

fractional distillation under vacuum gave diphenylmethylsilane, 45% yield, bp 93–95° (0.35 mm) [lit.²² 82° (0.15 mm)]. Diphenyldimethylsilane was prepared by the reaction of diphenyldichlorosilane with methylmagnesium iodide in ether. Fractional distillation under vacuum gave diphenyldimethylsilane, 82% yield, bp 115–118° (4.5 mm) [lit.³⁶ 113–115° (4 mm)]. Triphenylmethylsilane was prepared by the reaction of phenyllithium with methyltrichlorosilane in ether. Recrystallization of the crude product twice from benzene gave triphenylmethylsilane, 68% yield, mp 67–68° (lit.³⁷ 68.5–69.0°).

1,4-Bis(dimethylsilyl)benzene was prepared by the *in situ* reaction of dimethyldichlorosilane, 1,4-dibromobenzene, and magnesium in ether followed by lithium aluminum hydride reduction. A solution of dimethyldichlorosilane (219 g, 0.59 mol) and 1,4-dibromobenzene (134 g, 0.57 mol) in 200 ml of anhydrous ether containing magnesium turnings (42 g, 1.75 g-atoms) was refluxed for 12 hr. The reaction mixture was then distilled under vacuum and the distillate up to 92° (2 mm) was collected. This distillate was added slowly to a solution of an excess of lithium aluminum hydride dissolved in 300 ml of ether. Fractional distillation under vacuum gave 1,4-bis(dimethylsilyl)benzene: 69 g, 0.54 mol, 91% yield, bp 77–78° (8 mm) [lit.³⁸ 118° (35 mm)].

Preparation of Anion Radicals. Metallic reductions were carried out *in vacuo* by allowing $\sim 10^{-3}$ M solutions of the appropriate phenylsilane dissolved in THF, DME, or 2-methyl-THF at -76° to react with a potassium mirror. ESR spectra were recorded with

the resulting solutions of anion radicals contained in side-arm sample tubes out of contact with the metallic mirror.

Electrolyte reductions were performed using a sample cell containing two platinum electrodes. Anion radicals were generated directly in the ESR cavity using a Heath Model EUW-16 voltage reference source. The variable dc voltage source was increased until an ESR spectrum appeared. No reference electrode was employed. Polarographic grade tetra-*n*-butylammonium perchlorate ($\sim 10^{-2}$ M) was used as supporting electrolyte. This simple technique complemented the preparation of anion radicals by metallic reduction, allowing the characterization of three phenylsilane anion radicals that were subject to rapid further reduction in contact with a potassium mirror. No differences were noted in the hyperfine couplings for anion radicals which could be generated both metallically and electrolytically (Table I).

Electron Spin Resonance Measurements. ESR spectra were recorded on a Varian V-4502-15 ESR spectrometer using the X-band and a V4560 100-KHz field modulation unit. The temperature was controlled within $\pm 1^\circ$ using a Varian V-4557 variable-temperature controller. The controller was periodically calibrated with a copper-constantan thermocouple. Both the recorder and the sweep dial were calibrated using the resonance of the cyclooctatetraene anion radical in THF.³⁹

Coupling constants were measured directly from the strip chart recorder. Computer simulated spectra were obtained from a "Cal-Comp" adaptation to the IBM 360 computer. Spectra were simulated by the systematic variation of the coupling constants and the line widths until agreement between the calculated and experimental spectra was obtained.

Acknowledgment. Support of this work by the Robert A. Welch Foundation (Grant A-331) is gratefully acknowledged.

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(37) R. A. Benkeser, H. Landesman, and D. J. Foster, *J. Amer. Chem. Soc.*, **74**, 648 (1952).

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The Electron Paramagnetic Resonance Spectra of 4-Cyclopropylnitrobenzene Anion Radical and Related Compounds. Spin and Electron Density Distribution in the Cyclopropyl Group¹

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Abstract: The EPR spectra of nitrobenzene anion radicals with 4-vinyl, 4-cyclopropyl, *syn*-4-(*cis*-2,3-dimethylcyclopropyl), *anti*-4-(*cis*-2,3-dimethylcyclopropyl), and 3,5-dimethyl-4-cyclopropyl groups and radicals prepared from 5-nitroindan, 5-nitro-1,1-dimethylindan, 5-nitrospiro(cyclopentane-1,1'-indan), 5-nitrospiro(cyclopropane-1,1'-indan), and 6-nitro-3',4'-dihydrospiro(cyclopropane-1,1'(2*H'*)-naphthalene) are reported. The coupling constants for the β (methine) hydrogen atoms of the cyclopropane ring establish the conformational preference of the ring and the constants for the γ (methylene) and δ (methyl) hydrogen atoms indicate the extent of spin delocalization. These long-range interactions exhibit a distinctive stereochemical dependence which is compatible with the predictions of the INDO formulation and with an important role for carbon-carbon hyperconjugation.

Cyclopropane chemistry often reflects the intriguing interactions between electron-deficient p orbitals in carbonium ions and carbon radicals and neighboring p-rich carbon-carbon bonds. Recently, cyclopropylcarbinyl radical, its derivatives, and related anion and cation radicals have been investigated by EPR spectroscopy.³⁻⁵

This work established that the cyclopropyl group often preferentially adopts the bisected confor-

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

(4) (a) N. L. Bauld, R. Gordon, and J. Zoeller, Jr., *ibid.*, **89**, 3948 (1967); (b) N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller, Jr., R. D. Gordon, and J. S. Hyde, *ibid.*, **91**, 6666 (1969); (c) C. E. Hudson and N. L. Bauld, *ibid.*, **94**, 1158 (1972).

(5) (a) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, **91**, 1877 (1969); (b) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, **91**, 1879 (1969); (c) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971).

(1) This investigation was supported by Grants GP 13639 and GP 29574X from the National Science Foundation.

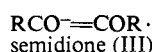
(2) Fellow of the New York State Board of Regents, 1968–1969; Fellow of the Petroleum Research Fund of the American Chemical Society, 1969–1970.



mation I rather than the perpendicular conformation II in accord with other results concerning cyclopropylcarbinyl carbonium ions and cyclopropylbenzene.⁶ The conclusion is based on the angular dependence of a_β , eq 1, where ρ_C^π is the spin density in the carbon p_z

$$a_\beta = \rho_C^\pi (B_0 + B \cos^2 \theta) \quad (1)$$

orbital, B_0 and B are constants near 0 and 50 G, respectively, and θ is the dihedral angle between the axis of the p_z orbital and the carbon-hydrogen bond.⁷ Thus, Russell and Malkus found that a_β for the cyclopropyl hydrogen atoms was substantially smaller than a_β for the related atom of the isopropyl group in the semidione III. The reduced a_β indicates that this atom in IIIb, on the average, lies close to the nodal plane of the



IIIa, R = isopropyl; $a_\beta = 1.92$ G (2 H); $a_\gamma = 0.05$ G (12 H)
 IIIb, R = cyclopropyl; $a_\beta = 0.57$ G (2 H); $a_\gamma = 0.37, 0.20$ G (4 H)
 IIIc, R = cyclopentyl; $a_\beta = 1.92$ G (2 H); $a_\gamma = 0.44, 0.22$ G (2 H)

π system of the semidione and that the cyclopropyl group prefers the bisected conformation. The γ (methylene) hydrogen atoms of the cyclopropane substituent also couple. Russell and Malkus pointed out that these couplings could result through electron delocalization from the cyclopropyl ring but that other interactions, e.g., spin polarization, could contribute to the appearance of spin density at the γ hydrogen atoms.³ In another investigation, Bauld and his students examined several arylcyclopropanes including the anion and cation radicals of 9-cyclopropylanthracene (IV).⁴

9-Alkylanthracene (IV)	a_β , cation, G	a_β , anion, G
CH ₃	7.8	4.3
CH(CH ₃) ₂	1.6	0.62
CH(CH ₂) ₂	4.8	6.64

