simple arguments would then lead to $a_{\text{anti}} \approx a_{\text{syn}}$, which is far from the case observed experimentally. Interactions represented by structures **91** and **92** have been referred to as *homohyperconjugation*.¹⁹

In connection with the question of the importance of the availability of unsaturated character in the σ moiety, Kosman and Stock^{42,43} have considered nonclassical structures such

as **93** to provide a possible explanation of the appearance of unpaired spin density at various centers in the σ skeleton.



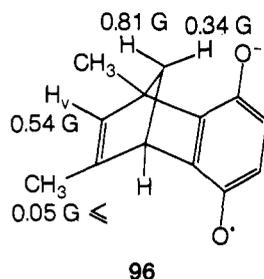
Nelsen and Trost³⁷ further proposed that a "back lobe overlap", as exemplified by structure **94**, takes place, which they suggest may provide a pathway for explaining the appearance of a_{syn} in several of the unsaturated derivatives. These authors also place emphasis on the possible "direct overlap" of the type depicted in **95**. While the trend that unsaturated



character in the σ moiety enhances long-range splittings seems evident, there appears to be no totally unambiguous evidence supporting the rationalization of such splittings constants by invoking "back lobe overlap" arguments.

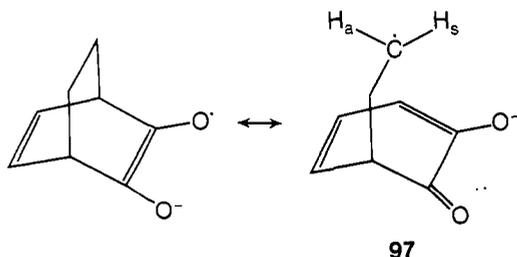
Kosman and Stock⁴⁴ have provided the following interesting argument as evidence *against* nonclassical structures such as **93**, which transfer spin density into the vinyl group of the σ moiety. They argued for the radical **96**, that

$$\frac{a_{\text{CH}_3}}{a_{\text{H}_v}} \approx \frac{\rho_C \pi B \cos^2 \theta}{\rho_C \pi Q} \approx -1$$

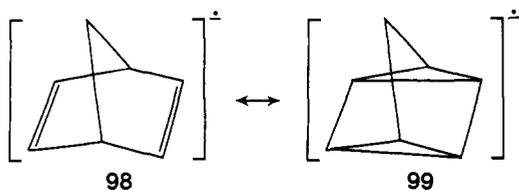


where B is about 50 G, $\cos^2 \theta$ is 0.5 and Q is approximately -25 G and ρ_{C^π} is the adjacent carbon π orbital unpaired spin density which appears to be approximately constant for the methylated and unmethylated derivatives based on a comparison of the hyperfine coupling constants. The experimental ratio is considerably different, and it was thus inferred that spin density is not "transferred" to the ethylenic π bond. The argument may be qualitatively correct but ignores the possibility that the C-H bonds of the methyl group or the C-H_v bond may experience, to very different extents, a through-space spin polarization (the meaning of this will be clarified later) directly from the π orbitals of the spin label. Such a mechanism could lead to a contribution of opposite sign to that obtained by the $B \cos^2 \theta$ mechanism, or of the same sign for the H_v proton. In this case the two mechanistic contributions could approximately cancel for the CH₃ protons and would be additive for a_{H_v} . In section IV it will be shown that spin polarization contributions of this size may appear. Such a consideration would, of course, invalidate the claim that electron exchange contributions (viewed classically or nonclassically) do not take place. The possibility that the $B \cos^2 \theta$ relationship may not be entirely valid for these systems has been raised.²²⁸

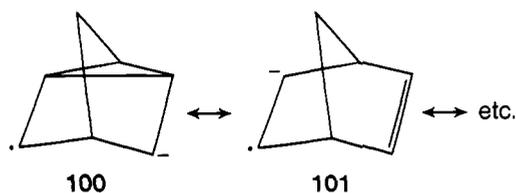
Russell et al.²⁰ have proposed a hybrid structure of the form of **97** to account for the observation that a_{anti} minus a_{syn} tends to remain roughly constant, when an ethylenic bond is introduced. In structure **97** both hydrogen atoms H_a and H_s would experience an additional equal increment. Before this simplistic picture can be adopted, it is necessary to understand the quantitative importance of hybrid structure **97** energetically, with respect to unsaturated analogues of structures such as **91** and **92**. Unfortunately, no group has been able to demonstrate via valance bond calculations that unsaturated analogues of structures **91** and **92** are much more important than **97**, which is required if the experimental results are to be rationalized. Other simple arguments such as that given by Nelsen and Trost cannot be totally excluded.



Hogevveen and de Boer¹²³ argued that the norbornadiene radical anion **98** did not rearrange to the anion of quadricyclene

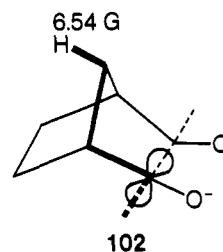


clene (**99**), since they were unable to prepare the radical anion by alkali metal reduction of quadricyclene. They have suggested that if structures such as **100** and **101** actually exist, and are not simply resonance hybrid structures, then rapid equilibration between different structures is proceeding at a rate greater than 6×10^8 c/s.

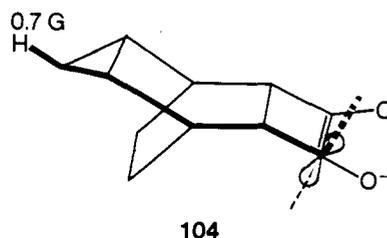
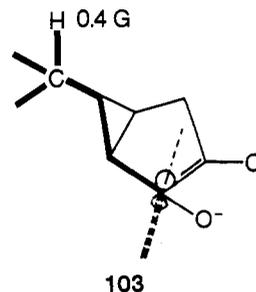


To this reviewer there appear to be no totally unambiguous or compelling data at the present time which can be unequivocally employed to demonstrate nonclassical structures for the bicyclic radicals. In other branches of norbornane chemistry, there has been considerable activity to resolve the question of the possibility of nonclassical structures. For the norbornane cation, at least, there appears to be evidence which supports the nonclassical structures in preference to a rapidly equilibrating set of classical structures.²²⁹⁻²³¹

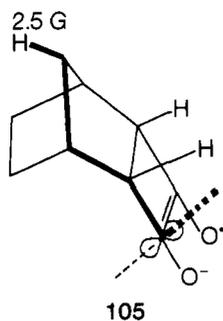
The most important empirical concept which has emerged is the so-called W plan proposed by Russell et al.^{13,14} to account for the stereoselectivity of long-range coupling constants. This concept embodies the basic stereochemistry that is usually required for sizable long-range coupling. Structure **102** illustrates the W plan or zigzag arrangement of bonds



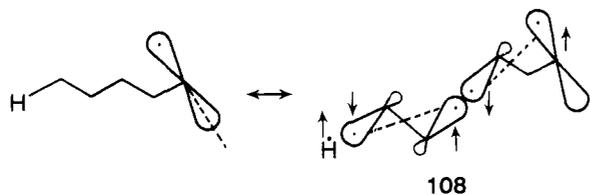
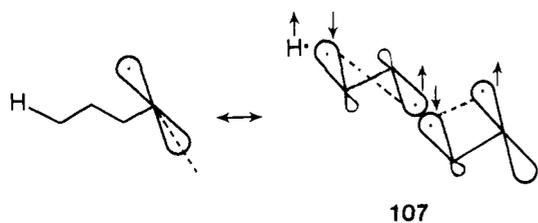
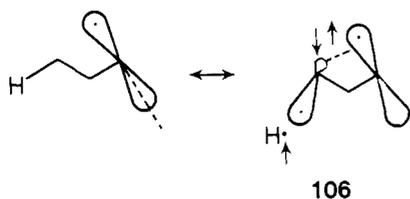
with respect to the $2p_\pi$ orbital of the semidione label. Russell et al.²⁴ have extended this empirical idea to even more distant protons by means of the 2.5V and 3V schemes. The W plan is simply the 2V arrangement of σ bonds with respect to the $2p_\pi$ orbital; 2.5V and 3V are illustrated in **103** and **104**. Russell and coworkers have suggested an approximate falloff of the hyperfine coupling by a factor of about three transgressing each step for $2V \rightarrow 2.5V \rightarrow 3V$. For example,



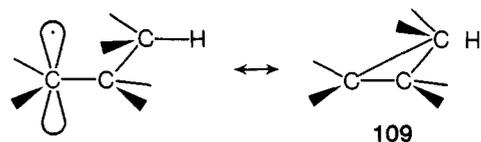
structures **102**, **105**, and **104** exemplify this trend. The hyperfine splitting for the CH₃ group of structure **103** does not arise from a rigid geometry, but rather a freely rotating group, and such cases are less easily correlated. There are, however, a number of examples which do not fit this trend. For example, the radical **85** can be represented by a 3V arrangement with a large coupling of $a_H = 3.01$ G, and **57** has a 10.1-G splitting for a 2V scheme. At the present time, no group has yet managed to predict any more reliable attenuation schemes than that suggested by Russell et al.²⁴ For spin labels other than the semidione, there is a shortage of information for these more remote coupling constants.



