lauroyl-(S)-valyl-*tert*-butylamide optically active stationary phase[20] (30 mg; from a 5% solution in DCM) (Miles Laboratories, Inc., Kankakee, Ill.) and installed in the Hewlett-Packard 5700A gas chromatograph. This was operated isothermally at 100 °C with a helium flow rate of 5 ml/min, and peak tracing and integration were accomplished with a Hewlett-Packard 3800A digital electronic integrator-recorder. As seen in Figure 3, these conditions permitted baseline resolution of the (R) and (S) enantiomers within ca. 22 min, with a peak separation of some 2.8 min. The results of this experiment are presented in Table V, while Table VI includes similar results from two replicate experiments.

Acknowledgment. We wish to express our gratitude to NASA for a research grant (No. NGL 05-020-582), which generously supported a portion of this investigation, and to Professor Michel Boudart of the Department of Chemical Engineering, Stanford University, and Mr. Jose J. Flores of Ames Research Center, Moffett Field, Calif., for their intellectual contribution and physical help in these studies.

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Contact Chemical Shifts for the Carbon Atoms of Nickel Complexes of the 4-Alkylanilines. The Factors Governing the EPR Hyperfine Constants of Carbon Atoms[1]

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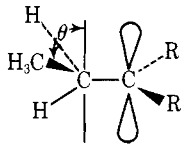
Abstract: The proton and carbon contact chemical shifts of the nickel acetylacetonate complexes of 20 aniline derivatives have been measured. The signs and magnitudes of the contact shifts for the meta and para carbon atoms of these anilines are consistent with the dominant π delocalization of spin density. The contact chemical shifts for the α carbon atoms of the substituents in 4-alkylaniline derivatives depend on the hybridization of the bonding orbital of the α-carbon atom and on the degree of substitution of the α atom. The contact chemical shifts for the β-carbon atoms in 4-alkylaniline derivatives exhibit an angular dependence. The results for molecules in which the dihedral anle is defined by structural constraints are well described by $a_\beta{}^C = \rho_C{}^\pi(-1.1 + 23\langle\cos^2\theta\rangle)$. In general, the contact chemical shifts both for the β-hydrogen and the β-carbon atoms of 4-alkyl groups conform to relationships based on $\langle\cos^2\theta\rangle$. The shifts for the 4-cyclopropylanilines deviate from this relationship. These data indicate that more spin density is delocalized to cyclopropyl groups in the bisected conformation than in the perpendicular conformation. The concept of carbon–carbon hyperconjugation provides a basis for the interpretation of the results.

Interest in the relative importance of carbon–carbon compared to carbon–hydrogen hyperconjugation prompted the initial studies of the electron paramagnetic resonance hyperfine constants, $a_\beta{}^C$, for β-carbon atoms in radicals.[3-5] The results established that spin delocalization to β-carbon atoms is just as important as spin delocalization to β-hydrogen atoms.[3] Progress in the definition of the factors governing spin delocalization to β carbon atoms has been impeded by the difficulties inherent in the spectroscopic study of ^{13}C in natural abundance and in the synthesis of enriched compounds. Consequently, there are few reports concerning these hyperfine interactions.[6-10] The work has, for the most part, focused on the definition of $B_2{}^C$ in eq 1, where $\rho_C{}^\pi$ is the spin density in the adjacent p orbital, θ is the dihedral angle, and $B_0{}^C$ and $B_2{}^C$ are empirical constants.



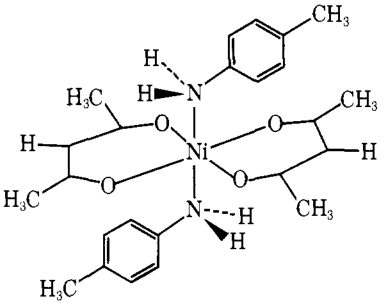
$$a_\beta{}^C = \rho_C{}^\pi(B_0{}^C + B_2{}^C\langle\cos^2\theta_C\rangle) \qquad (1)$$

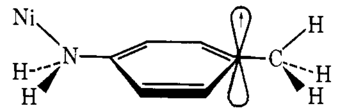
Experimental estimates of the angle-dependent term, $B_2{}^C$, which reflects the extent of spin delocalization range from about 15 to 25 G.[5-8] In the absence of experimental information most workers have assumed that the angle-independent term, $B_0{}^C$, is negligible.[6-8] For comparison, the theoretical results for the 1-propyl radical suggest that $a_\beta{}^C$ should be linearly dependent on $\langle\cos^2\theta_C\rangle$ with $B_0{}^C = 1.1$ G and $B_2{}^C = 13.8$ G.[11]

New interest in the concept of carbon–carbon hyperconjugation as an important factor governing the reactivity of organic molecules indicated that a thorough investigation of the hyperfine interactions of the β carbon atoms would be useful to gauge the impact of steric effects, hybridization changes, and the degree of substitution on electron release from carbon–carbon bonds. Our successful studies of β- and γ-hydrogen interactions[12] on the basis of the contact chemical studies observed for the nickel acetylacetonate complexes of aniline derivatives suggested that an investigation of spin delocalization to β-carbon atoms would resolve the key issues.

$$2C_6H_5NH_2 + Ni(C_5H_7O_2)_2 \rightleftarrows (C_6H_5NH_2)_2Ni(C_5H_7O_2)_2$$

In brief, this approach depends on favorably rapid ligand exchange and electron relaxation rates.[13,14] When these processes are rapid the resonances of the ligand are shifted but the lines are not unduly broadened. The extent of the shift depends, of course, on the concentration of the nickel complex. The method also depends on the idea that the π spin density at the para carbon atom of the aniline determines the chemical shifts of the nuclei of the para-substituent group. Clearly, the interpretation of nuclear resonance shifts in multistate metal complexes is much more difficult than in simple doublet state organic molecules.[14-16] For many complexes, the isotropic contact chemical shifts are altered by σ delocalization and dipolar shifts resulting from anisotropic dipolar interactions. Certain of these interactions could be especially significant for the carbon hyperfine constants. Fortunately, the octahedral nickel complexes have an orbitally nondegenerate ground state ($^3A_{2g}$) and the contact shifts for the ith nucleus can be described by the Bloembergen–McConnell expression,[16a]



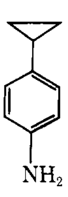


$$\sigma_i = \Delta H_i/H = -a_i(\gamma_e/\gamma_N)g\beta S(S+1)3kT \tag{2}$$

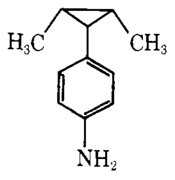
where the chemical shift, $\Delta H_i/H$, is measured relative to the shift in the uncomplexed ligand (or other suitable reference compound), S is the total spin quantum number, and the other symbols have their usual significance.