They too found that the cyclopropyl group often prefers the bisected form, especially in cation radicals, but that this preference can be attenuated by steric effects. Certain observations, for example, the temperature dependence of a_β for tris(4-cyclopropylphenyl)carbinyl radical V and the small a_β value for 4-(2-cyclopropyl-1-ethynyl)nitrobenzene anion radical, were identified with a negative value for B_0 (cyclopropane), eq 1. Bauld and his associates suggested that a cyclopropyl-cyclobutyl conjugative effect yields negative spin density on the β hydrogens.^{4b, 4c} The value of a_γ for V increases as the temperature is reduced. This result was identified with the more efficient conjugation in the bisected form through allylcarbinyl resonance.^{4b} Kochi, Krusic, and Eaton prepared cyclopropylcarbinyl radical VI.⁵ Their results indicate an important preference for the bisected form. The a_β value is temperature dependent and anomalously small.⁵ Krusic and his associates attributed this result, not to a negative B_0 , but rather to a structural distortion which reduces B .^{5c} INDO analyses support this view. These in-

(6) A resumé of the effort is presented by P. v. R. Schleyer and V. Buss, *J. Amer. Chem. Soc.*, **91**, 5880 (1969).

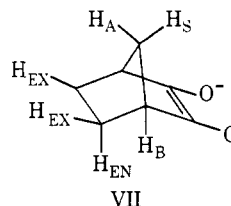
(7) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, Chapter 6.

VI, $a_\alpha = 20.7$ G, $a_\beta = 2.55$ G, $a_\gamma(\text{exo}) = 2.98$ G,
 $a_\gamma(\text{endo}) = 2.01$ G

vestigators noted that the large a_γ may result from spin donation from the p_z orbital to an antibonding ring orbital.

In summary, these studies establish that cyclopropylcarbinyl derivatives usually prefer the bisected conformation. Doubt exists concerning the best values of B_0 and B , and hence $\langle \theta \rangle$ because there are two different viable interpretations for the small a_β values. It is evident that more spin density appears at the γ nuclei when the radical adopts the bisected form. However, three rather different qualitative interpretations were advanced for this finding.

One path for the coupling of the γ hydrogen atoms involves the delocalization of electron density from the p-rich carbon-carbon bond of the cyclopropane ring to the electron-deficient p or π orbital of the spin label. Similar interactions are often considered for the appearance of spin density at the remote positions of spin-labeled bicyclic molecules.⁸⁻¹³ There is a close relationship between the coupling constants for the γ hydrogen atoms of the cyclopropane ring and the remote hydrogen atoms of the bicyclic compounds VII. We



have, therefore, examined the stereochemical dependence of the γ hydrogen coupling interaction through a study of new cyclopropanes in which the ring is oriented by steric or structural requirements. The success realized by McKinney and Geske in their investigation of the conformations of 4-alkylnitrobenzene anion radicals¹⁴ prompted the selection of these derivatives for study. Moreover, several important compounds of this class were known.¹⁵⁻¹⁷ Accordingly, we studied the spectra of anion radicals with the cyclopropane fragment constrained either to the bisected

(8) (a) G. A. Russell, T. Ku, and J. Lokensgard, *J. Amer. Chem. Soc.*, **92**, 3833 (1970); (b) G. A. Russell and G. R. Stevenson, *ibid.*, **93**, 2432 (1971), and related contributions concerning ketyl and semidiones.

(9) D. Kosman and L. M. Stock, *ibid.*, **91**, 2011 (1969), and related work concerning semiquinones.

(10) S. F. Nelsen, E. F. Travedo, and E. D. Seppanen, *ibid.*, **93**, 2913 (1971), and related work concerning semifurquinones.

(11) G. R. Underwood and V. L. Vogel, *ibid.*, **93**, 1058 (1971).

(12) A. Rassat and J. Ronzaud, *ibid.*, **93**, 5041 (1971), and related contributions concerning the bicyclic nitroxide radicals.

(13) (a) S. Terabe and R. Konaka, *ibid.*, **93**, 6323 (1971); (b) K. Tori, Y. Yoshimura, and R. Muneyuki, *ibid.*, **93**, 6324 (1971).

(14) T. M. McKinney and D. H. Geske, *ibid.*, **89**, 2806 (1967).

(15) G. L. Closs, H. B. Klinger, and S. H. Goh, unpublished results; H. B. Klinger, Thesis, The University of Chicago Library, 1967; S. H. Goh, Thesis, The University of Chicago Library, 1968.

(16) R. C. Hahn, P. H. Howard, S. Kong, G. A. Lorenzo, and N. L. Miller, *J. Amer. Chem. Soc.*, **91**, 3558 (1969). We thank Professor Hahn for advising us of his work prior to publication.

(17) L. M. Stock and P. E. Young, *ibid.*, **94**, 4247 (1972).

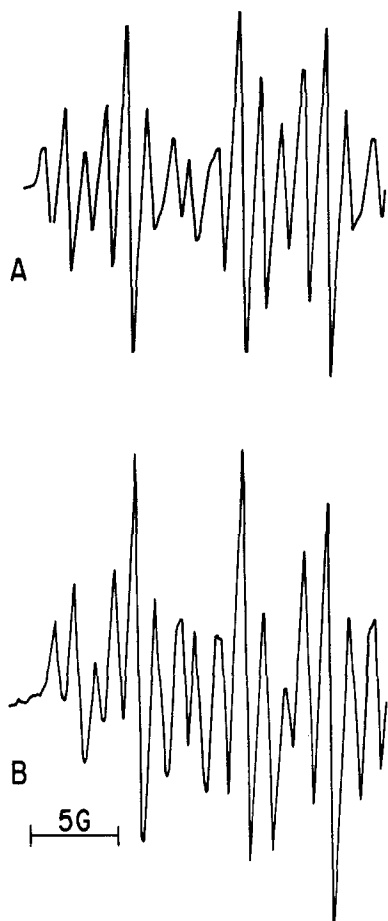
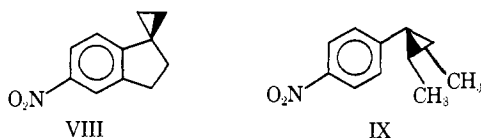


Figure 1. The low-field portion of the spectrum of *syn*-[4-(*cis*-2,3-dimethylcyclopropyl)]nitrobenzene anion radical is shown in B. A is the computer simulation of the spectrum.

conformation as in 5-nitrospiro(cyclopropane-1,1'-indan) (VIII) or largely to the perpendicular conformation as in *syn*-4-(*cis*-2,3-dimethylcyclopropyl)nitrobenzene (IX). To guide the interpretation of the long-



range constants we calculated the spin and electron density distribution in selected radicals by the INDO method.^{18,19}

Results

The aromatic nitro compounds were, with one exception, prepared in the study of the nitration reaction of the related hydrocarbons.¹⁷ Another reference compound 5-nitrospiro(cyclopentane-1,1'-indan) was synthesized from indene as described in the Experimental Section.