There have been few attempts to establish the W scheme on a more theoretically founded basis. One important study has been carried out by Ellinger et al.²³² who found that the calculated hyperfine coupling constants for γ protons of the propyl radical orientated in the W and in the opposite (anti-W) conformations exhibited marked changes. Unfortunately such a calculation does not really lead to any simple pictorial representation of the interactions taking place. From a semirigorous point of view, such a description is *not* possible from detailed ab initio calculations. However, intuitive understanding is considerably assisted by such simple models. Russell⁴ has attempted to provide a simple illustrative scheme for the interactions taking place in the 2V (**106**), 2.5V (**107**), and 3V (**108**) arrangements. Russell and coworkers³⁴ employed structures such as **106** to rationalize the low stereoselectivity of the long-range coupling constants in radicals such as **35**. The reviewer is not convinced by the utility of just this representation; however, it must be pointed out that these diagrams represent a simple extension of more familiar spin polarization diagrams, which have enjoyed considerable success as an

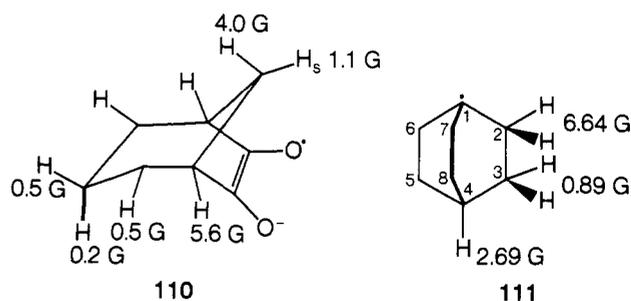


aid to understanding the mechanism producing a resultant spin density at protons in the node of the 2p_x orbitals in aromatic radicals. The limiting factor in these simple diagrams is that they provide no insight into the possible importance of other diagrams, and, equally important, they give no clear indication of the sensitive dependence of the hyperfine coupling constants on the stereochemistry. Similarly, the *homohyperconjugation* mechanism discussed earlier *does not* explain why there should be a preference for the anti proton and the syn proton to have widely differing hyperfine splittings. Eaton et al.²³³ and Underwood et al.²³⁴ have discussed the possibilities for hybrid structures such as **109**.



In summary, there have been no attempts to obtain semi-quantitative estimates of the importance of various hybrid structures **106**, **107**, **108**, and **109**, and hence there is no present way one can conclude that anti-W hybrid structures are unimportant. The intricate problem of the stereochemical dependence of long-range interactions has not yet been settled. The calculations of Ellinger et al.²³² are an important step in understanding the conformational dependence of the long-range couplings; however, their calculation has limitations which will be detailed in section IV.

The experimental findings do not all smoothly fit into the W plan. For example, radical **110** shows a sizable syn proton coupling constant²⁴ compared with other members of the semidione series. The cyclopropylcarbinyl radical (see Table XV) shows an even more noticeable lack of preferred stereoselectivity which is undoubtedly connected with the particular preference of this radical for the "bisected" conformation. The breakdown of stereoselectivity is noticeable in several of the radicals resulting from irradiation. Krusic et al.¹⁵⁷ found that for the 1-bicyclo[2.2.2]octyl radical (**111**), there is an appreciable δ coupling but a somewhat smaller γ coupling con-

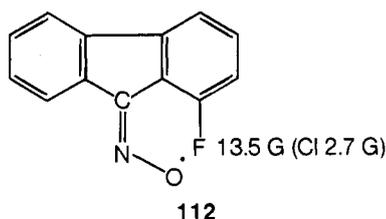


stant. These authors have attempted to rationalize these observations on the basis of a through-space delocalization via a parallel alignment of the C₁ π orbital and the bonds C₄-H, C₂-C₃, C₇-C₈, and C₅-C₆. However, Zimmerman and McKelvey²³⁵ found that for the anion radical of 1,4-diphenylbicyclo[2.2.2]octane, there was no evidence of electron delocalization between the two phenyl groups. If the suggestion of Krusic et al.¹⁵⁷ is significant, it points to the necessity of having a highly constrained and suitable geometry.

If the INDO assignment is correct, which should be at least slightly questionable, the bicyclobutyl radical (**78**) presents a drastic departure from the W plan. This example, however, requires verification by isotopic substitution studies. For the 7-norbornenyl radical (**79**) such an isotopic substitution study has been carried out by Kochi et al.¹¹⁸ Their findings of $a_{endo} \gg a_{exo}$ is contrary to expectations based on the W plan. If the assignment for bicyclobutyl radical is substantiated, then

the evidence suggests that some factors, presently not fully recognized as important, must be considered. Such a factor may be electron delocalization by more or less a simple spatial overlap of the appropriate orbitals. This mechanism, however, completely fails to provide a rationale for the observed coupling constants in the majority of bicyclic radicals. There is still completely lacking any satisfactory qualitative guide to an understanding of the appearance of an extensive number of smaller coupling constants (less than 1 G) which do not fit the W plan.

The concept of a direct overlap between the π orbitals of the label and the long-range protons has been emphasized by several authors. Indeed for radical 112²³⁶ it is difficult to envisage a mechanism as important as a through-space effect of one form or another. Such a mechanism may play a role in determining the values of some of the long-range coupled protons for the iminoxy radicals.



The main conclusions that seem to be supported by the majority of data concerning the stereochemical requirements may be summarized as follows. (i) Rigid or frozen σ skeletons are paramount to the observation of long-range couplings. (ii) An approximately coplanar zigzag arrangement of bonds with respect to the $2p_\pi$ orbital of the spin label consistently produce larger long-range interactions. (iii) Additional unsaturated character in the σ -moiety enhances such interactions. (iv) The magnitude of the long-range splittings changes dramatically with small structural changes which readjust the stereochemical location of the protons with respect to the spin label. (v) The magnitude of the coupling constant is frequently sensitive to substituents effects in the σ moiety.

An extensive amount of experimental data is available, which illustrates that long-range couplings are a sensitive probe of the stereochemistry, which in turn allows for the possibility of solving conformational problems, by incorporating various spin labels into the molecules of interest and monitoring the long-range splitting constants. Russell and co-workers^{25,30,31} have suggested this approach in several papers. The principal difficulty is the lack of concrete procedures to demonstrate that the radical derivatives and the precursors will maintain the same stereochemistry. This has been discussed by McConnell²³⁷ who has pioneered the idea of employing spin labels to study conformational effects. There still, however, remains considerable intrinsic interest in having a means to estimate the preferred conformations of radicals in solution and in frozen matrices.

Not too surprisingly, most of the studies which have made use of the stereoselectivity of long-range interactions have been restricted to the monocyclic radicals. Windle et al.⁷⁹ have made a particularly nice application of the observation of long-range interactions in the piperidine 1-oxyl radical. On the basis of the observed selective δ proton coupling, these authors were able to exclude conformations of the twist form, since for such a conformation the two δ protons would take up similar stereochemical conformations and hence be expected to couple equally, which is not the observed case. These authors have also noted for the same radical the collapse of the long-range hyperfine structure as the interconversion between different conformations begins to become rapid. Hence the observation of such couplings for the mono-

cyclic radicals can be taken as a guide to the temperatures at which frozen conformations occur. Russell and co-workers^{30,31} have made similar studies for monocyclic derivatives of various ring size for the semidione spin label. Russell et al.²⁵ have also attempted the study of a number of other systems, among them being some semidione steroid derivatives. Unfortunately, there was a pronounced lack of long-range interactions in these radicals. As Russell⁵ has remarked, it is considerably more reliable to make inferences based on the observation of long-range couplings rather than the lack of them.

Some interesting conformational applications have been made in the bicyclic radicals. Caldararu and Moraru⁹⁷ have been able to distinguish the two possible isomers in various substituted bicyclic iminoxy radicals. This is made possible by identifying the difference in the number of protons which are long-range coupled for the different isomers. Russell and Holland³³ have utilized the long-range interactions to monitor the stereochemical path of the reaction of 7-*anti*- and 7-*syn*-bromonorbornene with tri-*n*-butyltin deuteride. A number of valence isomerizations have been inferred by analyzing the long-range couplings for the various radical products produced. It is highly likely that many more applications of this kind will be carried out as the stereochemical implications of long-range interactions become quantitatively understood.

IV. Theoretical Analysis

A general theoretical understanding of long-range coupling has not yet been provided. The reasons for this situation are quite straightforward. The radicals exhibiting long-range interactions are fairly large and have far too many electrons to be attacked by anything other than semiempirical procedures. Equally important is the particular nature of the physical property that is being calculated. It is well recognized that accurate calculations of isotropic hyperfine coupling constants must incorporate various correlation effects if the results are expected to be of any value whatsoever. At the present time this is a very difficult assignment for large molecules. For long-range coupling constants, the magnitudes are small and this makes for further difficulties in calculating relatively accurate results.

A. σ - π Separability Problem

Before embarking on a discussion of the various model mechanisms which have been considered to play a role, the general question of σ - π separability requires some attention. This is a fairly central problem since a large majority of the systems exhibiting long-range coupling contain a π -electron moiety which is nonorthogonal to a σ -electron fragment. To make the language more precise, by π -electron moiety it is of course meant that the electrons occupy orbitals of π -symmetry and similarly for the σ -electron fragment, that orbitals of σ -symmetry are occupied. The σ - π separability problem encompasses considerations regarding the representation and construction of wave functions for groups of π and σ electrons.