Aniline (**1a**), 4-methylaniline (**2a**), and 4-trifluoromethylaniline (**3a**) were studied to examine the influence of substituents on the spin distribution in the benzene nucleus.[17] The other 4-alkylanilines (**4a–11a**) were examined to establish the extent of the spin delocalization to β-hydrogen and β-carbon atoms when steric effects were altered. Cyclopropane derivatives (**12a–16a**) were studied to establish the impact of changes in hybridization on the extent of spin delocalization to β-carbon atoms. To secure the relationship between $a_\beta{}^C$ and the dihedral angle, θ, we prepared a series of anilines (**17a–20a**) in which the angle is defined by the structure of the molecule.

CH_3	**2a**	CH_2CH_3	**4a**	$C(CH_3)_3$	**6a**
CH_2CH_3	**4a**	$CH_2CH_2CH_3$	**7a**	$C(CH_2CH_3)_3$	**10a**
$CH(CH_3)_2$	**5a**	$CH_2CH(CH_3)_2$	**8a**	1-adamantyl	**11a**
$C(CH_3)_3$	**6a**	$CH_2C(CH_3)_3$	**9a**		



12a



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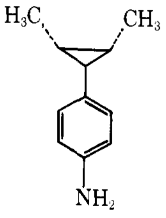

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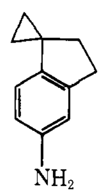

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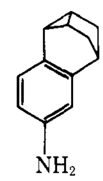

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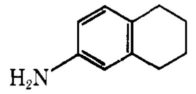
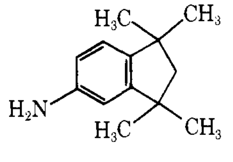
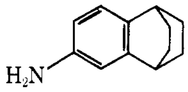


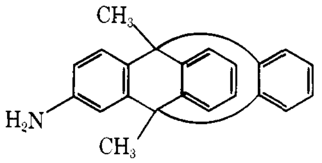
17a



18a



19a

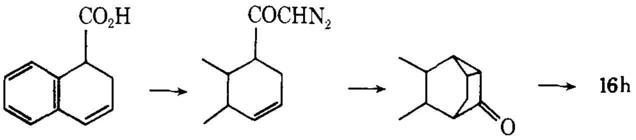


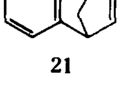
20a

Results

Preparations. The anilines which were not available commercially were obtained by reduction of the corresponding nitro compounds. These compounds were produced by the nitration of the parent hydrocarbons. Most of the necessary hydrocarbons were available. Others, (1-adamantyl)benzene, **11h**;[18] cyclopropylbenzene, **12h**;[19] and 2′,3′-dihydrospiro[cyclopropane-1,1′-indene], **15h**,[20,21] were synthesized by familiar routes. Phenylcarbene generated from benzyl chloride using lithium 2,2,6,6-tetramethylpiperidide by the method of Olofson and Dougherty[22] was added to (*Z*)-2-butene to give a 2:1 mixture of **13h** and **14h** in 77% yield. 1,3-Methano-1*H*-cyclopropa[*a*]naphthalene, **16h**, was previously prepared by Hahn and Rothman.[23] We used their di-π-methane rearrangement procedure and a second approach based on the preparation of tricyclo[2.2.2.0^{2,7}]octan-3-one[24] from 3-cyclohexenecarboxylic acid as shown in Chart I. 1,2-Dihydronaphthoic acid was converted to the diazo ketone which was decomposed over copper to give the ketone in 44% yield. The ketone was reduced to **16h** by a Wolff-Kischner procedure in which the hydrazone was formed before the addition of potassium hydroxide. This reaction gave a 2:1 mixture of **16h** and a new compound which we have tentatively identified as 8,9-dihydro-5,8-methano-5*H*-benzocycloheptene, **21**, on the basis of its NMR spectrum.[25] The other isomer, 1,4-dihydro-1,4-ethanonaphthalene, **22**, was not obtained in discernible amount.

Chart I





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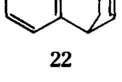


22

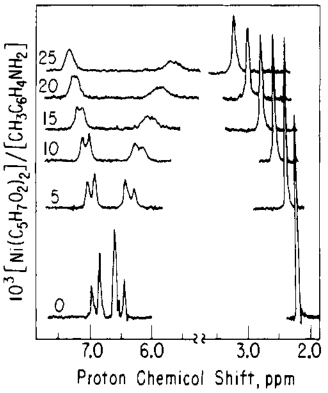
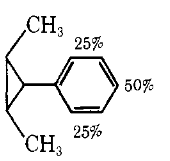
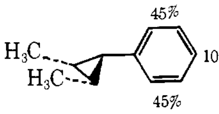


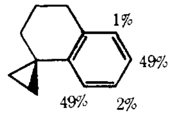
Figure 1. The proton NMR spectra of 4-methylaniline in the presence of variable amounts of nickel acetylacetonate.

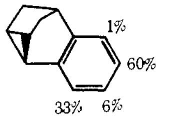
Tetramethylindan, **18h**, and 1,2,3,4-tetrahydro-1,4-ethanonaphthalene, **19h**, were also prepared by familiar methods.[26,27]

The nitration of the acyclic 4-alkylbenzenes and tetralin was accomplished with a mixture of nitric acid and sulfuric acid in nitromethane.[28] The lability of the arylcyclopropanes under strongly acidic conditions prompted the use of preformed acetyl nitrate.[29,30] The remarkable differences in the ortho/para ratios for molecules such as the isomers of (2,3-dimethylcyclopropyl)benzene have prompted discussions of an attractive interaction between the nitration agent and the cyclopropane ring in the transition state.[31] The ortho/para ratios for the nitration of 3′,4′-dihydrospiro(cyclopropane-1,1′(2*H*′)-naphthalene)[21] and its isomer, **16h**, offer a new test of this idea in molecules in which the cyclopropane nucleus is constrained to the bisected conformation. In **16h**, however, the cyclopropane nucleus is also constrained to a position in which favorable interactions between the cyclopropane ring and the nitronium ion are impossible in the transition state for the substitution reaction. The much smaller ortho/para ratio, 0.55, for **16h** compared to 1.0 for the isomer supports Hahn's suggestion.[31]









Contact Shift Measurements. Although solubility considerations sometimes limited the concentration of the amine, the freshly purified amine was usually dissolved in deuteriochloroform containing 2% tetramethylsilane to give a 1 to 2 M solution. The proton spectra were recorded at 60 or 270 MHz and the carbon spectra at 22.6 MHz. The carbon signals were assigned without difficulty. The proton signals were, for the most part, readily assigned on the basis of chemical shifts and coupling constants. However, the resonances of the exo and endo protons in the cyclopropane derivatives and in 1,2,3,4-tetrahydro-1,4-ethanonaphthalene, **19a**, could not be assigned in this way. Consequently, we investigated the pseudocontact chemical shifts of these amines with tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione)praseodymium(III). The results have been presented previously in connection with a discussion of the coupling constants of the exo and endo methylene protons in cyclopropylbenzene derivatives.[12,33]