The anion radicals were generated electrolytically in acetonitrile, dimethylformamide, or in these solvents with added water. The spectra were somewhat more highly resolved when water (1–2%) was present.¹⁴ The a_N value was altered by water but the other con-

(18) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

(19) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

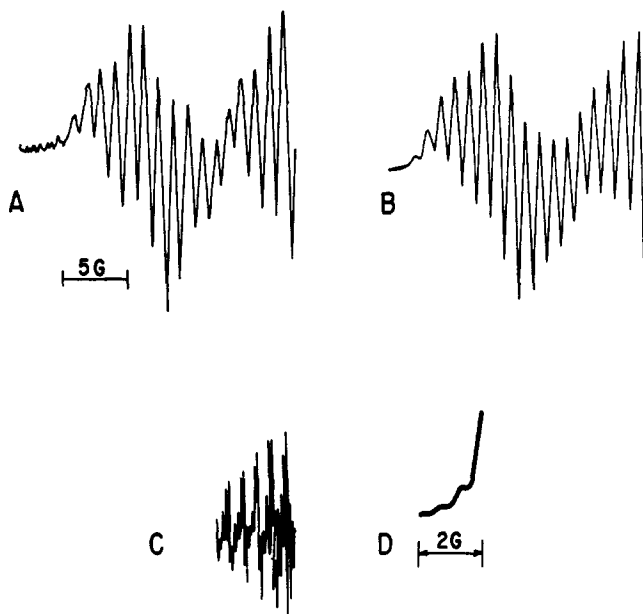
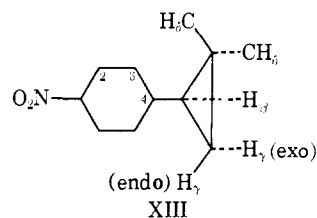


Figure 2. The low-field portion of the spectrum of *anti*-[4-(*cis*-2,3-dimethylcyclopropyl)]nitrobenzene anion radical at moderate resolution is shown in A. B is the computer simulation of this spectrum. C is the center portion of the spectrum at high resolution. D is the first three lines of the methyl septet recorded after multiple scans.

stants were unchanged. Because the solvent-induced changes in the constants are small, we only present the coupling constants, accurate within 0.03 G, for acetonitrile.

The atoms in the radicals are designated as shown in XIII. The constants assessed by a first-order analysis



of the spectra were tested by computer simulation.²⁰ Each analysis was based on the premise that the constants for the hydrogen atoms of the aromatic ring were similar to the known constants for 4-nitrotoluene, 4-nitrocumene, and 5-nitroindan.¹⁴ The correspondence between the observed and computed spectra is illustrated in Figure 1.

Unfortunately, we were unable to establish precise a values by computer simulation of the high-resolution spectrum (Figure 2C) of *anti*-[4-(*cis*-(2,3-dimethylcyclopropyl)]nitrobenzene. The low-resolution spectrum (Figure 2A) could be readily simulated (Figure 2B) by the constants $a_N = 10.90$, $a_2 = 3.33$, $a_3 = 1.17$, $a_\beta = 1.08$, and $a_\delta = 0.94$ G, respectively. The unusually large constant, a_δ , for the methyl hydrogen atoms was required by the spectrum width. The penultimate resonance of the septet due to these nuclei was detected at high gain and the outermost line was detected by time averaging methods (Figure 2D). The reasonable

(20) The observed and computed simulated spectra for all the compounds are presented by P. E. Young, Thesis, University of Chicago Library, 1971.

Table I. Coupling Constants for Nitrobenzene Anion Radicals in Acetonitrile

Compound	Coupling constant, G ^a					
	a_N	a_2	a_3	a_4	a_β	a_γ
Nitrobenzene ^b	10.32	3.39	1.09	3.97		
4-Methyl- ^b	10.70	3.39	1.11		3.98	
4-Ethyl- ^b	10.71	3.37	1.11		2.96	
4-Isopropyl- ^b	10.66	3.36	1.10		1.74	
4-Vinyl-	9.26	3.38	1.18		1.18	2.29
4-Cyclopropyl-	11.09	3.39	1.14		1.39	0.27
<i>syn</i> -[4-(<i>cis</i> -2,3-Dimethylcyclopropyl)]-	10.83	3.36	1.09		6.08	
<i>anti</i> -[4-(<i>cis</i> -2,3-Dimethylcyclopropyl)]- ^c	10.90	3.33	1.17		1.08	0.23
						$a_\delta = 0.94$
3,5-Dimethyl-4-cyclopropyl-	10.95	3.33	1.05		5.68	
4-(1-Methylcyclopropyl)-	10.95	3.37	1.13			
3,5-Dimethyl-	10.6	3.29	1.08	3.92		
5-Nitroindan ⁱ	10.84	3.54	1.11		1.38 ^d	
		3.30			5.40 ^e	
5-Nitro-1,1-dimethylindan	10.92	3.54	1.28		1.20	0.13 ^f
		3.30				
5-Nitrospiro(cyclopentane-1,1'-indan)	11.12	3.38	1.10		1.38	0.07 ^g
5-Nitrospiro(cyclopropane-1,1'-indan)	11.31	3.53	1.11		1.47	0.33
		3.28				
6-Nitrospiro(cyclopropane-1,1'-tetralin) ^h	11.00	3.53	0.99		1.40	0.33 ⁱ
		3.03				

^a The data for acetonitrile are reported. ^b Reference 14. ^c These results are discussed in the text. ^d For the 3 position. ^e For the 1 position. ^f This constant was observed only for 2% water in acetonitrile. ^g Estimated on the basis of the line width. ^h 6-Nitro-3',4'-dihydrospiro(cyclopropane-1,1'(2H')-naphthalene). ⁱ This constant was observed only for dimethylformamide. ^j D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Amer. Chem. Soc.*, **86**, 987 (1964).

Table II. Coupling Constants for Selected Nitrobenzene Anion Radicals and Cyclopropylcarbinyl Radicals Calculated by the INDO Approach

Compound ^a	Coupling constants, G											
	a_N	a_2	a_3	a_{α_1}	a_{α_2}	a_β	$a_{\gamma^{endo}}$	$a_{\gamma^{exo}}$	$a_{\gamma^{total} b}$	a_δ^{endo}	a_δ^{exo}	
Anion radicals												
Nitrobenzene	8.71	-2.88	1.47	-2.84 ^c								
4-Cyclopropyl-												
Bisected	8.49	-2.96 ^d	1.58 ^d			0.26	-0.17	0.15				
Perpendicular	8.34	-2.95	1.54			6.24	-0.15	-0.04				
<i>anti</i> -[4-(<i>cis</i> -2,3-Dimethylcyclopropyl)]-												
Bisected	8.39	-2.98 ^d	1.59 ^d			0.26	-0.22				0.26 ^e	
Perpendicular	8.26	-2.97	1.54			6.25	-0.15				0.04 ^e	
Neutral radicals												
Isobutyl												
Bisected				-21.68	-20.96	1.60	-1.08 ^f	2.06 ^f	-0.21			
Perpendicular				-21.14	-21.14	52.48	-2.16	0.23 ^f	-0.94			
Cyclopentylcarbinyl												
Bisected				-21.89	-20.82	1.67	-1.64	0.95		0.20	0.77	
Perpendicular				-20.95	-20.95	55.31	-1.55	-1.04		0.24	0.42	
<i>syn</i> -(<i>cis</i> -2,3-Dimethylcyclopropylcarbinyl)												
Bisected				-20.92	-20.41	1.33		1.32		0.82 ^e		
Perpendicular				-21.54	-21.54	43.41		-1.24		-0.02 ^e		
(1-Methylcyclopropyl)carbinyl												
Bisected				-20.31	-20.91	-1.48 ^e	-1.36	1.65				
Perpendicular				-21.58	-21.58	0.10 ^e	-1.07	-0.83				
Cyclopropylcarbinyl												
Bisected				-20.67	-21.54	1.34	-1.41	1.72				
Perpendicular				-21.54	-21.54	44.51	-1.26	0.90				
<i>anti</i> -(<i>cis</i> -2,3-Dimethylcyclopropylcarbinyl)												
Bisected				-20.50	-20.36	1.24	-1.53				1.76 ^e	
Perpendicular				-21.51	-21.51	44.09	-1.25				0.32 ^e	

^a The bond lengths and bond angles used for the calculations are discussed in the Experimental Section. ^b The average constant for the three hydrogen atoms. ^c The 4 position. ^d The average constant for the two slightly different hydrogen atoms of the 2 and 3 positions. ^e The average constant for the hydrogen atoms of the methyl group. ^f The constants for the hydrogen atoms held in the positions analogous to the positions of the exo and endo hydrogen atoms of the cyclopropyl and cyclopentyl rings.

values for a_N , a_2 , a_3 , and a_β , knowledge of the spectrum width and the hyperfine pattern (Figure 2C), suggest that a_γ is 0.23 G. The a values assigned for this radical are compatible with the INDO analysis discussed subsequently.