The σ - π separability problem is well known in the theory of isotropic hyperfine interactions. In contradistinction to most other physical properties, the σ - π separability question plays an important role even for simple aromatic radicals in which the protons lie in the nodal plane of the π orbitals. To calculate the hyperfine couplings for such protons, the σ - π interactions must be adequately accounted for. McLachlan et al.²³⁸ have required in their rigorous derivation of McConnell's equation²³⁹ that the electronic ground-state wave function for the relevant fragment be written in the form $U(\pi)V(\sigma)$, where $U(\pi)$ and $V(\sigma)$ contain π - π and σ - σ correlations, re-

spectively. This ground-state representation gives rise to no hyperfine coupling for the aromatic protons. The coupling constants are calculated by allowing for σ - π interactions in first-order perturbation theory. Such an assumption for the form of the ground-state wave function would be far from realistic for the situation of interest in long-range coupling. For this case the ground-state representation would give rise to a hyperfine coupling, since for an *orthogonal basis* the "pi-orbitals" have some 1s character. Furthermore, the σ - π interactions are no longer likely to be a small perturbation as required for a simple perturbation approach. Lykos and Parr²⁴⁰ give a fairly lucid account of the σ - π separability conditions and van der Hart and Fischer discuss other aspects.²⁴¹

The general problem with which one is faced is as follows. The physical properties of various systems hinge on the familiar and intuitive concepts of localized bonds and localized groups of electrons. In constructing wave functions for a molecule, two alternative approaches are possible. In the first instance, we could hope that our chemical intuition was valid and construct wave functions based on localized molecular orbitals (LMO's). The other procedure employs as building blocks molecular orbitals which are not localized to any atom or region, but span the entire molecule. These functions are referred to as the canonical molecular orbitals (CMO's). The net physical properties of the system, such as total energy, dipole moment, hyperfine coupling constants, etc., will in principle be the same, if a complete basis is employed in both cases. The question arises as to which description is the most useful from the point of view of chemical interpretation. In other words, can a useful partitioning scheme result for various physical properties, while at the same time, the traditional concepts on bonding be retained. We have become most accustomed to thinking about σ electrons being localized and π electrons being delocalized. This is of course only one description. Using the LMO approach, such partitioning seems more reasonable; however, some subtle effects may inadvertently be described poorly because of some traditional bias. The CMO approach circumvents this latter difficulty but poses another. Here the "catch 22" is whether or not suitable criteria can be found which allows the CMO's to be converted into a localized picture. There exist various criteria, and these have been discussed at length.²⁴²⁻²⁴⁶ There arises the enquiry as to whether the different localization criteria lead to the same results.

The main problem that is of concern is the partitioning of the spin density into the commonly discussed components ρ_π and ρ_σ for the π electrons and σ electrons, respectively. Population analysis of this form has been discussed.^{247,248} For radicals such as the bicyclic semidiones, the question arises as to whether criteria for a partitioning into ρ_σ and ρ_π can be found for a CMO or LMO basis. More importantly, in such radicals do the concepts of ρ_σ and ρ_π still have a useful unambiguous interpretation? It may be appreciated that, from the LMO point of view, it is not rigorously possible to obtain a description of bicyclic radicals in terms of ρ_π and ρ_σ alone. The overlap between the two separate moieties requires that the partitioning into ρ_π and ρ_σ will not be unique. However, it is possible to construct certain representations based on chemical intuition, which can be partitioned into contributions depending only on ρ_π , contributions depending on ρ_σ alone, and the remaining terms which arise from the σ - π interactions. This difficulty with a nonvanishing overlap factor is called the nonorthogonality problem.²⁴⁹ This has been discussed by Melchoir,²⁵⁰ who has stressed that, in formulating isotropic hyperfine interactions for simple hydrocarbons, previously neglected overlap factors can cause substantial changes. There are available well-known procedures for constructing an orthonormalized basis of MO's which reduce the computational difficulties considerably.^{249,251} However, the orthogonalized

basis no longer consists of orbitals of purely π symmetry or purely σ symmetry in the case of radicals of the bicyclic type.

There are two principal reasons for bothering to carry out a partitioning scheme. The first is a matter of economics. It seems generally well accepted that the current status of predicting the spin densities in a large array of aromatic radicals is well understood. Sales²⁵² and Bolton²⁵³ have reviewed a large part of these calculations. Hence in describing bicyclic radicals, it may prove possible to treat the σ skeleton with an adequate basis set, while restricting the description of the π electron spin labels to the minimal number of basis functions, i.e., the set of $2p_\pi$ orbitals, rather than including basis functions for all the spin label electrons. This short cut, though approximate, is likely to prove more valuable as attempts to carry out configuration interaction (CI) calculations take place. The second reason is that it is especially helpful in attempting to construct theoretical model mechanisms to rationalize the appearance of large long-range coupling constants.

The whole question of σ - π separability or more precisely in the present context, σ - π nonseparability, is intertwined with our notion that the σ electrons form localized bonds whereas the π electrons form delocalized bonds. The very concept of long-range coupling rests on this distinction. The question which of course remains unsettled is whether the region where these two overlap (synonymous with interact) can be best described in terms of LMO's, CMO's, or a combination of both, or whether the whole concept of partitioning should be totally discarded. The latter would seem rather unpalatable to the majority of chemists attempting a simple pictorial explanation of the observations. For further general discussion on the topic we refer the reader to the excellent review by Kutzelnigg, Del Re, and Berthier.²⁵⁴

B. Symmetry and Mechanistic Considerations

The most controversial topic which remains incompletely resolved is the question of the importance of various mechanisms. The problem arises out of a desire to understand, in simple terms, which factors govern the appearance of unpaired spin density at various sites. When large-scale accurate configuration interaction calculations become available for such radicals, the question of mechanisms will be a moot issue, since the CI wave functions will inevitably be so complex that it would be highly inappropriate to breakdown the wave function into various mechanistic contributions. Only the total coupling constant will be meaningful. The attempt to approach the conformationally sensitive long-range couplings within the framework of the single determinant approximation must be regarded with considerable caution. Many approaches have started with the model concept that the "unpaired electron" is localized on the spin label and then attempt to rationalize under what likely conditions a fraction of the unpaired spin density, will relocate into various other sites of the σ framework. It must, of course, be kept in mind that this is a simple though quite convenient model and is based on our preconceived concepts of LMO's. Other approaches start from a few relevant geometric and empirical parameters and construct a wave function such that the electrons are not described in a localized description, but extend over the entire radical. This approach then attempts to identify what mechanistic features are contained within this CMO description.

There are two basic mechanisms which enter this problem and have been briefly referred to in previous sections. These are spin polarization (synonym, exchange polarization) and spin delocalization. The synonym for spin polarization is a possibly misleading nomenclature (though frequently employed), since other nonexchange terms also contribute to the coupling in general. These mechanisms have been dis-



Figure 1. Polarization in C-H fragment.

cussed in many contexts in semiempirical approaches to the calculation of isotropic hyperfine interactions.²⁵⁵⁻²⁶¹ There are several other words which have entered the vocabulary of the long-range ESR spectroscopist. Some are valuable descriptive terms; others have been overworked and in some cases have been misused to the extent that they have lost their meaning by referring to entirely different mechanisms.

Spin polarization embraces those configurations which results in spin density being induced at a particular center, without any transfer of electron density. To illustrate this, consider the C-H fragment for which there are fairly lucid accounts. Employing the approximation of perfect pairing, the structures in Figures 1a and 1b would be equally important. If the interaction between σ and π electrons is taken into account, structure a will be energetically more favored as determined by the size of various exchange integrals. This fact implies that the electrons of the C-H bond are slightly polarized. The π electron thus induces a departure from perfect pairing which results in a finite unpaired spin density at both the hydrogen and carbon nuclei. This process can be clearly applied to systems with more than one intervening bond. For such systems, three different spin polarization processes may be distinguished. The first mechanism is the direct polarization of the electrons of the C-H bond of interest (i.e., those involving long-range coupled protons) as a result of the unpaired π electron density. This is depicted in Figure 2a. The second contribution arises from terms representing spin polarization of a mixed direct-indirect character, i.e., polarization of one of the intervening bonds and subsequent polarization of the C-H bond as a result of the induced spin density at the intermediate center as shown in Figure 2b. There may be many such terms depending on the size of n . The third mechanism is a purely indirect process whereby each bond between the "pi-center" and the long-range proton is successively polarized. All spin polarization contributions involve only an electron pair decoupling process and do not, by definition, induce π -electron migration into the σ skeleton. However, both polarization and transfer processes may be operative simultaneously.

Spin delocalization refers to those contributions which arise from spin density being induced at a certain center, either by fractional migration of electrons away from or toward the particular center. These processes depend critically on the particular orbitals involved in the delocalization mechanism. The most reasonable migration route is through the classical bonding pathway, i.e., an indirect process. Some interesting studies have been carried out to test the hypothesis of spin delocalization and spin localization in a number of radicals with various π -electron moieties mutually perpendicular, parallel, or partially separated by a σ framework.^{235,262-266} Spin delocalization may also take place via a direct route between *nonbonded* atoms. This mechanism is governed by the geometry of the situation, which in turn determines the relative overlap of orbitals on the *nonbonded* centers. Such delocalization mechanisms are similar to those often referred to in the literature as being hyperconjugative interactions. As has been pointed out,²⁶⁷ hyperconjugation may in a restricted sense be associated with electron-delocalization mechanisms. However, in a more general way, hyperconjugation

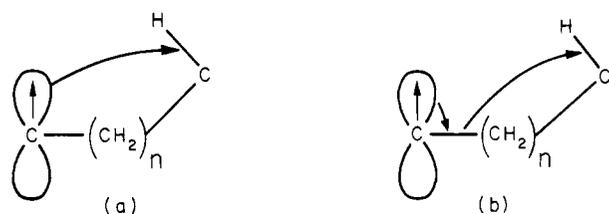


Figure 2. Direct and indirect spin polarization pathways for an aliphatic fragment.

may be taken to include other interactions between atoms, e.g., nonconventional pairing schemes. Hyperconjugation then includes both spin-transfer and spin-polarization mechanisms. In view of the general confusion regarding this term, it appears preferable to avoid its use and retain only the terms spin delocalization and spin polarization. Alternatively, it should be clearly defined what is meant by the term in the particular context in which it is used. Similar comments apply to the term *homohyperconjugation*. Spin delocalization will depend on the relative electronegativities of the different centers.