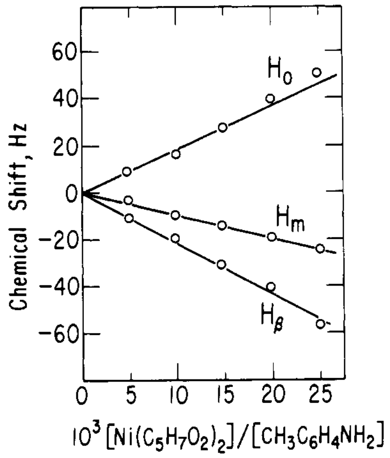


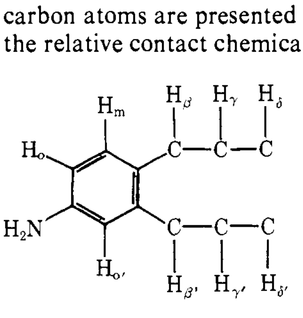
Figure 2. The relationship between the chemical shifts for the ortho, meta, and β protons of 4-methylaniline and the concentration of nickel acetylacetonate.

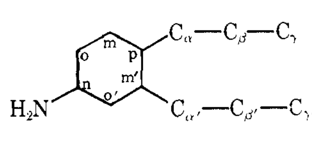
Incremental amounts, 10–20 μl, of a solution of nickel acetylacetonate, 0.25 M, in deuteriochloroform were added to a solution of the amine in the same solvent. The same solution was used for the proton and the carbon contact shift measurements to avoid errors arising from the reaction of traces of water with the micromolar quantities of nickel acetylacetonate.

Ordinarily, the Ni/amine ratio was about 10^{-2}. The formation constant for the complex is very large and all the nickel is complexed under the conditions of these experiments. Dilution shifts are negligible. However, all the signals including tetramethylsilane exhibit a small, but perceptible, upfield susceptibility shift for which we have not compensated. Typical results for 4-methylaniline obtained at 60 MHz are shown in Figure 1.

The slope of the linear relationship, Figure 2, between the observed contact chemical shift for each resonance and the nickel acetylacetonate/amine ratio was determined by the least-squares method under the restriction that the line pass through the origin. The slope determined in this way was divided by 2 to yield the contact shift, σ_i, for each nucleus in ppm. These values of σ_i depend on the concentration of the amine and presumably on differences in the binding interactions between the nitrogen atoms of the different ligands and the nickel atom. To compensate for these effects, we selected the ortho proton and the meta-carbon atom in each molecule as an internal reference. The relative values, $\sigma/\sigma_o{}^H$ and $\sigma/\sigma_m{}^C$, are independent of the initial concentration of the amine over a wide concentration range.

The σ_i values for the ortho-hydrogen atoms and the meta-carbon atoms are presented in Tables I and II together with the relative contact chemical shifts for the other atoms.





Discussion

The contact chemical shifts are directly proportional to the carbon and hydrogen atom s orbital spin density. The transfer of spin density from the orbitals of the metal atom to the orbitals of the carbon and hydrogen atoms of the ligand may

Table I. Proton Contact Chemical Shifts for the Nickel Acetylacetonate Complexes of Aromatic Amines in Chloroform

Amine	Contact shift σ_o^H, ppm	Relative contact chemical shift, σ/σ_o^H					
	H_o	H_o	$H_{o'}$	H_m	H_β	$H_{\beta'}$	H_γ
Aniline, **1a**[a]		1.00		−0.42	1.00		
4-Methyl, **2a**	16.4	1.00		−0.42	−1.12		
4-Trifluoromethyl, **3a**	15.5	1.00		−0.41	−2.85[b]		
4-Ethyl, **4a**	19.9	1.00		−0.47	−0.86		
4-Isopropyl, **5a**	18.8	1.00		−0.44	−0.40		0.048
4-*tert*-Butyl, **6a**	26.1	1.00		−0.40			0.022
4-Propyl, **7a**	31.2	1.00		−0.47	−0.79		
4-Isobutyl, **8a**	19.6	1.00		−0.51	−0.74		
4-Neopentyl, **9a**	20.4	1.00		−0.45	−0.60		
4-(1,1-Diethylpropyl), **10a**	26.4	1.00		−0.42			
4-(1-Adamantyl), **11a**	26.0	1.00		−0.41			
4-Cyclopropyl, **12a**	14.1	1.00		−0.43	−0.32		0.052 (endo) −0.33 (exo)
4-1α,2α,3α-(2,3-Dimethylcyclopropyl), **13a**	8.83	1.00		−0.47	−1.72		−0.25
4-1α,2β,3β-(2,3-Dimethylcyclopropyl), **14a**	9.08	1.00		−0.50	−0.27		0.11
2′3′-Dihydrospiro[cyclopropane-1,1′-inden-5-amine], **15a**	20.1	1.00	1.00	−0.41			0.076 (endo) −0.11 (exo)
1a,2,3,7b-Tetrahydro-1,3-methano-1*H*-cyclopropa[*a*]naphthalen-5-amine, **16a**	19.5	1.00	1.00	−0.61	−0.038	−0.068	−0.23[c]
1,2,3,4-Tetrahydronaphthalen-6-amine, **17a**	23.7	1.00	1.08	−0.51	−1.46	0.050	
1,1,3,3-Tetramethyl-2,3-dihydro-1*H*-inden-5-amine, **18a**	22.4	1.00	1.04	−0.43			−0.039
1,2,3,4-Tetrahydro-1,4-ethanonaphthalen-6-amine, **19a**	24.2	1.00	1.00	−0.45	0.069	−0.050	0.32 (exo) 0.026 (endo)
9,10-Dimethyl-9,10[1′,2′]benzenoanthracen-2-amine, **20a**	28.4	1.00	1.23	−0.56			

[a] Reference 15c. [b] For β-F. [c] The results for the γ′ protons are 0.053 for the exo proton and −0.008 ± 0.008 for the endo proton.

occur through dipolar interactions as well as σ and π interactions.[15,16] Critical analyses of the prior experimental work by Roberts, Morishima, Kurland, and McGarvey and their associates indicate that the contact chemical shifts for the ortho-, meta-, para-, and β-hydrogen atoms and for the ortho-, meta-, para-, α-, and β-carbon atoms result almost exclusively from spin density in the π system, rather than the σ system of the electron deficient aniline ligands.[15,16] Both theory and experiment suggest that positive spin density arises at the nitrogen atom via electron transfer to the nickel d orbitals.[34] Morishima and his associates point out that the equal values of σ_o^H and σ_p^H and the modestly different values of σ_o^C and σ_p^C for aniline are compatible with equal π spin density at the ortho- and para-carbon atoms.[15b,c] Delocalization into the σ framework would, of course, lead to very different results. Although not rigorously excluded,[15d] there is little reason to expect significant dipolar contributions for the remote carbon atoms of the ligands in the nickel–aniline complexes. Our observations are compatible with these suggestions. First, the signs of the shifts alternate as expected for a dominant interaction with π spin density with upfield shifts for C_n and C_m but downfield shifts for C_o and C_p. The ratios for these carbon atoms, Table II, are essentially constant for all the alkylanilines. Second, the results are consistent with the predictions of the Karplus–Fraenkel relationship