The very small constants for certain γ hydrogen atoms could not be measured under the same conditions. For 5-nitro-1,1'-dimethylindan, a_γ was determined in acetonitrile with 2% water. For the spiro-tetralin, a_γ was measured in dimethylformamide. For

5-nitrospiro (cyclopentane-1,1'-indan), a_γ could not be resolved in any solvent. However, the large line width, about 0.4 G, suggests that a_γ is significant, 0.07 ± 0.02 G.

The results are summarized in Table I.

Pople and his associates obtained impressive agreement between the predictions of INDO theory and the coupling constants for many radicals including nitrobenzene anion radical.^{18,19} We calculated the constants for selected nitrobenzene anion radicals and for certain cyclopropylcarbinyl radicals to evaluate alternative charge and spin transfer mechanisms. The results are summarized in Tables II and III.

Table III. Calculated Energy of Radicals

Compound	Energy, kcal mol ⁻¹		
	Bisected conformation	Perpendicular conformation	Difference
Anion radicals			
4-Cyclopropylnitrobenzene	-72,064.68	-72,063.62	1.06
<i>anti</i> -[4-(<i>cis</i> -2,3-Dimethylcyclopropyl)-nitrobenzene]	-82,648.74	-82,647.48	1.26
Neutral radicals			
Isobutyl	-21,447.73	-21,446.34	1.39
Cyclopentylcarbinyl	-31,116.39	-31,115.00	1.39
<i>syn</i> -(<i>cis</i> -2,3-Dimethylcyclopropyl)carbinyl	-31,051.60	-31,048.43	3.17
(1-Methylcyclopropyl)carbinyl	-25,758.24	-25,754.51	3.73
Cyclopropylcarbinyl	-20,468.03	-20,462.88	5.15
<i>anti</i> -(<i>cis</i> -2,3-Dimethylcyclopropyl)carbinyl	-31,052.06	-31,046.36	5.70

Discussion

Coupling Constants for Nitrogen Atoms. Linear relationships between a_N and the partial rate factors for electrophilic substitution and Hammett σ constants have been examined to define the electron distribution in nitrobenzene anion radicals.^{21,22} The para partial rate factors and the a_N values for the radicals examined in this work are presented in Table IV.

Table IV. Nitrogen Atom Coupling Constants for Anion Radicals, $\text{RC}_6\text{H}_4\text{NO}_2$, and Para Partial Rate Factors for Nitration, RC_6H_5

Compound	p_r^a	a_N , G
Benzene	1	10.32
Toluene	185	10.70
<i>syn</i> -(<i>cis</i> -2,3-Dimethylcyclopropyl)benzene	416	10.83
(1-Methylcyclopropyl)benzene	658	10.95
1,3-Dimethyl-2-cyclopropylbenzene	944 ^b	10.95
Cyclopropylbenzene	947	11.09
<i>anti</i> -(<i>cis</i> -2,3-Dimethylcyclopropyl)benzene	2430	10.90
Indan	1130 ^b	10.84
1,1-Dimethylindan	1220 ^b	10.92
Spirotralin	6270 ^c	11.00
Spiroindan	9140 ^b	11.31

^a Reference 17. ^b The 5 position. ^c The 6 position.

(21) (a) P. L. Kolker and W. A. Waters, *Proc. Chem. Soc.*, 55 (1963);
 (b) P. L. Kolker and W. A. Waters, *J. Chem. Soc.*, 1136 (1964).
 (22) E. G. Janzen, *Accounts Chem. Res.*, 2, 279 (1969).

Values of a_N for the alkyl and cyclopropyl compounds are larger than a_N for nitrobenzene. The a_N values also parallel the partial rate factors. These findings are in accord with previous analyses^{21,22} and with the idea that the aromatic nucleus is electron deficient in the anion radical.^{21,22} Only the result for *anti*-[4-(*cis*-2,3-dimethylcyclopropyl)]nitrobenzene departs from this trend. The reduced a_N value for this molecule may result from a somewhat greater delocalization of spin density to the cyclopropyl group. This interpretation is compatible with the large constants for the γ and δ hydrogen atoms of the cyclopropane ring, Table I. Similar but accentuated changes appear in the coupling pattern for 4-vinylnitrobenzene anion radical with a_N reduced to 9.26 G and large a_H values for the hydrogen atoms of the vinyl group.

Rather substantial changes in the conformational preference of the cyclopropyl group have only a small influence on a_N . The structure of spiro(cyclopropane-1,1'-indan) constrains the cyclopropyl group to the bisected conformation, whereas steric interactions force the cyclopropyl group in the *syn*-[4-(*cis*-2,3-dimethylcyclopropyl)] derivative to deviate from this conformation. For these two radicals, a_N differs by only 0.5 G. There is an even smaller difference between a_N constants when the cyclopropyl groups have comparable substituents. The difference between a_N for the *syn*- and *anti*-[4-(*cis*-2,3-dimethylcyclopropyl)]nitrobenzene anion radicals which prefer the perpendicular and bisected conformations, respectively, is 0.07 G. The calculated a_N values for the bisected and perpendicular conformations of two typical radicals, Table II, predict a small difference, 0.15 G, in agreement with the experimental results.²³

Coupling Constants for α and β Hydrogen Atoms. The constants for the aromatic hydrogen atoms, a_2 and a_3 , of the monoalkyl derivatives are near 3.35 and 1.10 G, respectively, Table I. The interactions responsible for these couplings are well understood and theoretical methods for their analysis are quite advanced.²⁴ The INDO approach, for example, yields values, a_2 about -3 G and a_3 about +1.4 G, in good agreement with experiment.

The constancy of a_2 and a_3 for the 4-alkylnitrobenzene radicals indicates that the spin density at the 2 and 3 positions is independent of the character of the 4 substituent. These data suggest that the spin density at the 4 position, ρ_{C-4}^π , is also essentially constant. The findings that the variations in a_N are small and that the calculated ρ_{C-4}^π values range only from 0.141 for the cyclopropyl to 0.146 for *anti*-*cis*-2,3-cyclopropyl groups support this conclusion.

Interest in the conformational preference of alkyl groups led McKinney and Geske to define R , eq 2,

$$R = \frac{a_\beta}{a_{\beta-\text{CH}_3}} = 2\langle \cos^2 \theta \rangle \quad (2)$$

where a_β is the constant for the β nuclei of the group under study, $a_{\beta-\text{CH}_3}$ is the constant for the corresponding radical with a methyl group at the selected position, and $\langle \cos^2 \theta \rangle$ is the average value for the di-

(23) The absolute a_N values, Table II, are not completely reliable. Prior work established that the theory underestimates a_N by about 25%.¹⁹

(24) Several models for the methyl radical are compared by D. M. Schrader and K. Morokuma, *Mol. Phys.*, 21, 1033 (1971).

hedral angle. This expression is applicable when ρ_C^π is constant and when B_0 is negligible. More detailed tactics focusing on the potential barrier, V_0 , to rotation about the bond between the radical site and an alkyl group have been used by Bauld and Krusic and their associates.^{4,5c} Curiously, a_β for the cyclopropane derivatives is smaller than predicted by the usual values of B and B_0 . As noted, two interpretations have been advanced. Hudson and Bauld^{4c} suggested that spin delocalization produced negative spin density at the β hydrogen atom and proposed eq 3 for the conforma-

$$\frac{a_\beta}{a_{\beta\text{-CH}_3}} = 1.85(\cos^2 \theta) - 0.10 \quad (3)$$

tional analysis of cyclopropanes based on a negative B_0 parameter. Krusic, in contrast, inferred that a structural deformation reduced B .^{5c} Sufficient data are not yet available to distinguish between these interpretations.²⁵ Fortunately, only a minor uncertainty develops in the conformational preferences of the cyclopropyl groups examined in this study. Pertinent a_β values, the related quantities, R and $\langle\theta\rangle$, and the potential barrier V_0 , estimated by an approximate method,^{4b} are summarized in Table V.