There are some other descriptive terms which are employed in mechanistic discussions. These include the expressions *direct* and *indirect*, which mean that the contributions arise from interactions of a through-space character or through the classical bonding pathway, respectively. The terms have also been used to denote contributions arising from the ground-state wave function (in CMO basis), the direct contribution, and admixture of excited-state contributions, the indirect contribution.²³² For those cases in which there is an "electron-paired" inner core, contributions to the hyperfine coupling will arise from inner-core polarization. This amounts to an exchange polarization of the inner-core electrons by the "unpaired electron" in the outer valence shell.

Some qualitative considerations about the importance of various contributions may be given without reference to any particular long-range coupled system. The general importance of each of the outlined mechanisms depends on factors such as stereochemistry, nature of atom under consideration, and substituent effects among others. The work of McConnell²³⁹ and Luz²⁶⁷ pointed out that consecutive spin polarization (indirect process) along an aliphatic chain will be quickly attenuated after the first bond adjacent to the "pi-orbital containing a fraction of the unpaired electron". This can be seen by treating the σ - π interaction as a small perturbation. For consecutive polarization, the only manner by which this mechanism can be accommodated into simple molecular orbital methodology is to include descriptions of the system containing multiple excitations from bonding to antibonding molecular orbitals of the intervening bonds of the chain. Multiple polarizations will therefore enter only as second- and higher order terms. The most important contributions for a reasonably convergent perturbation expansion will accordingly arise from terms involving single excitations, and this automatically restricts the polarization to only one bond. Transmission of direct through-space spin decoupling in saturated systems does not depend on the dihedral angles of the system for "limited fragment" calculations.

Essentially the same ideas will apply to mixed direct-indirect contributions to the hyperfine coupling. In this case, the geometry of the entire framework of the saturated system is involved. Mixed direct-indirect contributions will only be expected to give rise to a fairly small collective contribution to the first-order hyperfine coupling, and only in those cases where the geometry is highly favorable. Indirect spin-polarization processes over more than one bond have received little attention. Colpa and de Boer²⁶¹ have made a very approximate estimate for the \dot{C} -C-H radical and showed that such

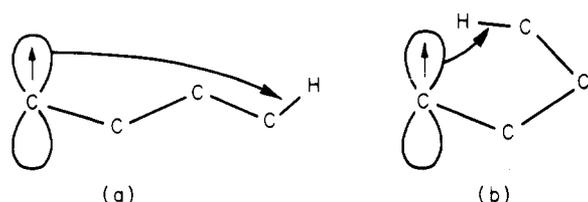


Figure 3. Possible orientation for hypothetical C_4H fragment.

contributions are much too small to explain the experimental results. Their conclusion is intuitively correct and will apply even more appropriately to the extended systems of interest in long-range coupling.

Direct spin polarization will be highly stereoselective. For the hypothetical saturated system C_4H , oriented as shown in Figure 3a, the direct spin decoupling will be negligible. However, for the orientation in Figure 3b, the stereochemistry is such that a reasonable interaction may occur. These types of interactions have been essentially neglected in the work of some authors,^{267,268} apparently owing to the fact that the appropriate integrals did not appear in the literature at that time. The conclusion to be drawn is that saturated systems for which Figure 3a is a prototype will not be expected to have very large hyperfine interactions resulting from this mechanism. On the other hand, oriented radicals such as the bicyclic derivatives have some C-H bonds constrained in a geometry resembling Figure 3b and may be expected to have a sizable portion of the observed hyperfine coupling arise through direct spin polarization.

Spin-delocalization mechanisms can be accounted for in the molecular orbital approach employing LMO's, by construction of configurations in which an electron from an orbital centered at one atom is shifted to an orbital centered elsewhere. The importance of this redistribution of charge will depend on the extent of overlap between the participating orbitals. The overlap dependence appears to be the factor governing delocalization processes, and this is sharply dependent on the stereochemical restrictions of the molecule.

For consideration of proton hyperfine coupling constants, core polarization terms are not involved. Such contributions could not be neglected in a discussion of other nuclei, for example, ^{13}C hyperfine splittings.²⁶⁹ There is a scarcity of experimental work for such hyperfine splittings for situations of interest in long-range coupling.²⁷⁰

Specific comments about the quantitative contributions of the various mechanisms depend on the computational approach employed. The results for semiempirical and ab initio studies are described below. There is, however, one important feature which can be applied to all the radicals which have a π -electron moiety as the source for introducing spin density into the σ skeleton. This is the criteria of symmetry of the highest occupied π molecular orbital (HOMO) of the spin label. The idea as applied in long-range coupling arises from the work of Whiffen,²⁷¹ although general symmetry arguments were in use in ESR before this study. The importance of this symmetry consideration has been discussed extensively for long-range coupling.^{34,45,107} The experimental trend observed, for which there does not appear to be any exception at present, is as follows. For radicals whose HOMO is symmetric with respect to a plane bisecting the σ and π moieties (this plane being perpendicular to the plane of the spin label), as illustrated in Figure 4a, the long-range hyperfine coupling constants of various protons are observed to be larger, usually by a factor of 2 or 3 compared with those radicals whose HOMO is antisymmetric. This simple observation is a fairly useful guide for predicting a priori the general trends expected with spin labels of different HOMO symme-

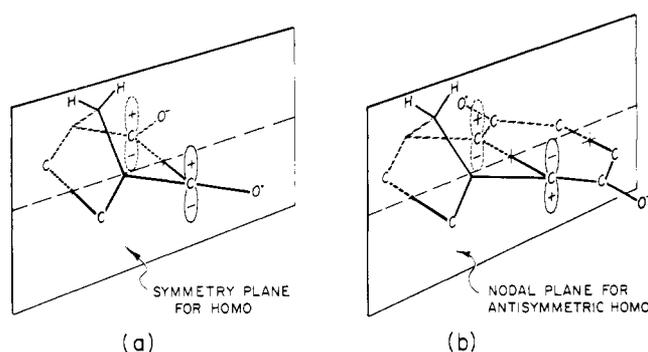


Figure 4. Symmetry properties of HOMO.

try. The reasons for this are straightforward. For situations in which the HOMO is antisymmetric (see Figure 4b), then by symmetry considerations alone, spin delocalization vanishes for protons in the plane bisecting the HOMO. However, when the HOMO is symmetric, spin delocalization is *not* prevented on symmetry grounds and may be nonvanishing. The distinction between the two cases gives a possible guide to the importance of spin delocalization. There are, however, complications to this approach. Comparing the long-range splittings for the same σ moiety, attached to different spin labels exhibiting opposite symmetries for the HOMO's, may lack validity, since there are two factors which have been altered. One is that there is limited knowledge on how constant the stereochemistry of the σ skeleton remains. This is a very important point, since the hyperfine coupling constants are fairly sensitive to small geometric changes. Further, the unpaired spin densities on the two adjacent centers for different spin labels will be unequal, in some cases differing by a factor of 2 or more, and this will in part correlate with the observed differences in the hyperfine couplings. It is not intended to suggest that there is a linear dependence of long-range splittings on the unpaired spin populations at the adjacent centers of the spin label. In fact, quite the opposite has been suggested.⁴⁸ A nonlinear dependence seems more likely based on the experimental results. Unfortunately, no situations have been reported in which a bicyclic radical has been prepared in both states: one in which the HOMO is symmetric, the other in which the same spin label has an antisymmetric HOMO. There are at first sight some anomalies which deserve mention. The 7-syn proton couplings of some bicyclo[2.2.1]heptyl derivatives are approximately the same (in magnitude, sign not known) for spin labels with different HOMO symmetries. This may be rationalized by assuming that spin delocalization, when a symmetric HOMO is present, is highly stereoselective to various centers. For those radicals whose σ frameworks contain an ethylene group, arguments concerning the possibilities of overlap are not affected since the vinyl π orbitals do not lie in a node of the HOMO. The situation with respect to various C-H bonds which do not lie exactly in the nodal plane is less clear. For example, the exo protons of the bicyclo[2.2.1]heptyl derivatives of the semidione, semiquinone, and semifuraquinone spin labels are 2.49, 0.70, and 2.04 G, respectively. For spin labels which are asymmetrically substituted, e.g., the nitrobenzene label, the HOMO cannot be strictly classified as symmetric or antisymmetric; however, qualitative conclusions similar to those outlined above may be formulated.