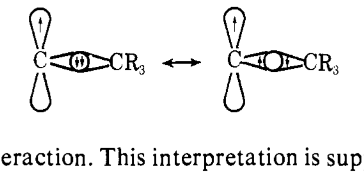
$$a_i^C = (S^C + \sum_{j=1}^{3} Q_{CX_j}^{\ C})\rho_i^\pi + \sum_{j=1}^{3} Q_{X_jC}^{\ C}\rho_j^\pi \tag{3}$$

where S^C is the carbon atom 1s orbital spin polarization constant, $Q_{CX_j}^{\ C}$ is the spin polarization constant between the p orbital on atom *i* and the CX_j σ bonds, and $Q_{X_jC}^{\ C}$ is the spin polarization constant between the p orbitals on atom *j* and the CX_j σ bonds.[35] Substitution of the *Q* parameters suitable for the meta- and para-carbon atoms[36] of 4-methylaniline yields

$$\frac{\sigma_p^C}{\sigma_m^C} = \frac{a_p^C}{a_m^C} = \frac{31.1\rho_p^\pi + 13.9(2\rho_m^\pi)}{35.6\rho_m^\pi - 13.9(\rho_o^\pi + \rho_p^\pi)} \tag{4}$$

The contact shifts for the ring protons of aniline indicate that $\rho_p^\pi = \rho_o^\pi$ and that $\rho_o^\pi = -0.42\rho_m$. Substitution of these quantities into eq 4 gives $\sigma_p^C/\sigma_m^C = -1.1$. Two groups of investigators have recently proposed new sets of *Q* constants.[37] Using their parameters, we calculate σ_p^C/σ_m^C to be −1.2. The experimental values cluster about −1.3 in reasonable agreement with the theory, and judging from the results for other complexes, in a direction opposite to that expected for σ delocalization or a dipolar interaction. These results, consequently, favor the view that π electron spin density dictates the contact shifts for the meta- and para-carbon atoms and the nuclei of the para substituents.[38,39]

α-Carbon Atom Coupling Constants. The contact chemical shifts for the α-carbon atoms of the para substituents indicate that a_α^C is negative. The shifts for the α-carbon atoms of the meta substituents are smaller and exhibit the opposite sign. These results are compatible with the idea that spin polarization of the electrons of the C_p–C_α bond, as illustrated, is the dominant interaction.



This interpretation is supported by the finding that the $\sigma_\alpha^C/\sigma_m^C$ value, 0.43, for 4-isopropylaniline is about 16% smaller than the value, 0.50, for 4-cyclopropylaniline. Although other factors, as discussed subsequently, influence the spin population at the α-carbon atom, the more negative value of a_α^C for the cyclopropyl carbon atom is in accord with the concept of spin polarization because the s character of the exocyclic carbon bonding orbital of the cy-

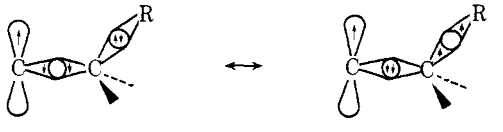
Table II. Carbon Contact Chemical Shifts for Nickel Acetylacetonate Complexes of Aromatic Amines in Chloroform

Amine	Contact shift σ_m^C, ppm	Relative contact shift, σ/σ_m^C									
		C_n	C_o	$C_{o'}$	C_m	$C_{m'}$	C_p	C_α	$C_{\alpha'}$	C_β	$C_{\beta'}$
Aniline, **1a**[a]		2.78	−2.47		1.00		−1.50				
4-Methyl, **2a**	130	2.52	−1.62		1.00		−1.17	0.50			
4-Trifluoromethyl, **3a**	30.5	2.77	−1.59		1.00		−1.20	0.60			
4-Ethyl, **4a**	118	2.69	−1.63		1.00		−1.30	0.45		0.67	
4-Isopropyl, **5a**	108	2.67	−1.56		1.00		−1.22	0.43		−0.51	
4-*tert*-Butyl, **6a**	148	2.66	−1.55		1.00		−1.28	0.38		−0.34	
4-Propyl, **7a**	145	2.61	−1.68		1.00		−1.35	0.42		−0.72	
4-Isobutyl, **8a**	112	2.60	−1.62		1.00		−1.29	0.45		−0.69	
4-Neopentyl, **9a**	111	2.61	−1.57		1.00		−1.30	0.46		−0.70	
4-(1,1-Diethylpropyl), **10a**	147	2.59	−1.56		1.00		−1.33	0.40		−0.36	
4-(1-Adamantyl), **11a**	139	2.54	−1.59		1.00		−1.22	0.38		−0.36	
4-Cyclopropyl, **12a**	69.0	2.59	−1.62		1.00		−1.30	0.50		−0.45	
4-1α,2α,3α-(2,3-Dimethylcyclopropyl), **13a**	84.5		−1.72		1.00			0.50		−0.35	
4-1α,2β,3β-(2,3-Dimethylcyclopropyl), **14a**	73.0		−1.60		1.00			0.55		−0.48	
2′3′-Dihydrospiro[cyclopropane-1,1′-inden-5-amine], **15a**	105	2.63	−1.59	−1.53	1.00	1.00	−1.21	0.49	−0.15	−0.47	
1a,2,3,7b-Tetrahydro-1,3-methano-1*H*-cyclopropa[*a*]naphthalen-5-amine, **16a**	151		−1.51	−1.32	1.00	1.03	−1.30	0.49	−0.16	−0.51	
1,2,3,4-Tetrahydronaphthalen-6-amine, **17a**	125	2.78	−1.72	−1.59	1.00	1.06	−1.30	0.45	−0.16	−0.14	0.071
1,1,3,3-Tetramethyl-2,3-dihydro-1*H*-inden-5-amine, **18a**	175	2.65	−1.65	−1.62	1.00	1.06	−1.31	0.37	−0.15	−0.62	0.22
1,2,3,4-Tetrahydro-1,4-ethanonaphthalen-6-amine, **19a**	135	2.60	−1.68	−1.52	1.00	0.97	−1.23	0.39	−0.13	−0.61	0.21
9,10-Dimethyl-9,10[1′,2′]benzenoanthracene-2-amine, **20a**	195	2.40	−1.54	−1.39	1.00	0.96	−1.28	0.39	−0.13	0.013	−0.009

[a] Reference 15c.

clopropane is about 25% greater than that for the relevant carbon bonding orbital of the isopropyl compound.