Table V. Experimental and Theoretical Parameters Related to the β Coupling Constants

Compound	a_β , G	R^a	$\langle\theta\rangle$, deg Eq 2 Eq 3	V_0 , ^b kcal mol ⁻¹
4-Methylnitrobenzene	3.98	1.00	45 45	
4-Isopropylnitrobenzene	1.74	0.44	62	1.7 ^c
4-Cyclopropylnitrobenzene	1.39	0.35	65 60	2.0 ^c (1.2) ^e
<i>syn</i> -[4-(<i>cis</i> -2,3-Dimethyl- cyclopropyl)]nitrobenzene	6.08	1.53	28 20	1.5 ^d
<i>anti</i> -[4-(<i>cis</i> -2,3-Dimethyl- cyclopropyl)]nitrobenzene	1.08	0.27	68 63	2.8 ^c
3,5-Dimethyl-4-cyclo- propylnitrobenzene	5.68	1.43	32 24	1.1 ^d

^a Based on eq 2. ^b Rotational barrier estimated by the procedure outlined in Figure 2, ref 4b. ^c Preference for bisected form. ^d Preference for perpendicular form. ^e Reference 4c.

The extreme a_β values are realized for *anti*- and *syn*-[4-(*cis*-2,3-dimethylcyclopropyl)]nitrobenzene anion radical. The other results for a_β are intermediate but differ importantly from the free rotation value for the methyl group. The quantities R , θ , and V_0 measure the extent of the conformational preference. Thus, the preference of the *cis*-2,3-dimethylcyclopropyl group in the *anti* compound for the bisected conformation ($R = 0.27$, $V_0 = 2.8$ kcal mol⁻¹) is greater than that of the cyclopropyl ($R = 0.35$, $V_0 = 2.0$ kcal mol⁻¹) or the isopropyl ($R = 0.44$, $V_0 = 1.6$ kcal mol⁻¹) groups in the related anion radicals. In contrast, the *cis*-2,3-dimethylcyclopropyl group of the *syn* compound ($R = 1.53$, $V_0 = 1.5$ kcal mol⁻¹) and the cyclopropyl group of 3,5-dimethyl-4-cyclopropylnitrobenzene ($R = 1.43$, $V_0 = 1.1$ kcal mol⁻¹) exhibit a preference for the per-

(25) Analyses of data for a_β for isopropyl derivatives²⁶ and cyclopropane bonded to sp carbon atoms^{4c} support the view that B_0 is negative. On the other hand, INDO analyses^{5c} and the related behavior of certain 2-substituted ethyl radicals²⁷ suggest that B is unusually small.

(26) N. L. Bauld, C. E. Hudson, and J. S. Hyde, *J. Chem. Phys.*, **54**, 1834 (1971).

(27) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

pendicular conformation. The cyclopropyl substituent in the anion radicals prefers the bisected conformation. However, steric interactions can, as observed previously,⁴ dictate the conformational preferences of cyclopropyl groups in radicals. The observations for the *syn* and *anti* compounds illustrate this point with an estimated potential energy barrier difference of 4.3 kcal mol⁻¹. The barrier, V_0 , to rotation in 4-cyclopropylnitrobenzene anion radical is estimated to be 2 kcal mol⁻¹ by an approximate method.^{4b} A more rigorous procedure suggests a lower barrier, about 1.2 kcal mol⁻¹.^{4c} The calculated energy differences, Table III, between the bisected and perpendicular conformations of the anion radicals are in good accord with the lower value.

Coupling Constants for γ and δ Hydrogen Atoms. Measurable constants for the γ -cyclopropyl methylene hydrogen atoms and the δ hydrogen atoms of methyl groups are observed when the cyclopropyl group is constrained by steric or structural requirements to the bisected form. Thus, a_γ is 0.33 G for the spiroindan and spiroindalin and 0.27 G for 4-cyclopropylnitrobenzene anion radical. In contrast, a_δ is below the detection limit for the anion radicals which prefer the perpendicular conformation. The γ couplings, therefore, have an important angular dependence. The four γ hydrogen atoms of the radicals derived from 4-cyclopropylnitrobenzene and both spiro compounds exhibit, within the resolution limit, the same constant even though these atoms are not equivalent. Their apparent equivalence is almost certainly accidental because the γ hydrogen atoms of semidiones (III) and cyclopropylcarbinyl radicals VI do exhibit unequal couplings. In the reference compounds, 4-ethyl- and 4-isopropylnitrobenzene anion radicals, a_γ is undetectable. The constants for the γ atoms of 5-nitro-1,1'-indan and 5-nitrospiro(cyclopentane-1,1'-indan) anion radical are above the detection limit, but about threefold smaller than the values for the cyclopropanes.

The finding that the methyl hydrogen atoms of *anti*-4-(*cis*-2,3-dimethylcyclopropyl)nitrobenzene are coupled importantly is surprising. Indeed, the constant for these δ hydrogen atoms, 0.94 G, is about threefold larger than the constants for the *exo* or *endo* γ hydrogen atoms in anion radicals which prefer the bisected conformation. The hydrogen atoms of the methyl groups of the related *syn* derivative and 4-(1-methylcyclopropyl)nitrobenzene are uncoupled as are the δ hydrogen atoms of 4-nitro(spirocyclopentane-1,1'-indan).

Several ideas have been advanced to account for the appearance of important spin density at the remote γ and δ positions.^{3-5,8-13} Explanations based on the concept of spin polarization with the transfer of spin density without charge transfer and on the concept of electron delocalization with charge transfer have been considered. For the most part, these ideas are incorporated in the INDO theory^{18,19} and in the spin polarization models developed by Luz and Barfield.^{28,29} These theories yield estimates of spin density at the nuclear sites and therefore have an inherent advantage over theories based exclusively on the concept of elec-

(28) Z. Luz, *J. Chem. Phys.*, **48**, 4186 (1968).

(29) M. Barfield, *J. Phys. Chem.*, **74**, 621 (1970).

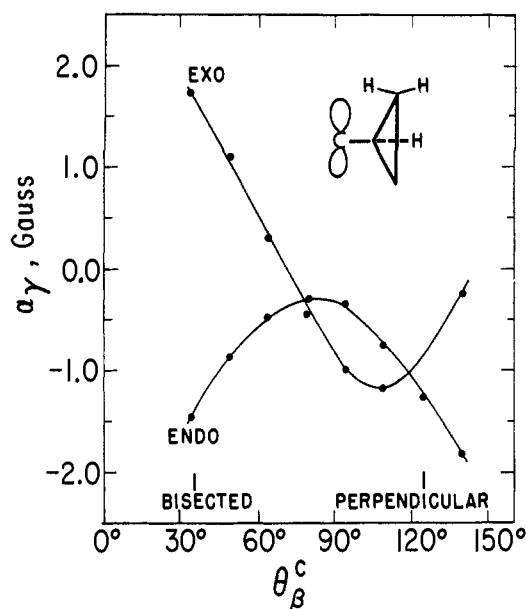


Figure 3. The relationship between the coupling constants for the endo and exo hydrogen atoms and the angle, θ_{β}^C , based on the INDO theory.

tron delocalization. Luz and Barfield developed their quantitative approach for the interpretation of a_{γ} and a_{δ} on the basis of exchange integrals and other parameters for strain-free molecules with a focus on the internuclear angles rather than on the interorbital angles important in strained molecules. Both theories consider the indirect paths, XI and XII, important. However, Barfield included several other paths, e.g., XIII for the transmission of spin information. Both positive and negative a_{γ} values can be obtained depending on the geometry of the radical. We calculated the constants for the γ and δ hydrogen atoms of two representative simple molecules, cyclopropylcarbinyl and *cis*-2,3-dimethylcyclopropylcarbinyl radicals, by both spin polarization models and INDO theory to evaluate the predictive capabilities of these methods. We used the procedure and notation, XIV, of Rassat and Ronzaud.¹²