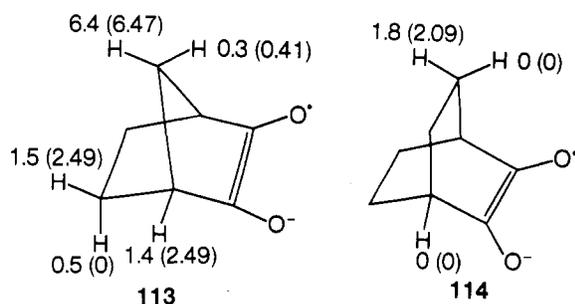
Mechanistic discussions for other nuclei for which long-range couplings have been observed are lacking. A number of long-range coupled fluorine splittings have been recorded, but the magnitudes have not been calculated via ab initio methods. The corresponding problem for β -fluorine splittings has attracted considerable attention.²⁷²⁻²⁸¹

C. Semiempirical Computation Schemes

The problem of long-range hyperfine coupling from a theoretical point of view has two facets. One approach to the study of long-range coupling constants is to take the simplest possible procedures which admit various adjustable parameters and attempt to account for the magnitudes of the splittings on a correlative basis. The hope is that, once a set of empirical parameters is obtained, these may be transferred and employed for molecules of similar structural types. This group encompasses the methods such as extended Hückel²⁸²⁻²⁸⁴ and the intermediate (complete) neglect of differential overlap INDO (CNDO) procedures.²⁸⁵⁻²⁹¹ The alternative approach starts from assumptions only of the stereochemistry (which could also be optimized) and, without recourse to any empirical parameters, attempts to compute the coupling constants using more theoretically sound approximations. The semiempirical approach is of considerable value to the ESR spectroscopist, since it may be employed with little difficulty and is valuable for assigning various coupling constants to particular protons. Additionally, complex spectra can often be unraveled by using semiempirical calculations as a "first guess". This is especially true now that computer simulation of spectra is widely available. The disadvantage, however, is that the semiempirical schemes are usually restrictive in terms of how they accommodate different mechanisms. However, this inadequacy can be accounted for by selective adjustment of the empirical parameters. There is, however, a tendency to attempt to draw definitive conclusions on the contributions of various mechanisms from such schemes. This is obviously an incorrect approach and is, no doubt, part of the reason for conflicting opinions, where in reality no comparison should be made. The *ab initio* approach attempts to be a beneficial aid to the ESR spectroscopist, but a prime motivation is also to provide a test of molecular theories for such radicals.

1. Extended Hückel

General accounts of the approximations employed in the extended Hückel procedure may be found in the articles by Jug,²⁸⁴ Blyholder and Coulson,²⁸³ and Dewar.²⁹⁰ Several applications of the extended Hückel formalism to the calculation of hyperfine coupling constants have appeared.²⁹²⁻²⁹⁴ A few applications to the bicyclic radicals have been made by Underwood and Givens²⁹⁵ and Russell et al.⁴⁰ Two examples from the calculations of Underwood et al.²⁹⁵ are (in gauss) shown in structures 113 and 114, where the experimental results are in parentheses. The results presented are for more



or less the optimum geometry reported. The results for the bicyclo[2.2.1]heptane semidione radical anion were found to be particularly sensitive to variations of various geometric parameters. Unfortunately, there is a lack of structural data available for such radicals (or related systems), so it is particularly difficult to estimate reliable geometries for these radicals. Aside from questions of the validity of the approximations involved, it seems difficult to place any reliance on such

calculations as an aid to spectroscopic assignments. Part of the reason for this is the somewhat limited experience with radicals like the bicyclic derivatives and the lack of optimum semiempirical parameters. The sensitivity to geometric parameters has not been explored beyond the above preliminary studies. It is unlikely, however, that much work in this area will be forthcoming, especially because of the availability of more rigorous semiempirical schemes such as INDO and *ab initio* programs.²⁹⁶

There are certain intrinsic features of the extended Hückel formulation as currently used which limit its usefulness in considerations of mechanistic contributions. The neglect of spin polarization in the single determinant approximation renders it meaningless to attempt to estimate its importance by attributing the difference between calculated and experimental observations as arising from this cause, especially in view of the fact that the adjustment of various available semiempirical parameters can overcompensate for the degree to which spin delocalization takes place. The calculated long-range coupling constants using the extended Hückel formalism appear with positive sign, and this is at variance with some of the experimental results for selected long-range coupled protons. The extended Hückel scheme appears at best to be limited to applications when rough trends are sought.

2. INDO Method

The intermediate neglect of differential overlap (INDO) scheme is an SCFMO approach whose approximations have been outlined in detail.^{285,290} The INDO method is a somewhat more rigorous extension of the complete neglect of differential overlap (CNDO) scheme.^{290,291} The latter method has been employed for the calculation of spin densities;²⁹¹ however, the results are not likely to be satisfactory since among the approximations CNDO neglects one-center atomic exchange integrals. This makes it impossible to give a proper account of spin polarization.

In the INDO scheme, the electronic wave function Ψ is written in the unrestricted Hartree-Fock formalism as a Slater determinant of the form

$$\Psi = |\psi_1^\alpha(1)\alpha(1)\psi_2^\alpha(2)\alpha(2) \dots \psi_p^\alpha(p)\alpha(p)\psi_1^\beta(p+1)\beta(p+1) \dots \psi_q^\beta(p+q)\beta(p+q)| \quad (1)$$

and the spatial orbitals for different spins, ψ_i^α , ψ_i^β are expressed as a linear combination of valence shell atomic orbitals (LCAO approach) as

$$\psi_i^\alpha = \sum_{\mu} C_{\mu i}^{\alpha} \phi_{\mu} \quad (2)$$

$$\psi_i^\beta = \sum_{\mu} C_{\mu i}^{\beta} \phi_{\mu} \quad (3)$$

The schemes in which various integrals over the basis ϕ_i are retained or deleted give rise to the approximations CNDO, INDO, etc. The isotropic hyperfine coupling constant is then obtained as the expectation value of the Fermi contact operator with respect to Ψ . At high magnetic fields, the isotropic electron-nuclear interaction is adequately approximated by

$$H_F = \frac{8\pi}{3} g_e g_N \beta_e \beta_N \sum_{\mathbf{k}} \delta(\mathbf{r}_{\mathbf{k}N}) S_{\mathbf{k}z} I_{Nz} \quad (4)$$

and hence the isotropic hyperfine coupling constant (in gauss) for nucleus N is

$$a_N = \langle \Psi | H_F | \Psi \rangle \{g_0 \beta_e \langle S_z \rangle \langle I_{Nz} \rangle\}^{-1} = \frac{8\pi}{3g_0} g_e g_N \beta_N \langle \Psi | \rho(r_N) | \Psi \rangle \quad (5)$$

where

$$\rho(r_N) = \sum_k \delta(r_{kN}) \sigma_{kz} \quad (6)$$

The symbols g_e and g_N , are respectively g factors for the electron and nucleus, β_e and β_N are the Bohr magneton for the electron and nucleus, $\langle S_z \rangle$ is the expectation value of the electron spin angular momentum, $\rho(r_{kN})$ is the spin density operator evaluated at nuclear position r_N , $\delta(r_{kN})$ is the Dirac δ function, and σ_{kz} is the Pauli spin operator. g_0 is the g value of the radical.

There is one serious limitation to the INDO formulation as briefly outlined above. This concerns the problem that a single determinant wave function in the unrestricted Hartree-Fock formalism is not an eigenfunction of S^2 . This means that calculations conducted with a Ψ given by eq 1 includes contributions from other multiplicities; i.e., the doublet ground state contains an admixture of the quartet state and higher multiplet states. This consideration has not been taken into account in almost all the studies pertaining to long-range coupling nor, for that matter, other simpler radicals. Beveridge and Dobosh²⁸⁸ have found from a somewhat limited study that the approximation of ignoring the contamination from higher multiplet states is not serious for the semiquantitative calculation of hyperfine coupling constants. Considerable attention has been directed toward this problem for more semiempirically based schemes,²⁹⁷⁻³⁰⁵ and it may be possible that the conclusion generally reached that this approximation is usually satisfactory may also apply in the INDO scheme. In any event it would be of value to test the effect of annihilating at least some of the higher multiplet states for a few of the bicyclic radicals, to get some idea of the usefulness of this approximation for situations of interest in long-range coupling.

Aside from the approximation involved in rejecting many integrals, the INDO scheme and, of course, other similar semiempirical single determinant approaches are unable to account fully for spin polarization mechanisms of a direct through-space classification because of the neglect of all two-center exchange integrals in these schemes. Various through-bond spin-polarization contributions are also inadequately represented. These can only be satisfactorily accounted for in a configuration interaction approach. The inclusion of one-center exchange integrals in the INDO scheme allows the effect of local spin polarization contributions to be accounted for.²⁸⁷ It is evident that the mechanistic interpretations from the INDO method are somewhat restricted, though far less so than the extended Hückel procedure. From such calculations, a rough guide to the mechanistic contributions might be expected, but it would be a fairly tenuous proposition to suppose that semiquantitative estimates can be found by this method.