It is evident that $\sigma_\alpha^C/\sigma_m^C$ depends on structure. The results for the α-carbon atoms of the methyl, 0.50, ethyl, 0.45, isopropyl, 0.43, and *tert*-butyl, 0.38, groups exhibit variations which are well beyond the limit of experimental error. In addition, the four primary groups, ethyl, propyl, isobutyl, and neopentyl, all have a very similar value, 0.44 ± 0.02, for this ratio, whereas the tertiary groups, *tert*-butyl, 1,1-diethylpropyl, and 1-adamantyl, all exhibit a smaller value, 0.38 ± 0.01. These observations indicate that there is less negative spin density at the α-carbon atoms of the tertiary alkyl groups than at the same atoms of the primary alkyl groups. We infer that at least two distinct interactions influence a_α^C importantly. The negative sign of the coupling constant for the 4-alkyl groups establishes that spin polarization of the electrons of the C_p–C_α bond is the dominant interaction. The diminished absolute values of a_α^C for the tertiary groups suggest that spin delocalization of the electrons of the C_α–H_β and C_α–C_β bonds contributes positive spin density. The two contributions are illustrated in the resonance structures. The positive contribution apparently depends on the extent of spin delocalization of the electrons of the C_α–H and C_α–C_β bonds. The differences in a_α^C for the methyl, primary, secondary, and tertiary alkyl groups may, therefore, be related to the greater electron release from carbon–carbon bonds than from carbon–hydrogen bonds.[40] The explicit interactions responsible for the changing values of a_α^C are not defined by our results. However, in the absence of direct overlap between the carbon p orbital and the carbon 2s orbital of C_α, we suggest that an indirect mechanism operates with positive s orbital spin density at C_β relayed to C_α.[41]



negative contribution   positive contribution

β-Carbon Atom Coupling Constants. The contact chemical shifts for all the β-carbon atoms, Table II, indicate that a_β^C is positive for the 4-alkylaniline derivatives except when the β carbon atom is constrained by a rigid structure to the nodal plane of the π electron system as in **20a**. The contact shifts for the β-carbon atoms clearly depend on the dihedral angle, θ_C. We have used several procedures to establish these angles to enable an analysis of the relationship between the chemical shift and the angle. In some cases, θ_C is defined by the structure of the strain-free, but rigid molecules, **17a–20a**. For the anilines with tertiary substituents, **6a**, **10a**, and **11a**, for which rotation about the C_p–C_α bond is rapid, $\langle\cos^2\theta_C\rangle$ is 0.5. In the other cases, the values of $\langle\cos^2\theta_C\rangle$ can be calculated from the values of $\langle\cos^2\theta_H\rangle$ determined from the relationships which govern the β-hydrogen interactions, Table III.[42]

The relationship between the chemical shift and the dihedral angle was examined in three ways. First, we assessed the quantitative relationship between σ_β^C and σ_m^C via eq 5.

$$\frac{\sigma_\beta^C}{\sigma_m^C} = \frac{a_\beta^C}{a_m^C} = \frac{\rho_p^\pi(B_0^C + B_2^C\langle\cos^2\theta_C\rangle)}{Q\rho_m^\pi + Q'(\rho_o^\pi + \rho_p^\pi)} \tag{5}$$

This expression may be simplified on the basis of the results for aniline which indicate that $\rho_o^\pi = \rho_p^\pi$ and that $\rho_m^\pi = -0.42\rho_o^\pi$ to yield eq 6.

$$\frac{\sigma_\beta^C}{\sigma_m^C} = \frac{(B_0^C + B_2^C\langle\cos^2\theta_C\rangle)}{2Q' - 0.42Q} \tag{6}$$

The relationship between $\sigma_\beta^C/\sigma_m^C$ and $\langle\cos^2\theta_C\rangle$ is shown in Figure 3.

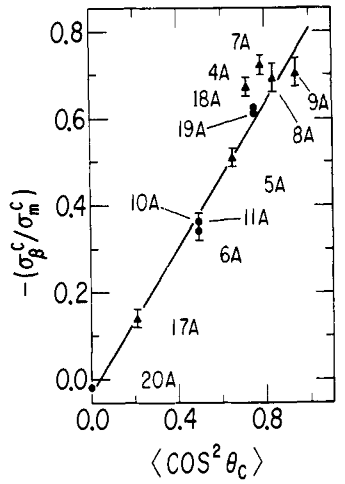


Figure 3. The relationship between $\sigma_\beta{}^C/\sigma_m{}^C$ and $\langle\cos^2\theta_C\rangle$ for the 4-anilines. The results for molecules for which θ_C is defined by structure are indicated by the circles.

Table III. Values for $\langle\cos^2\theta_H\rangle$ and $\langle\cos^2\theta_C\rangle$ Based on Contact Chemical Shifts of 4-Alkylaniline Complexes with Nickel Acetylacetonate

4-Substituent	$\langle\cos^2\theta_H\rangle^a$	$\langle\cos^2\theta_C\rangle^b$
4-Methyl, **2a**	0.50	
4-Ethyl, **4a**	0.39	0.72
4-Isopropyl, **5a**	0.20	0.65
4-Propyl, **7a**	0.36	0.78
4-Isobutyl, **8a**	0.33	0.84
4-Neopentyl, **9a**	0.28	0.94
4-Cyclopropyl, **12a**	0.17	0.69

[a] Reference 42. [b] Based on the relationships: $\langle\cos^2\theta_C\rangle = 1.5 - 2\langle\cos^2\theta_H\rangle$ for primary groups, $\langle\cos^2\theta_C\rangle = 0.75 - 0.5\langle\cos^2\theta_H\rangle$ for secondary groups, and $\langle\cos^2\theta_C\rangle = 0.79 - 0.58\langle\cos^2\theta_H\rangle$ for the cyclopropyl group.

Second, the *tert*-butyl substituent was adopted as the reference group in the same way that the methyl substituent is used for the analysis of β-hydrogen atom couplings to yield

$$\frac{\sigma_\beta{}^C/\sigma_m{}^C}{(\sigma_\beta{}^C/\sigma_m{}^C)_{t\text{-Bu}}} = 2\langle\cos^2\theta_C\rangle \qquad (7)$$

The expression is applicable under the conditions that $B_0{}^C$ may be neglected and that the spin distributions in the aromatic π electron systems are, in a relative sense, the same. The results are illustrated in Figure 4.