The calculated values are derived from eq 4 in the Luz analysis

$$a_{\gamma} = -1.14 \cos^2 \theta_{\beta}^C - 0.88 \cos^2 \theta_{\gamma}^H \quad (4a)$$

$$a_{\delta} = +1.35 \cos^2 \theta_{\beta}^C \cos^2 \theta_{\delta}^H \quad (4b)$$

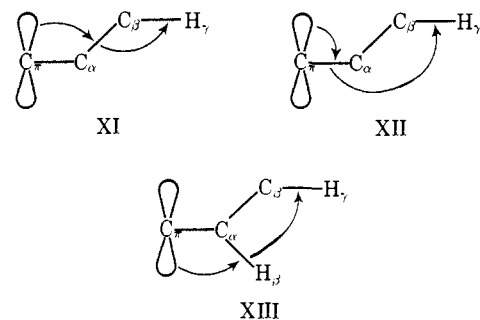
and from eq 5 in the Barfield analysis

$$a_{\gamma} = 1.65 \cos^2 \theta_{\beta}^C - 0.84 \cos^4 \theta_{\beta}^C + 2.62K(\theta_{\gamma}^H) - 0.68 \cos^2 \theta_{\beta}^C [K(\theta_{\gamma}^H) + 120] + K(\theta_{\gamma}^H - 120)] + 0.15[\cos^2(\theta_{\beta}^C + 120)K(\theta_{\gamma}^H + 120) + \cos^2(\theta_{\beta}^C - 120)K(\theta_{\gamma}^H - 120)] + 0.17 \quad (5a)$$

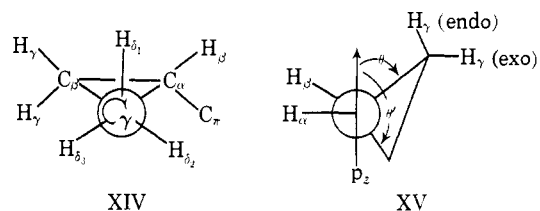
$$a_{\delta} = -8.42K(\theta_{\delta}^H)\cos^2 \theta_{\beta}^H \quad (5b)$$

$$K(\theta) = -0.287 \cos^2 \theta + 0.016 \cos \theta + 0.015 \quad (5c)$$

where θ_{β}^C is the angle between the p_z orbital and the plane $C_{\pi}C_{\alpha}C_{\beta}$, θ_{γ}^H is the angle between the planes $C_{\pi}C_{\alpha}C_{\beta}$ and $C_{\alpha}C_{\beta}C_{\gamma}$, and θ_{δ}^H is the angle between the planes $C_{\alpha}C_{\beta}C_{\gamma}$ and $C_{\beta}C_{\gamma}H_{\delta}$. The angles are measured in a clockwise sense. Contributions from the γ path defined by θ_{β}^C and the δ path defined by θ_{δ}^H were



added to yield a_{γ} for one pair of endo and exo hydrogen atoms, XV. The single contribution for the δ



hydrogen atoms of the methyl groups was derived for conformation XIV where the $C_{\gamma}H_{\delta}$ bond bisects the angle $C_{\beta}C_{\beta}C_{\alpha}$. The results are summarized in Table VI.

Table VI. Calculated Coupling Constants for γ and δ Hydrogen Atoms of Cyclopropylcarbinyl and *syn*- and *anti*-(*cis*-2,3-Dimethylcyclopropyl)carbinyl Radicals Based on Spin Polarization Models and the INDO Model

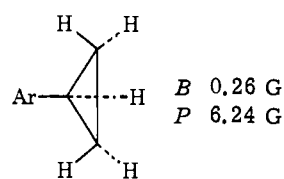
Dihedral angle, θ_{β}^C	Coupling constant, G				
	a_{γ} Cyclopropyl Endo	a_{γ} Cyclopropyl Exo	a_{δ_1} 2,3-Dimethylcyclopropyl	a_{δ_2} 2,3-Dimethylcyclopropyl	a_{δ_3} 2,3-Dimethylcyclopropyl
Luz Spin Polarization Model					
0°	-2.0	-1.7	+0.9	+0.01	+1.1
Bisected	-1.5	-1.2	+0.6	+0.005	+0.7
90°	-0.8	-0.5	0.00	0.00	0.00
Perpendicular	-1.2	-0.9	+0.3	+0.002	+0.4
Barfield Spin Polarization Model					
0°	+0.4	+0.6	+1.6	-0.1	+2.0
Bisected	+0.7	+0.9	+1.0	-0.08	+1.3
90°	-0.6	-0.3	0.00	0.00	0.00
Perpendicular	+0.1	+0.6	+0.4	-0.04	+0.6
Pople INDO Model					
Bisected	-1.4	1.7			
Perpendicular	-1.3	-0.9			
Bisected ^a	-1.5		+0.3	+0.6	+4.4
Perpendicular ^a	-1.3		+0.08	+0.2	+0.7
Bisected ^b		+1.3	+0.3	+0.4	+2.0
Perpendicular ^b		-1.2	-0.3	+0.2	+0.07

^a Dimethyl derivative, *anti* isomer. ^b Dimethyl derivative, *syn* isomer.

Because the Luz and Barfield models are based on parameters for strain-free molecules, these approaches only suggest limiting values for a_{γ} and a_{δ} in strained molecules. The Barfield model suggests that a_{γ} for the endo and exo atoms is positive in both conformations. The Luz model suggests negative values. In each case, the constant predicted for the exo γ atom is, in an absolute sense, more positive than the value for the endo γ atom. Both models suggest a_{δ} is positive. However, neither model distinguishes between the endo and exo groups because only one interaction, that between the $C_{\alpha}-C_{\beta}$ bond and the $C_{\gamma}-H_{\delta}$ bond, is considered. The INDO theory yields different results. Certain

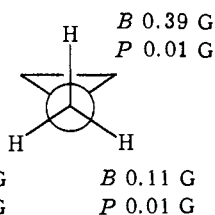
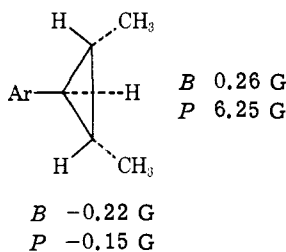
differences almost certainly originate in the adaptability of the INDO method to strained molecules. In brief, this theory indicates that a_γ is negative for the endo hydrogen atoms in both conformations and also for the exo atoms for the perpendicular form. On the other hand, a_γ for the exo hydrogen atom is large and positive for the bisected conformation. The angular dependence of a_γ is shown in Figure 3. As the spin polarization models, this approach suggests that a_δ is positive. However, the INDO model distinguishes between the methyl groups of the isomeric syn and anti compounds with the quite remarkable value, 4.4 G, predicted for hydrogen atom δ_3 in the bisected conformation of the anti isomer XIV. This constant is threefold larger than the constant predicted for the exo γ hydrogen atoms.

The constants suggested by the INDO theory for the anion radicals examined in this study are shown in XVI and XVII.