Underwood et al.,²³⁴ Sullivan et al.,³⁰⁶ and Abronin et al.³⁰⁷ have applied the INDO method to the study of alkyl radicals, in particular the propyl radical, in order to calculate the γ -proton coupling constants. Underwood et al. have produced a three-dimensional hyperfine coupling constant surface for the variation of a_γ as a function of the two dihedral angles shown in Figure 5. These authors found that an empirical fit to the surface is described by the equation

$$a_\gamma = A + B \sin^2 \theta_\beta^C \sin^2 \theta_\gamma^H + C(1 - \sin^2 \theta_\beta^C) \sin^6 (\frac{1}{2}\theta_\gamma^H - \frac{1}{5}\theta_\beta^C) + D \sin \theta_\gamma^H \sin^2 (2\theta_\beta^C) \quad (7)$$

where the parameters A , B , C , and D have respectively the values, -1.54 , -0.48 , 4.8 , and -0.7 G. The main feature found from this calculation is that the total hyperfine coupling for the γ protons is a sum of a positive spin-delocalization contribution and a negative spin-polarization contribution. The

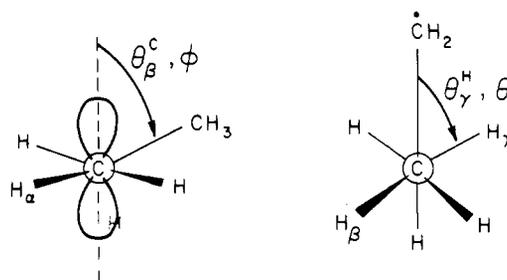
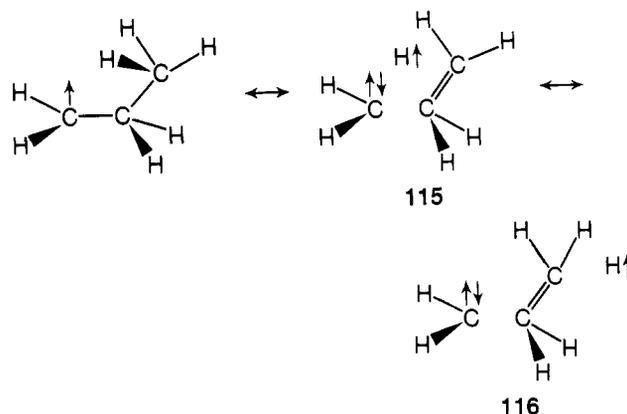


Figure 5. Specification of dihedral angles for the Underwood-Vogelorio expression for a_γ (eq 7) and the Barfield expression eq 10.

outcome is that the total value of the hyperfine coupling a_γ appears as a balance of these two contributions which is fairly sensitive to the conformation. For some geometries the total coupling constant is negative, whereas for other conformations it is positive, in some cases over 3 G. Equation 7 may prove to be a fairly useful guide to estimating geometries, even though the parameters A , B , C , and D have not yet been fully optimized.

The statements of Underwood et al.²³⁴ concerning the mechanistic contributions are not well founded. These authors tentatively suggest that the large values of the spin polarization for certain conformations are due to structures such as 115 and 116. This suggestion seems somewhat tenuous since such a scheme as previously explained is a third-order mechanism based on a perturbation theory analysis, and, further, this mechanism is not fully accounted for within the approximations of the INDO scheme. It is more likely that direct through-space spin polarization is much more important, since such a contribution appears as a first-order contribution. As referred to previously, Colpa and de Boer²⁶¹ have considered this problem at a simple semiempirical level, and they find that direct through-space spin polarization is ap-



proximately three times that estimated for the through-bond spin polarization for the fragment $\dot{C}-C-H$. The difference between through-bond and through-space contributions would be expected to be even greater for the fragment $\dot{C}-C-C-H$ in various favorable conformations. The problem of fully describing this through-space spin polarization is beyond the reach of the present INDO schemes, since the required two-center exchange integrals necessary to properly account for the appropriate structures are not retained.

Corvaja et al.³⁰⁸ have proposed an alternative suggestion for the angular dependence of the γ -proton splittings of the form

$$a_\gamma = A + B \cos^2 \theta_C + C \cos^2 \theta_H \quad (8)$$

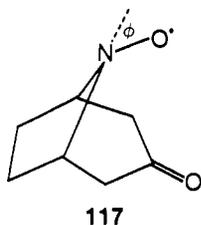
where θ_C is the angle between the π orbital and the $\dot{C}-C-C$ plane and θ_H is the angle between the $\dot{C}-C-C$ and $C-C-H_\gamma$ planes. These authors did not provide any values for A , B , and C , and calculations are required to determine these parameters.

Sullivan and Wright³⁰⁶ concluded from their study that INDO calculations of γ -proton splittings for freely rotating or torsionally oscillating protons could not account for the experimental observations. Despite its shortcomings, the INDO procedure is still of considerable usefulness in making assignments. We now illustrate a few examples for long-range coupled systems.

Stock and Young,¹³⁶ Krusic et al.,¹³¹ and Danen³⁰⁹ have carried out INDO calculations on the cyclopropylcarbinyl radical and analogues in different conformations. For this radical, the very small β -proton splitting acts as a sensitive gauge of the preferred conformation. For the bisected conformation (β proton in the node of the carbon $2p_\pi$ orbital), the calculated splittings were $a_\beta = 1.34$ G, $a_{\gamma,endo} = -1.41$ G, and $a_{\gamma,exo} = 1.72$ G which compares with the experimental values $a_\beta = 2.55$, $a_{\gamma,endo} = 2.01$, and $a_{\gamma,exo} = 2.98$ G (absolute values). The assignment of a_{exo} and a_{endo} by Krusic et al.¹²⁸ was based on comparison with Russell's W plan. Calculations for the perpendicular conformation gave $a_\beta = 44.51$, $a_{endo} = -1.26$, and $a_{exo} = 0.90$ G. Considering the closeness of $|a_{exo}|$ and $|a_{endo}|$ as calculated from the INDO scheme for the bisected conformation, it would be difficult to justify the assignment of the absolute values of the coupling constants obtained experimentally. The difference in sign for the calculated values may be taken advantage of if the particular signs for the γ splittings could be ascertained. For some cyclopropyl derivatives, Stock and Wasielewski¹³⁴ have determined from NMR studies that the endo protons have negative sign while the exo protons have positive coupling constants. These results are consistent with the conclusions from the INDO calculations.

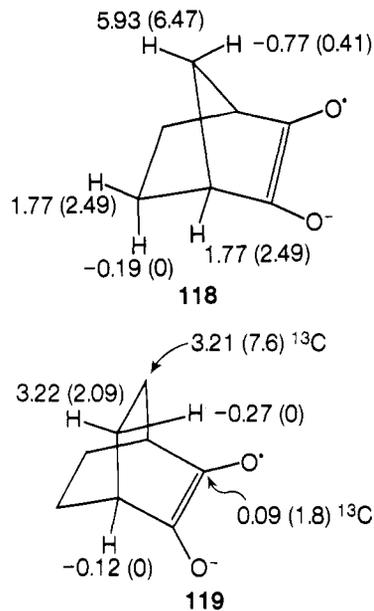
A number of applications of the INDO scheme have been made for various bicyclic radicals. As remarked earlier, INDO calculations for the bicyclobutyl radical¹²⁰ lead to results for the γ -proton coupling constants which would not be anticipated on the basis of Russell's W plan. Lloyd and Rogers¹⁵⁶ and Krusic et al.¹⁵⁷ have made calculations on the 2- and 1-adamantyl radicals, respectively. Lloyd and Rogers found a substantial δ -proton coupling was predicted compared with somewhat smaller γ -proton couplings. On the basis of this evidence, these authors assigned a long-range coupling of 3.55 G to the δ proton, rather than to a β proton as had been previously assigned by Ferrell et al.¹⁵⁵ Similar conclusions were obtained by Krusic et al.¹⁵⁷ for the 1-bicyclo[2.2.2]octyl radical, and additional evidence was provided by examining the spectra of the 4-alkyl derivative. This latter case is a good example in which INDO has proved its value in making assignments of the long-range splittings. Kochi et al.¹¹⁸ have carried out extensive calculations for the 7-norbornenyl radical for which they found restricted geometric orientations for which agreement with experimental coupling constants could be reproduced. Interestingly, they found these regions do not correspond to local energy minima on the conformational energy surface.

Rassat and Ronzaud⁹⁰ have carried out calculations on a typical bicyclic nitroxide **117**. They found variations of sign for



the spin densities at the endo and exo protons as a function of the angle ϕ . Underwood and Vogel³¹⁰ have studied a number of semidione derivatives. Structures **118** and **119** illus-

trate typical results of their INDO calculations. The experiment values (absolute) are given in brackets. For **119** the proton coupling constants are in satisfactory agreement, although the ^{13}C splittings compare less favorably with the results of Russell et al.²⁷⁰ Part of the discrepancy for the ^{13}C splittings may result from the neglect of inner-shell polarization in the INDO scheme. The calculated results shown are the best of several possible sets given by Underwood and Vogel for different geometries. Although a systematic geometric variation was not performed, the calculations for a few different geometries for **118** showed that as the 7-syn coupling becomes more negative, the 7-anti coupling decreased



initially and then increased. Undoubtedly the coupling constants are sensitive to a combination of geometric variables. Overall, the agreement between theory and experiment appears satisfactory.

3. Other Semiempirical Approaches

In this subsection we discuss briefly two interesting attempts by Luz²⁶⁷ and Barfield²⁶⁸ to calculate the hyperfine splittings for aliphatic radicals. Bailey and Golding³¹¹ have also carried out a study of the aliphatic systems. These calculations neglect a number of interactions of the through-space classification and hence they should not be expected to apply to highly strained conformations of the aliphatic radicals. Barfield has pointed out this restriction of his work. Nevertheless, several authors have attempted to utilize these relations for structurally strained radicals. This is not a valid procedure.