Third, we used the ortho-hydrogen atom as the reference point. The familiar McConnell relationship[43] is combined with eq 1 to yield eq 9 where γ is the gyromagnetic ratio.

$$a_o{}^H = \rho_o{}^\pi Q^H \qquad (8)$$

$$\frac{\sigma_\beta{}^C\gamma^C}{\sigma_o{}^H\gamma^H} = \frac{a_\beta{}^C}{a_o{}^H} = \frac{\rho_p{}^\pi(B_0{}^C + B_2{}^C\langle\cos^2\theta_C\rangle)}{\rho_o{}^\pi Q^H} \qquad (9)$$

The relationship between $\sigma_\beta{}^C\gamma^C/\sigma_o{}^H\gamma^H$ and the dihedral angle is shown in Figure 5.

In all three cases, the results for the rigid molecules and for the anilines with tertiary alkyl groups define a precise linear relationship which, of course, does not pass through the origin. The observations for most alkyl groups which experience restricted rotation also adhere to the relationship. However, the results for the ethyl, propyl, isobutyl, and neopentyl groups exhibit a clear trend with deviations for the ethyl and neopentyl groups which appear beyond the limit of experimental error.[44]

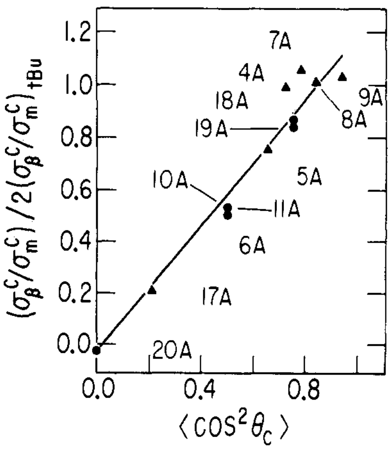


Figure 4. The relationship between $(\sigma_\beta{}^C/\sigma_m{}^C)/(\sigma_\beta{}^C/\sigma_m{}^C)_{t\text{-Bu}}$ and $\langle\cos^2\theta_C\rangle$.

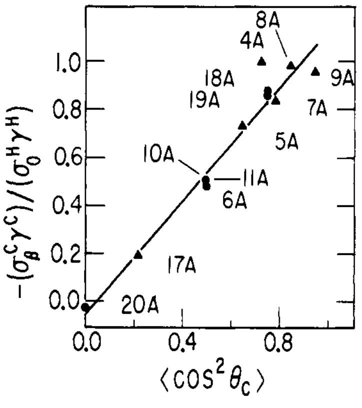


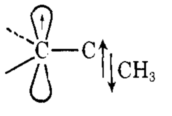
Figure 5. The relationship between $\sigma_\beta{}^C\gamma^C/\sigma_o{}^H\gamma^H$ and $\langle\cos^2\theta_C\rangle$.

The slopes and intercepts of relationships 6, 7, and 9 can be used to define $B_0{}^C$ and $B_2{}^C$. The values deduced from these relationships depend critically on the values adopted for the Q parameters and the spin density distribution. These uncertainties are minimized when the ortho-hydrogen atom is selected as the reference, eq 9. With equal spin density at the ortho and para positions, the adoption of a Q constant, -25 G acceptable for the modestly electron deficient aniline ligand yields $B_0{}^C$ as -1.1 G and $B_2{}^C$ as 23 G. The $B_2{}^C$ value determined in this way is somewhat larger than the values estimated previously for hexamethylacetone ketyl,[45] 15-20 G, di-*tert*-butyl nitroxide,[5] 20 G, alkylsemidiones,[7] 17-21 G, and carboxylic acid dianion radicals,[8] 20 G. An estimate of $B_2{}^C$ based on eq 6, although somewhat less certain, also yields a larger value. We believe that the difference is real and that the more positive value observed for the aniline ligand reflects the fact that electron delocalization is more important in the modestly electron deficient amine complex than in the other anionic or neutral radicals.

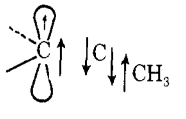
It has been suggested that the *tert*-butyl substituent might not be an adequate reference group for the definition of $B_2{}^C$ because its steric requirements are rather large.[7] The 1,1-diethylpropyl derivative, **10a**, and the 1-adamantyl derivative, **11a**, were synthesized and studied to determine whether or not steric effects had an important influence on $a_\beta{}^C$. The observed values of $\sigma_\beta{}^C/\sigma_m{}^C$, $\sigma_\beta{}^C\gamma^C/\sigma_o{}^H\gamma^H$, and other appropriate ratios for these tertiary groups, **9a–11a**, are, Figures 3-5, within experimental error. We conclude that steric effects of these groups do not lead to significant molecular distortions in the anilines and that such tertiary groups with $\langle\cos^2\theta_C\rangle = 0.5$ can be used to estimate $B_2{}^C$ when the $\rho_C{}^\pi$ values are known.

The $\langle \cos^2 \theta_C \rangle$ values determined from the $\langle \cos^2 \theta_H \rangle$ values of the proton couplings are large for the ethyl, propyl, isobutyl, and neopentyl groups. Curiously, the $\sigma_\beta{}^C/\sigma_m{}^C$ values for these molecules do not change in a corresponding way and the results for the ethyl and neopentyl groups deviate from the linear relationships, Figures 3-5, established for the other anilines. The origin of the discrepancy is not clear. However, the results do suggest that caution is necessary in detailed interpretations of ESR observations.

The experimental results, $\sigma_\beta{}^C/\sigma_m{}^C = 0.013 \pm 0.002$ and $\sigma_{\beta'}{}^C/\sigma_m{}^C = -0.009 \pm 0.003$, for the triptycene, **20a**, require the negative value for $B_0{}^C$. We previously pointed out that the negative $B_0{}^H$ value was compatible with a long-range direct-spin-polarization interaction as first proposed by Colpa and de Boer.[12b,46] The same interpretation is apparently suitable for the β-carbon atoms.

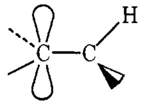


dominant interaction

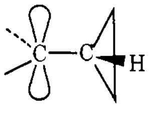


minor interaction

Cyclopropanes. The cyclopropanes, **12a–16a**, were investigated to establish the contact chemical shifts for α- and β-carbon atoms in strained molecules in which the p character of the C_α–C_β bonding orbitals is large. The results presented in Table II indicate that the contact shifts for both the α and β carbon atoms of the cyclopropane derivatives differ from the values observed for the simple alkyl groups. The coupling constants for the α-carbon atoms of the cyclopropane, as discussed previously, are more negative than the constants for the α carbon atoms of the other alkyl groups because, in large part, of the increased s character of the exocyclic carbon bonding orbital in the strained molecule. Hybridization changes and conformational preferences both influence the contact shifts for the β-carbon atoms of these strained molecules. The large preferences of the syn and anti isomers of 4-(2,3-dimethylcyclopropyl)aniline, **13a** and **14a**, for the perpendicular and bisected conformations, respectively, are well established by the shifts observed for the β-hydrogen atoms. There is a corresponding difference in the shifts for the β-carbon atoms in these molecules with less spin density delocalized to the β-carbon atoms of the syn isomer, $\sigma_\beta{}^C/\sigma_m{}^C = -0.35$, perpendicular conformation, than to the β-carbon atoms of the anti isomer, $\sigma_\beta{}^C/\sigma_m{}^C = -0.48$, bisected conformation. The results for the two rigid molecules, **15a** and **16a**, in which the cyclopropane groups are constrained to the bisected position exhibit similar values of $\sigma_\beta{}^C/\sigma_m{}^C$, -0.47, and -0.49, respectively. The value for the simple cyclopropane, **12a**, which also exhibits a preference for the bisected conformation is only modestly smaller, -0.45. These results indicate that more spin density is delocalized to the cyclopropyl group when the molecule adopts the bisected conformation.