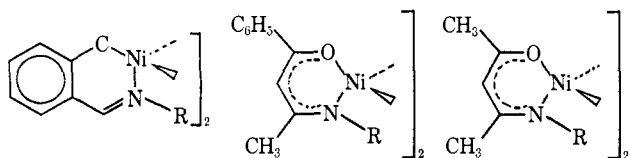
B -0.17 G B 0.15 G
P -0.15 G P -0.04 G

XVI



XVII

A thorough comparison of theory and experiment is difficult because the signs of many constants are not yet established with confidence. However, the contact chemical shifts for three nickel complexes, XVIII-XX,



XVIII, R = cyclo-Pr XIX, R = cyclo-Pr XX, R = cyclo-Pr

indicate that the constants of the exo and endo hydrogen atoms are distinctly different and suggest that the signs are indeed opposite.³⁰ More recent work on the contact chemical shifts of these atoms in a nickel complex of 4-aminocyclopropylbenzene³¹ indicates a_γ (endo) is negative and a_γ (exo) is positive.³¹ These results are compatible with the findings of the French and Japanese groups in their study of bicyclic molecules.^{12,13} On this basis, we shall adopt the view that a_δ is positive and that a_γ is positive for the exo atoms and negative

(30) P. E. Young, Thesis, University of Chicago Library, 1971.

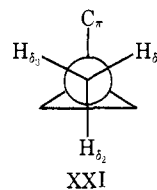
(31) Unpublished results with M. R. Wasielewski.

for the endo atoms of the anion radicals which prefer the bisected conformation. The experimental results indicate that the radicals in which the cyclopropane ring prefers the perpendicular form have only small spin populations at the γ and δ hydrogen atoms, but that rather important spin populations appear at these hydrogen atoms in the anion radicals in which the cyclopropane ring prefers the bisected conformation. Both the Barfield and the Pople models yield a reasonably satisfactory portrayal of these results. For the radicals that prefer the perpendicular form, both theories suggest that the constants for the endo and exo atoms change importantly when the dihedral angle, θ_β^C , deviates from 124° . For example, the Barfield model indicates a_γ for both the endo and exo atoms changes from positive to negative between the perpendicular and 90° conformations, Table VI. Similarly, the INDO theory, Figure 3, suggests that the a_γ for these hydrogen atoms undergo changes in sign and magnitude for the conformations near the perpendicular form. The spectroscopic data reveal that $\langle\theta\rangle$, Table V, is about 30° for these anion radicals. This angle defines the carbon angles, θ_β^C as about 90° and θ'_β^C as about 200° . Thus, within the framework of both theories, the undetectably small couplings for the exo and endo hydrogen atoms in the anion radicals with perpendicular geometry arise from compensating negative values of a_γ at 90° and positive values at 200° .³²

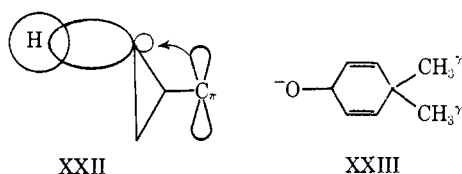
The constants for the radicals that prefer the bisected form have more regular features. There are, however, significant differences in the predictions of the spin polarization models and the INDO theory. Although the calculated a_γ and a_δ values XVI are threefold smaller than observed, the Pople theory does correctly infer that the constants are similar in magnitude and opposite in sign for the anion radicals with bisected geometry and that the constants for the γ atoms of the strained molecules are larger than the constants for unstrained compounds such as the spirocyclopentane or 1,1-dimethylindane. Impressively, this theory indicates that a_δ for the methyl groups of *anti*-(*cis*-2,3-dimethylcyclopropane)nitrobenzene anion radical is about threefold larger than the value for the γ hydrogen atom. The general agreement realized for the cyclopropane derivatives is paralleled by successful analyses of the observations for bicyclic semidiones and nitroxides.¹² We infer that the INDO model is very reliable for the estimation of the sign and approximate magnitude of long-range coupling constants.

In a sense the success achieved with the INDO approach disposes of the problems concerning the interpretation of long-range couplings. However, we believe that it is valuable, insofar as possible, to identify the principal interactions that, in the more traditional

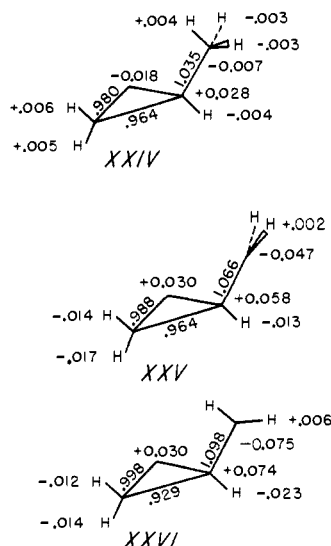
(32) Compensating positive and negative terms also may reduce a_δ for the methyl group of 4-(1-methylcyclopropane)nitrobenzene anion radical below the detection limit. This suggestion is based on the finding that $a_{\delta_1} = a_{\delta_2} = -1.3$ G and $a_{\delta_3} = +3.0$ G for the perpendicular conformation of 1-methylcyclopropylcarbinyl radical XXI.



qualitative sense, are responsible for long-range coupling in the cyclopropanes. Many interactions are included in a natural way in the INDO analysis. They blend to yield either a net α spin or β spin at a specific nucleus. Because the s orbital spin density is determined by the spin populations in many neighboring orbitals, the changes in the observed constants cannot be related with full confidence to variations in bond indices or electronic charge distributions. Certain features are, however, discernible. One interaction that has received particular attention in discussions of long-range coupling is the direct interaction between a p_z orbital and a $C_\beta-H_\gamma$, or a $C_\gamma-H_\delta$ bond, XXII.⁸⁻¹¹ To examine this point, we evaluated the bond indices³³ for the $C_\pi-C_\gamma$ and the $C_\pi-C_\delta$ bonds. These bond indices are small, about 0.004, and similar for both the perpendicular and bisected forms of the cyclopropanes. We infer that this interaction plays only a modest role. Other indirect interactions involving the p_z orbital and the $C_\pi-C_\alpha$ and the $C_\alpha-C_\beta$ bonds have also received attention. Russell and Stevenson,^{8b} for example, proposed that the modest a_γ for XXIII resulted from com-



pensating positive and negative contributions akin to the leading terms depicted in XI and XII. We probed for the importance of the first component, XI, through the evaluation of the bond indices. These values and charge distributions at carbon, ± 0.000 , and hydrogen, $\pm .000$, are summarized for three typical molecules, methylcyclopropane (XXIV) and the perpendicular (XXV) and bisected (XXVI) forms of cyclopropyl-



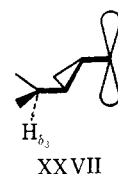
carbonyl radical. The indices for the $C_\alpha-C_\beta$ bond are smaller for the bisected form than for the perpendicular form. Similar but accentuated differences were found for the corresponding cations.¹⁷ The decreased bond indices suggest that a leading interaction which produces positive spin density at the exo γ hydrogen atom occurs between the p_z orbital and the $C_\alpha-C_\beta$ bond in accord with

(33) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

the Russell proposal and the concept of carbon-carbon hyperconjugation. This interaction is, of course, important only in the bisected conformation. The disparity between the spin polarization model and the INDO theory may arise from an enhanced electron delocalization in the bisected molecules. Although the charge distributions XXIV-XXVI do not suggest a deep-seated reorganization of valence electron density, careful analysis does suggest that there is a modest, but significant depletion of electron density from the $C_\alpha-C_\beta$ bond. This difference, also discernible in the anion radicals, is apparent in the radicals and quite pronounced in the cations.¹⁷ Such variations in charge are compatible with the viewpoint expressed by Rassat and others¹² that the positive coupling constants often signal electron as well as spin delocalization. For completeness, we note that the spin polarization mechanisms may also produce positive long-range coupling constants and that sign determinations cannot always uniquely distinguish between the alternative mechanisms.

The importance of the second component, XII, may be inferred from the prediction of the INDO theory that negative spin density appear at both the exo and endo hydrogen atoms of the cyclopropylcarbonyl radical in the perpendicular conformation. The theory indicates that spin density in the p_z orbital polarizes the electron density in the $C_\pi-C_\alpha$ bond in a negative sense and that this imbalance in spin is propagated without sign change to the $C_\beta-H_\gamma$ bond.