Luz's approach in essence is a valence-bond treatment with the various integrals being evaluated empirically or nonempirically where possible. The treatment is restricted in the sense that only spin polarization is taken into account. Luz assumes that the γ - and δ -proton hyperfine coupling constants can be represented by

$$a_H = Q_H \rho \quad (9)$$

where ρ is the π spin density population and Q_H 's are σ - π interaction parameters which are dependent on the conformation of the chain, etc. The values for $Q_{H\gamma}$ and $Q_{H\delta}$ were estimated by perturbation theory to be -1.0 and $+0.34$ G, respectively. Rassat and Ronzaud⁹⁰ have employed Luz's formulation to obtain an expression for the γ and δ proton coupling constants, though these authors do not make it clear which particular approximations they have employed. Satisfactory agreement for γ couplings were found by these au-

thors. The agreement, however, is likely illusory in view of the neglect of far too many of the necessary integrals. The treatment of Luz in the opinion of the reviewer is best restricted to simple aliphatic radicals, and no attempt should be made to employ this formulation for the bicyclic radicals.

Barfield has carried out a valence-bond calculation using an intergroup configuration interaction procedure in the generalized product approximation of McWeeny et al.³¹² The necessary integrals were estimated empirically. As with Luz's treatment, no account was taken of through-space interactions, and this limits the treatment to aliphatic radicals. Barfield obtained the following formula for a_γ :

$$a_\gamma = 1.65 \cos^2 \phi - 0.84 \cos^4 \phi + 2.62K(\theta) - 0.68 \cos^2 \phi [K(\theta + 120^\circ) + K(\theta - 120^\circ)] + 0.15 [\cos^2(\phi + 120^\circ) K(\theta + 120^\circ) + \cos^2(\phi - 120^\circ) K(\theta - 120^\circ)] + 0.17 \quad (10)$$

$$K(\theta) = -0.287 \cos^2 \theta + 0.016 \cos \theta + 0.015$$

The angles θ and ϕ are as specified in Figure 5. Barfield found satisfactory agreement between experimental values and those obtained from eq 10 for some aliphatic radicals. An important advantage of the Barfield formulation is that it allows for both positive and negative γ -proton coupling constants. A semiempirical correlation between long-range hyperfine couplings and spin-spin coupling has been noted.³¹³

D. Ab Initio Calculations

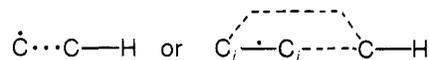
There has not been very rapid progress in the general area of calculating hyperfine coupling constants by nonempirical approaches. This stems from the fact that to treat the rather sensitive dependence of the coupling constants on correlation effects requires configuration interaction calculations. However, the difficulties of implementing such an approach for large molecules makes the problem intractable with present-day computers. Most groups working on the ab initio calculation of hyperfine couplings have been restricted to relatively small molecular systems.^{232,247,314-325} The simplest means of taking at least partial account of correlation effects has been to apply perturbation theory to the single Slater determinant wave function of ab initio quality. Almost all the ab initio calculations of hyperfine coupling constants for molecules have been restricted to single determinant calculations, with the effect of annihilation of higher multiplet states usually being considered for unrestricted Hartree-Fock calculations.

There are a few criteria such as the virial theorem, etc., for which a wave function of "reasonable quality" ought to satisfy. It has been pointed out that, to obtain a satisfactory description for the electronic properties near the nucleus, the wave function should satisfy the cusp conditions^{247,323} which arise from the fact that the wave function has a cusp at the nucleus if the corresponding Hamiltonian has a coulomb singularity at that nucleus. Chang et al.,²⁴⁷ Konishi et al.,³²³ and Poling et al.³²⁴ have tested wave functions for a number of organic radicals, e.g., C-H, $\cdot\text{CH}_3$, to see how well such conditions are satisfied. However, it does not appear to have been adequately established how poor the calculated hyperfine coupling constants will be for wave functions which only satisfy the cusp constraints approximately.

Ab initio work concerning long-range coupling constants has been extremely limited. Ellinger et al.²³² have carried out a study of the propyl radical, and King and Adam³²⁸ have investigated model fragments for long-range interactions. The philosophy involved in approximating the long-range coupled bicyclic radicals by suitable fragments involves providing a

minimal description of the π -electron spin label, but concentrated efforts toward an adequate description of the σ - π interactions arising between the spin label and the σ moiety. The model fragment approach has been a corner stone in the theoretical development of our present-day understanding of hyperfine interactions. A number of authors have employed this approach for various problems (see ref 238, 239, 261, 267, 268, 329, and 330). This approach is difficult to circumvent for radicals like the bicyclic derivatives, since all electron ab initio treatments taking at least partial account of correlation effects would be very expensive propositions at the present time.

All of the essential features of the bicyclic systems can be represented by the σ - π interactions of a weakly bound



fragment which incorporates the geometric factors appropriate to the long-range interactions. While these model fragments are somewhat naive, they do allow a fairly rigorous nonempirical calculation to be effected. As far as the mechanisms for long-range interactions are concerned, this approach would appear superior to other empirically based formulations, which by their nature, are restricted to spin polarization or to spin delocalization, and to which correlation with experiment is achieved by arbitrary adjustment of the available parameters. The calculations of King and Adam involved a minimal basis configuration interaction calculation with all integrals being evaluated nonempirically. Calculations carried out for the simpler of the above two fragments are appropriate for a system such as the 2-norbornyl radical. The results are quite instructive. The basic features were that the total hyperfine coupling is a sensitive balance of positive and negative contributions to the total coupling constant. The spin-delocalization contributions dominated for an anti proton orientation while for the syn proton orientation, the total coupling constant arises from a sum of many small contributions (mostly positive). Configurations describing electron delocalization to the radical site were found to be totally negligible, whereas a direct through-space delocalization to the C-H bonds in question was found to be significant for the anti-proton conformation but far less important for the syn-proton configuration. Calculations carried out for which excited configurations representing electron delocalization were excluded led to smaller values for the hyperfine couplings constants, with the ground-state configuration giving rise to the largest contribution, rather than the contributions from spin polarization configurations.³³¹

The second of the above-mentioned fragments allows the symmetry properties of the spin label to be taken into consideration. The π -molecular orbital of the spin label is restricted to the two adjacent centers, i.e.

$$\pi_r \approx C_{ir}\phi_i + C_{jr}\phi_j \quad (11)$$

and this allows for a treatment involving a symmetric HOMO ($C_{ir} = C_{jr}$) or an antisymmetric HOMO ($C_{ir} = -C_{jr}$). Detailed arguments for the model fragments have been discussed.³²⁸ In order to discuss the significance of various mechanistic contributions, King and Adam found it useful to partition the hyperfine interactions into various mechanistic contributions. For the symmetric HOMO,

$$a_{H_s} = (\rho + R_s^2)^{-1} \{ R_s^2 Q_{tt_s} + \rho^2 Q_{pp_s} - \rho R_s \text{sgn}(W_{ip}) Q_{tp_s} \} \quad (12)$$

and for the antisymmetric HOMO,

$$a_{H_a} = \rho(1 + R_a^2)^{-1} \{ R_a Q_{pp_a} + Q_{gg_a} - R_a \text{sgn}(W_{gp}) Q_{gp_a} \} \quad (13)$$

TABLE XVII. Calculated 7-Syn and 7-Anti Proton Coupling Constants (in gauss) for the Bicyclo[2.2.1]heptyl Skeleton

Spin label	Spin density at adjacent site	Calculated		Observed ^c	
		7-syn	7-anti	7-syn	7-anti
Radical Anions					
Semidione	0.294 (s) ^b	1.62	5.01	0.41	6.54 ^d
Semiquinone	0.110 (a)	-0.08	0.10	0	0.66 ^e
Semifuraquinone	0.299 (a)	-0.21	0.27	0.47	1.03 ^f
Dicyanoethylene	0.146 (a)	-0.10	0.13		
2,5-Semidione ^a	0.238 (a)	-0.17	0.22		
Radical Cations					
Semidione	0.088 (a)	-0.16	0.08		
Semiquinone	0.250 (s)	1.37	4.28		
Semifuraquinone	0.384 (s)	2.11	6.49		
Dicyanoethylene	0.212 (s)	1.17	3.64		
2,5-Semidione	0.373 (s)	2.05	6.31		

^a Assumed bound as a spin label across 3-4 bond. ^b Symmetry of HOMO designated by "a" for antisymmetric, "s" for symmetric. ^c Absolute values of the coupling constant reported. ^d Data from ref 13. ^e Data from ref 37. ^f Data from ref 48.

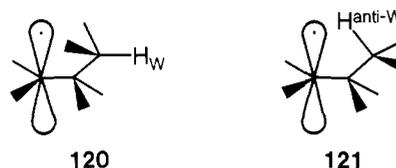
where ρ is the spin density at the adjacent site of the spin label, the Q 's are various σ - π interaction constants, R_a , R_s , W_{ip} , and W_{gp} are matrix element factors, and sgn denotes the sign of an appropriate electronic matrix element. At the sophisticated level of a CI calculation for the model fragments of the bicyclic radicals, *there is not a natural partitioning into spin-delocalization and spin-polarization contributions. There are important contributions which arise from cross terms between these two descriptions*, and this makes it impossible to discuss the two independently of each other. The philosophy expressed by Stock and Young¹³⁶ for INDO calculations, concerning the lack of need to pursue individual mechanistic arguments, is an actual reality for CI calculations. For more involved CI calculations, the possibilities of singling out particular contributions becomes progressively more unrealistic.