perpendicular



bisected

Direct comparison of the results for the β-carbon atoms of the cyclopropanes with the results for the other alkyl groups is awkward because interorbital angles rather than internuclear angles must be considered for the cyclopropanes and because the s character of the endocyclic bonds in the cyclopropanes is reduced to about 18%. Nevertheless, a rather primitive analysis of the results for the cyclopropyl group and the isopropyl group, $(\sigma_\beta{}^C/\sigma_m{}^C)_{c\text{-}C_3H_5}/(\sigma_\beta{}^C/\sigma_m{}^C)_{i\text{-}C_3H_7} = 0.88$, with adjustments both for the change in the average dihedral angle, 0.65/0.69, and for the difference in hybridization, 0.25/0.18, suggests that the spin population at the β-carbon atom is about 15% greater in the cyclopropyl group in these molecules.[47]

Summary. The carbon contact chemical shifts may be qualitatively discussed on the basis of spin polarization and spin delocalization. The results for the carbon atoms of the aniline nucleus are compatible with the Karplus–Fraenkel relationship. The hyperfine constants for the α-carbon atoms depend on structure. Two factors, the hybridization of the exocyclic carbon bonding orbital and the degree of substitution of the α carbon atom, are discernible. The latter influence may be identified with the greater importance of carbon–carbon hyperconjugation compared to carbon–hydrogen hyperconjugation. The observations for the β carbon atoms indicate that there is a linear relationship between the hyperfine constant for this atom and the dihedral angle. The results for the ethyl and neopentyl groups, curiously, deviate from this linear relationship. The B_0 constant for carbon, as for hydrogen, is negative. The results for the β-carbon atoms of the cyclopropyl substituents depend sharply on the conformational preference of the group and suggest that more spin density is delocalized to the p rich carbon–carbon bonds of these strained rings.

Experimental Section

Hydrocarbons. Many needed hydrocarbons, **5h**, **6h**, **7h**, **8h**, **9h**, **10h**, and **17h**, were obtained commercially. Others such as the adamantane derivative, **11h**,[18] the simple cyclopropane derivative, **12h**,[19] the spirocyclopropane-1,1′-indene, **15h**,[20] the tetramethylindan, **18h**,[26] and the tetrahydroethanonaphthalene, **19h**,[27] were prepared by well established routes. All these materials exhibited physical and spectroscopic properties in accord with the literature.[33] The syntheses of **13h**, **14h**, and **16h** are described here.

1α,2α,3α- and 1α,2β,3β-(2,3-Dimethylcyclopropyl)benzene (13h) and (14h). These compounds were prepared by the method described by Olofson and Dougherty[22] by the reaction of benzyl chloride (0.1 mol), (*Z*)-2-butene (1.3 mol), and lithium 2,2,6,6-tetramethylpiperidide (0.1 mol) in ether. Distillation of the crude product gave a colorless mixture of **13h** and **14h** (11.2 g, 77%, bp 84–85 °C (11 Torr)). The isomers were separated by VPC (17 ft × 0.25 in., 8% SE 30 on Chromosorb P, 155 °C, 30 ml min^{-1} He) and identified by NMR spectroscopy.

1a,2,3,7b-Tetrahydro-1,3-methano-1*H*-cyclopropa[*a*]naphthalen-2-one (16k). 1,2-Dihydro-1-naphthoic acid was converted to 1,2-dihydro-1-naphthoyl chloride (mp 46–48 °C) in the customary way. A solution of this acid chloride (11.3 g, 0.059 mol) in ether (100 ml) was added dropwise to a cold solution of ethereal diazomethane (ca. 0.7 M, 250 ml). The reaction mixture was stirred for 24 h at room temperature. Ether and excess diazomethane were removed in vacuo prior to the addition of fresh ether (50 ml). After 1 h a small amount of a white precipitate formed. The mixture was then filtered and the filtrate was concentrated to yield an oil (1,2-dihydro-1-naphthoyl)-diazomethane (11.0 g, 94%). The oil was dissolved in tetrahydrofuran (100 ml) and slowly added via a Soxhlet apparatus to a refluxing mixture of copper powder (12 g) in tetrahydrofuran (1 l.) over 4 h. The mixture was refluxed for 20 h. The solution was filtered and the solvent was removed in vacuo to yield a dark brown oil (10.8 g). The oil was chromatographed in 1.5-g portions on silica gel (75 × 2 cm column) using petroleum ether:ether (1:1) to give 1a,2,3,7b-tetrahydro-1,3-methano-1*H*-cyclopropa[*a*]naphthalen-2-one as a light yellow waxy solid (4.2 g, 44%): NMR ($CDCl_3$) δ 7.06 (m, 4 H), 2.74 (d, $J = 5$ Hz, 1 H), 2.69 (t, $J = 7.8$ Hz, 1 H), 2.36 (m, 2 H), 1.89 (m, 1 H), 1.41 (d, $J = 11$ Hz, 1 H); IR (CCl_4) 1740 cm^{-1}. The ketone was converted to its semicarbazone derivative (mp 229–230 °C) prior to analysis.

Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.71, H, 5.76, N, 18.49. Found: C, 68.53, H, 5.82, N, 17.74.