Finally, the long-range couplings of the δ hydrogen atoms may be related quite specifically to the W plan structural relationship between H_δ and the radical center that passes through the $C_\alpha-C_\beta$ bond in the bisected structure XXVII.



In summary, many structural components present in bicyclic molecules are also present in the cyclopropanes and many, apparently similar, long-range coupling interactions are observed in both compounds. The INDO theory presents a very reasonable portrayal of the spin density distribution in the cyclopropanes. Finally, certain aspects of the theoretical analysis may be identified with conventional ideas, for example, carbon-carbon hyperconjugation and W plan relationships, concerning the mode of propagation of spin density.

Experimental Section

Spiro(cyclopentane-1,1'-indan). This compound was prepared by the alkylation of indene with 1,4-dibromobutane followed by diimide reduction as described for the preparation of spiro(cyclopropane-1,1'-indan).¹⁷ The alkylation of indene (0.5 mol) provided spiro(cyclopentane-1,1'-indene) (bp 88-91° (1.5 Torr), 28% yield). The nmr spectrum (1.50 (8 H, s), 5.90 (1 H, d, $J = 5.5$ Hz), 6.17 (1 H, d, $J = 5.5$ Hz), 6.8 (4 H, s)) and the mass spectrum (calcd for $C_{13}H_{14}^+$, 170.1095; found, 170.1057) establish the structure.

The compound (0.1 mol) was reduced to spiro(cyclopentane-1,1'-indan) (bp 73-74° (0.5 Torr), 75% yield). The nmr spectrum (1.40 (8 H, s), 1.50 (2 H, t, $J = 7$ Hz), 2.42 (H, t, $J = 7$ Hz), 6.41 (4 H, s)) and the mass spectrum (calcd for $C_{13}H_{16}^+$, 172.1252; found, 172.1219) establish the structure.

5-Nitrospiro(cyclopentane-1,1'-indan). The nitration of spiro(cyclopentane-1,1'-indan) (0.01 mol) with nitric acid and acetic anhydride in methylene chloride was carried out at about 5° by the procedure used for other spiro compounds.¹⁷ The 5- and 6-nitro compounds obtained in nearly equal amounts were separated by vpc. 5-Nitrospiro(cyclopentane-1,1'-indan) (mp 60–62°, 10% yield) was purified by sublimation. The nmr spectrum (1.77 (8 H, s), 2.0 (2 H, t, $J = 7$ Hz), 2.90 (2 H, t, $J = 7$ Hz), 7.14 (1 H, d, $J = 9$ Hz), 7.97–8.10 (2 H, m) and the mass spectrum (calcd for $C_{13}H_{15}NO_2^+$, 217.1103; found, 217.1109) establish the structure. For comparison, the nmr spectrum of the 6-nitro derivative exhibited the following signals: 1.77 (8 H, s), 2.0 (2 H, t, $J = 7$ Hz), 2.90 (2 H, t, $J = 7$ Hz), 7.13–7.37 (1 H, m), 7.85–8.06 (2 H, m). The m/e value observed for this isomer was 217.1096.

Electron Paramagnetic Resonance Spectra. The anion radicals of the nitrobenzene derivatives were generated electrolytically. In a typical experiment, 4-(1-methylcyclopropyl)nitrobenzene (2.0 mg, 9.013 mmol) was dissolved in acetonitrile containing tetra-1-propylammonium perchlorate. This solution was placed in the bulb section of an electrolytic cell³⁴ and degassed. The solution was then introduced into the capillary portion of the cell which contained 0.5 cm of mercury (D. F. Goldsmith). The solution was

(34) C. P. Poole, "Electron Spin Resonance, A Comprehensive Treatise on Experimental Techniques," Interscience, New York, N. Y., 1967, p 628.

continuously electrolyzed at -1.8 V. The spectrum was recorded in the usual way. The spectrum was analyzed by computer simulation.

Acetonitrile was washed with saturated potassium hydroxide solution. The nitrile was decanted and dried over sodium carbonate for 12 hr. The dry material was refluxed for 8 hr over phosphorus pentoxide in a nitrogen atmosphere. Acetonitrile was then collected by distillation and stored under nitrogen. Tetra-1-propylammonium perchlorate was prepared by the neutralization of the ammonium hydroxide (10% solution, 50 ml) with perchloric acid (70% solution, 7.5 ml) at 0°. The white crystals were collected and washed with water. The product was then recrystallized twice from 80:20 water-acetonitrile and dried at 80° over phosphorus pentoxide.

Computations. Program 141, Quantum Chemistry Program Exchange, Indiana University, was used for the INDO calculations. The bond lengths and angles used in these calculations are based on known structural data.³⁵ The general structures of 4-cyclopropyl-nitrobenzene (W) and cyclopropylcarbonyl radical (X) are shown in Figure 1, ref 17.

(35) (a) R. G. Ford and R. A. Beaudet, *J. Chem. Phys.*, **48**, 4671 (1968). (b) R. W. G. Wyckoff, *Crystal Struct.*, **6**, 11 (1969). R. W. G. Wyckoff, "Crystal Structures," John Wiley and Sons, Inc., New York, New York, 1969.

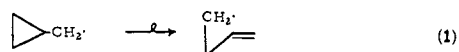
Homolytic Rearrangements and the Conformations of Alkyl Radicals by Electron Spin Resonance

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Abstract: Homolytic rearrangements are studied by esr in the allylcarbonyl, ω -hexenyl, β -acetoxyethyl, neophyl, and 4-phenylbutyl systems, which have been scrutinized previously in chemical studies. The presence and location of unsaturation (vinyl, acetylenyl, carbonyl, or phenyl) in the alkyl chain are employed as possible probes for conformational effects on cyclizations in these systems. The magnitude and the temperature dependence of the hyperfine splitting of the β protons, together with the observation of alternating line widths in the esr spectra, are used as guides to deduce equilibrium conformations. A carbonyl group specifically located in the 4 position relative to the radical center has a unique effect on the selective broadening of only the $M_I = \pm 1$ lines of the β -proton triplets caused by in-phase modulation of the coupling constants. The effects of C=C unsaturation and phenyl groups on the conformation of alkyl radicals are also discussed.

Electron spin resonance spectroscopy (esr) has been used in a direct study of homolytic rearrangements. For example, the esr spectrum of the cyclopropylcarbonyl radical from the photolysis of cyclopropylacetyl peroxides can be readily observed at low temperatures ($< -140^\circ$), whereas only that of the allylcarbonyl radical can be obtained above -100° .¹ At intermediate temperatures the esr spectrum consists of a superposition of these two individual spectra. The reverse process, *viz.* the ring closing of allylcarbonyl



radical to cyclopropyl carbonyl radical, on the other hand, cannot be observed by esr, since only the spectrum of the allylcarbonyl radical is obtained from the photolysis of allyl acetyl peroxides even at -140° . The

kinetic analysis of the vinyl rearrangement of allylcarbonyl radicals, however, indicates that it proceeds *via* cyclization.² The latter is not inconsistent with the esr studies since the concentration of the cyclopropylcarbonyl intermediate may be too low to observe. Similar results have been obtained in an esr examination of the irreversible cyclization of the ω -hexenyl radical to the cyclopentylmethyl radical.³ Both of these systems are unusual for alkyl radicals, since they proceed at relatively high rates. For example, the first-order rate constant for ring opening in eq 1 is in excess of 10^8 sec^{-1} and that for cyclization of the ω -hexenyl radical is approximately 10^5 sec^{-1} at 25° .⁴

Generally, the rearrangement of organic free radicals is less common than that of the analogous carbonium ions.⁵ Homolytic cyclizations, when they have been

(2) L. K. Montgomery, J. W. Matt, and J. R. Webster, *ibid.*, **89**, 923 (1967).

(3) R. A. Sheldon and J. K. Kochi, *ibid.*, **92**, 4395 (1970).

(4) D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).

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