Q factors appropriate for the syn and anti protons of the bicyclo[2.2.1]heptyl moiety have been calculated using nonempirical procedures. These values together with eq 12 and 13 have been used by King³³² to calculate the splitting constants for the latter radical based on a few different spin labels including some predictions for the cationic analogues for these systems. The results are summarized in Table XVII. The major difficulty is the calculation of the Q factors for the various proton positions in the different σ moieties. General Q factors exhibiting explicit dependence on the various angular variables could be given; however, they would be far too complex to be useful. An alternative exercise may be to obtain appropriate "experimental estimates" of the Q factors and hope for transferability for systems whose σ - π interactions arise from similar stereochemical situations.

The interesting calculation of Ellinger et al.²³² has been previously discussed with respect to its bearing on the W plan. There are a few additional comments which appear relevant to their calculation. These authors designate the ground-state term which contains the spin-delocalization mechanism as the direct contribution, which should not be confused with the usage of direct to imply various through-space interactions, which may be of either spin-delocalization or spin-polarization character. These authors then apply first-order perturbation theory to obtain an indirect contribution which accounts for the spin polarization. The hyperfine coupling constant is then given by

$$a_H = a_{\text{direct}} + a_{\text{indirect}} = \frac{8\pi}{3} (g_e/g_0) g_H \beta_H (\rho_{\text{direct}} + \rho_{\text{indirect}}) \quad (14)$$

where ρ_{direct} and ρ_{indirect} are the spin densities at the proton from the two different mechanisms. These authors have calculated the two conformations shown in structures **120** and **121**. Their conclusions can be summarized as follows. For



the anti-W proton (**121**), the contributions found were 1.11 and -0.91 G for spin delocalization (direct term) and spin polarization (indirect term), respectively. For the W proton (**120**), the contribution for spin delocalization was 2.64 G and from spin polarization 1.73 G. From these results, the empirically formulated W plan of Russell is well supported. For the W proton, both contributions have the same sign, and the coupling is appreciable. However, for the anti-W proton, the contributions are of opposite sign, and the resultant coupling is fairly small. These ab initio calculations lend support to the widely held view that long-range couplings are highly stereoselective. Unfortunately there are no experimental results for different frozen conformations of the propyl radical which can support these calculations. For the freely rotating γ protons, it was found that spin delocalization is not appreciable, whereas spin polarization leads to a value $a_\gamma = -0.21$ G, which is in satisfactory agreement with experimental results. Such an agreement must be considered to be at least partly fortuitous considering the method of calculation and the very small size of the coupling constant to be calculated.

The partitioning scheme of Ellinger et al.²³² which splits the total hyperfine coupling into direct and indirect contributions has one limiting drawback. It is possible to include in a perturbation analysis terms which are not spin polarization contributions by the conventional definition. In the localized MO description, these contributions would amount to spin delocalization into the σ -antibonding regions of the appropriate long-range C-H bonds. For freely rotating methyl groups in the propyl radical, such a contribution would be expected to be fairly small and need not be considered. However for the W-plan conformation, this requires extensive investigation. This factor makes estimates of the various mechanistic contributions difficult. From the procedure outlined by these authors, *higher order* (i.e., beyond first order delocalization perturbative contributions have not been incorporated. It should thus be stressed that their results for the propyl radical should be considered a semiquantitative guide to the values for the hyperfine coupling constants. These remarks aside, the work of Ellinger et al. on the conformational dependence of long-range couplings by way of the propyl radical is a significant contribution to our understanding of such interactions.

V. Summary and Concluding Remarks

This review has been concerned with illustrating the diverse variety of radicals which have been found to exhibit long-range hyperfine coupling constants. Some notable features such as the high stereoselectivity, the preference for rigid configurations, and the correlation of hyperfine couplings to some extent with the symmetry properties of the HOMO of the spin label have been discussed. The theoretical calculations at the present stage of development have been considered and found to be lagging behind the experimental developments. The mechanistic contributions have been considered at length.

There are several areas in which future work could answer important questions. From a theoretical standpoint, this is a

wide open area with additional work required for obtaining nonrigorous semiempirical approaches to predicting hyperfine coupling constants for the strained radicals, without employing parameters limited to only aliphatic fragments. The computation of long-range coupling constants still remains a challenge for more exact nonempirical studies, both as an intrinsic amplification of our knowledge in this area and as an aid to checking semiempirical calculations. Additional studies at this level may assist in verifying the assignment of coupling constants for radicals such as bicyclobutyl, adamantyl, etc.

Further applications of long-range interactions to explore conformational problems seem likely. There are a number of possible spin labels which could be synthesized and this would be a considerable aid in attempting to correlate adjacent π -orbital spin densities with measured long-range coupling constants. Presently, there does not appear for a given HOMO symmetry, a sufficient sequence of bicyclic radicals based on different spin labels for which a satisfactory test of expressions such as eq 12 and 13 can be made. An important contribution, both from the point of understanding the problems of mechanistic contributions and the importance of HOMO symmetry and, possibly, as yet unrealized charge effects, may be explored by examining the long-range couplings originating from both the anion and cation of the same spin label. Additional work for ^{13}C and long-range fluorine splittings would be of considerable interest.

VI. Addendum

This addendum attempts to indicate briefly the most relevant research papers which have appeared after the date of submission of this review. I have been restricted to those journals which have been received by the Radcliffe Science Library at Oxford before 15 December, 1975.

The most interesting paper to appear, which probably reflects the reviewers bias, is a theoretical investigation of the γ -proton coupling in the *n*-propyl radical by Ellinger et al.³³³ These authors have calculated the angular variation of the γ -proton hyperfine coupling constant for this radical. They have also provided informative plots of the variation of the contributions to the γ -proton hyperfine coupling as a function of various conformations. Another problem which has an important bearing on the mechanistic discussions of long-range coupling is the particular choice of the MO basis. This question has been considered by Ellinger et al.³³⁴

King and Schlegel have carried out preliminary investigations of the bicyclobutyl radical³³⁵ and the cyclopropylcarbinyl radical,³³⁶ using single determinant uhf wave functions. For the bicyclobutyl radical, qualitative support for an anti-W assignment of the long-range coupling constants was obtained, in agreement with the results of semiempirical INDO calculations. Disagreement was found between the ab initio calculations and the semiempirical results, regarding the vital question of the proper choice of sign for the long-range coupling constants of the cyclopropylcarbinyl radical.

A number of interesting experimental papers have appeared over the past year. Russell and associates³³⁷⁻³⁴⁵ continue their exhaustive investigations of the semidione spin label. The variety of radicals examined continues to grow rapidly. A number of extended Hückel and INDO calculations of many of the semidione radicals have been reported by Russell and coworkers. Also presented are further discussions on the mechanism of long-range coupling.

One of the most interesting reports to be published concerns the observation of the bicyclo[2.1.1]hex-5-yl radical by Matsunaga and Kawamura.³⁴⁶ These authors have assigned a remarkably large long-range coupling constant of $|26.8 \text{ G}|$ to the 6-endo proton of this radical. Equally interesting is the as-

signment of the long-range coupling constant of the 6-exo proton to be $|0.50 \text{ G}|$. This assignment establishes an appreciable difference in the proton coupling constants at the 6 position of this radical. The reviewer would like to see additional experimental work on this radical before he accepts the proposed assignment. If the long-range splittings prove verifiable in this system, related radicals might prove to be of considerable interest. INDO calculations for this radical have been reported for several geometries; however, the optimum geometry does not yield very good agreement with the experimental results. Kawamura and coworkers^{347,348} have also investigated the 1-norbornyl radical, the 9-benzonorbornenyl radical, and the 9-benzonorboradienyl radical. Faucitano et al.³⁴⁹ have examined the ESR spectra of some substituted cyclopentadienes, including the radical resulting from γ -irradiation of tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene. A long-range coupling constant of approximately 6 G has been assigned on rather tenuous evidence.

Gillbro et al.³⁵⁰ have estimated the principal values of the coupling tensor of the γ -proton splitting for the 2-hexyl radical. Another paper (see ref 313) dealing with the correlation of long-range hyperfine splitting constants with coupling constants in NMR has appeared.³⁵¹ Danen and Rickard³⁵² have reported a preliminary communication of their results on radicals derived from 1-azaadamantane, 1-azabicyclo[2.2.1]heptane, and 1-azabicyclo[2.2.2]octane.

Sahini and coworkers³⁵³ have continued their investigations of the bicyclic iminoxy radicals. Ingold and Brownstein³⁵⁴ examined the ESR and NMR spectra of the di-*tert*-butyliminoxy and di(1-adamantyl)iminoxy radicals. Morishima and Yoshikawa³⁵⁵ have investigated the induced contact shifts of 2-azabicyclo[2.2.2]oct-5-ene and related compounds. These authors have also reported a number of INDO calculations of some hydrocarbon σ -radical analogues of the aza compounds.

Dodd and coworkers^{356,357} reported the ESR spectra of naphthobicyclobutane, 2,3-naphthobarrelene, and 2,3-naphthobarrelane. All long-range coupling constants were observed to be less than 1 G. Bauld and Farr³⁵⁸ have provided a brief discussion on mechanistic considerations (the reader should consult sections III and IV for an expanded discussion dealing with the suggestions of these authors).

Heterocyclic radicals continue to receive attention. Some have been found to exhibit moderately large long-range interactions, particularly those involving an ether linkage.³⁵⁹⁻³⁶¹ Dixon and coworkers have provided a semiempirical approach to understanding long-range interactions. In view of the expense of carrying out detailed ab initio calculations, the approach by Dixon and associates³⁶¹ appears to have some merit.

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