1a,2,3,7b-Tetrahydro-1,3-methano-1*H*- cyclopropa[*a*]naphthalene (16h). Compound **16k** (2.10 g, 12.4 mmol), hydrazine hydrate (3.5 g, 98%), and diethylene glycol (5 ml) were refluxed for 30 min. The solution was cooled to ambient temperature and potassium hydroxide (1.6 g, 25 mmol) was added. The solution was refluxed for 30 min. The cooled solution was poured into water and the product was extracted into carbon tetrachloride (2 × 50 ml). The extract was washed with

Table IV. Preparation of Nitro Compounds

Compd	Method	Yield, %	Separation method[a]	Physical property	
				Obsd	Lit.
4-(1-Methylethyl)nitrobenzene, **5n**	A	80	SB	bp 120–122 °C (10)	124–125 °C (11)[b]
4-(1,1-Dimethylethyl)nitrobenzene, **6n**	A	82	SB	bp 125–128 °C (10)	125–130 °C (10)[c]
4-Propylnitrobenzene, **7n**	A	84	SB	bp 133–135 °C (14)	154 °C (20)[d]
4-(2-Methylpropyl)nitrobenzene, **8n**	A	86	SB	bp 138–141 °C (14)	138–141 °C (14)[e]
4-(2,2-Dimethylpropyl)nitrobenzene, **9n**	A	87	SB	mp 25–26 °C	29 °C[f]
4-(1,1-Diethylpropyl)nitrobenzene, **10n**	A	87	SB	bp 161–165 °C (10)	163–165 °C (10)[g]
4-(1α,2α,3α-(2,3-Dimethylcyclopropyl))-nitrobenzene, **13n**	B	78	VPC	mp 43–45 °C	43–45 °C[h]
4-(1α,2β,3β-(2,3-Dimethylcyclopropyl))-nitrobenzene, **14n**	B	87	Cryst	mp 108–109 °C	109–110 °C[h]
5-Nitro-2′,3′-dihydrospiro[cyclopropane-1,1′-indene], **15n**	B	21	CC	mp 79–81 °C	81–82.5 °C[i]
5-Nitro-1a,2,3,7b-tetrahydro-1,3-methano-1*H*-cyclopropa[*a*]naphthalene, **16n**	B	53	VPC	mp 56–58 °C	
6-Nitro-1,2,3,4-tetrahydronaphthalene, **17n**	A	77	SB	bp 160–161 °C (10)	169 °C (13)[j]
5-Nitro-1,1,3,3-tetramethyl-2,3-dihydro-1-*H*-indene, **18n**	A	80	Cryst	mp 48–49 °C	48.5–49 °C[k]
6-Nitro-1,2,3,4-tetrahydro-1,4-ethanonaphthalene, **19n**	A	85	Cryst	mp 59–61 °C	60–61 °C[l]

[a] The method used for the separation of the 4 isomer from the mixture. Spinning band distillation and vapor phase chromatography were generally useful. For **9n**, the product crystallized in the receiver; for **14n**, the product crystallized from the oil obtained upon evaporation of the extraction solvent, and it was recrystallized from petroleum ether at −30°; for **15n**, the product was chromatographed on silica gel with 15% ether in hexane, and it was recrystallized from hexane; for **18n**, the product crystallized at −20 °C from the oil obtained upon evaporation of the solvent, and it was recrystallized from ethanol–water; for **19n**, the product crystallized as the extraction solvent was removed. [b] Reference 48. [c] J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 2339 (1938). [d] Reference 53. [e] Reference 54. [f] Reference 55. [g] Reference 56. [h] Reference 21. [i] Reference 31. [j] Reference 57. [k] Reference 58. [l] Reference 28.

water (3 × 50 ml) and then dried over magnesium sulfate. The yellow oil (1.1 g) obtained upon evaporation of the solvent was chromatographed (20% SF-96 on Chromosorb W, 6 ft × 3/8 in., 170 °C, 50 ml min^{-1} He) to yield about 0.3 g of 8,9-dihydro-5,8-methano-5*H*-benzocycloheptene and **16h** (0.74 g, 38%). Compound **16h** was also prepared by the di-π-methane approach.[23] The samples obtained by the two routes were identical in all respects and readily identified by the NMR spectrum: ($CDCl_3$) δ 6.96 (m, 4 H), 2.90 (t, J = 4.5 Hz, 1 H), 1.97 (t, J = 7.5 Hz, 1 H), 1.67 (d of d, J = 4.5, 12 Hz, 2 H), 1.48 (d, J = 7.5 Hz, 2 H), 0.87 (d, J = 12 Hz, 2 H).

A second compound tentatively identified as 8,9-dihydro-5,8-methano-5*H*-benzocycloheptene, **21**, was obtained in 10% yield by VPC. This assignment was prompted by several distinctive features of the NMR spectrum including the aryl hydrogen atom resonances at δ 6.92 (4 H), the vinyl hydrogen atom resonances at δ 6.20 (1 H), δ 5.75 (1 H), the resonances of the syn and anti 8 hydrogen atoms at δ 1.75 (1 H) and δ 1.92 (1 H) as well as the close similarity of the entire upfield region of the spectrum to that of bicyclo[3.2.1]octa-2,6-diene.[25]

Nitro Compounds. The procedures for the nitration of **5h** and **16h** illustrate the two methods, A and B, useful for the preparation of these compounds. The results for other molecules are shown in Table IV. Other procedures as described subsequently were adopted for the preparation of the adamantane derivative, **11n**, the cyclopropane, **12n**, and the triptycene, **20n**.

Procedure A, 4-(1-Methylethyl)nitrobenzene (5n). Compound **5h** (12.0 g, 0.1 mol) was dissolved in nitromethane (75 ml). A nitration reagent was prepared by the dropwise addition of 70% nitric acid (4.5 ml, 0.1 mol) to 98% sulfuric acid at less than 20 °C. The acid mixture was stirred for 10 min and then added dropwise over 20 min to the stirred nitromethane solution maintained at 20 °C. The solution was then stirred for 2 h at 20 °C. The solution was then poured onto ice and the products were extracted into chloroform (2 × 50 ml). The extract was washed with 10% sodium bicarbonate (3 × 50 ml) and water (2 × 50 ml) and then dried over magnesium sulfate. The solvent was removed in vacuo to yield a yellow oil (13.2 g, 80%). Spinning band distillation gave pure **5n** (6.2 g, bp 120–122 °C (10 Torr); lit.[48] bp 124–125 °C (11 Torr)). The nuclear magnetic resonance spectrum indicated that the product was not contaminated with isomeric impurities.

4-(1-Tricyclo[3.3.1.1^{3,7}]decyl)nitrobenzene (11n). 1-Phenyltricyclo[3.3.1.1^{3,7}]decane (**11h**) was prepared by the method of Stetter, Schwarz, and Hirschhorn.[18] This hydrocarbon was nitrated as described by Stetter, Weber, and Wulff[49] to give **11n** (mp 128–130 °C; lit.[49] mp 130 °C) in 83% yield.

4-Cyclopropylnitrobenzene (12n). Cyclopropylbenzene (**12h**), prepared by the method of Peterson and Skell,[19] was nitrated by fuming nitric acid in acetic anhydride as described by Hahn, Corbin, and Schechter.[30] The para isomer, **12n**, was obtained by spinning band distillation (bp 109–110 °C (3 Torr)).

Procedure B, 5-Nitro-1a,2,3,7b-tetrahydro-1,3-methano-1*H*-cyclopropa[*a*]naphthalene (16n). Fuming nitric acid (90%, 0.45, g, 6.4 mmol) was added dropwise with stirring to acetic anhydride below 25 °C. The solution was stirred for 15 min and then methylene chloride (5 ml) was added. A solution of hydrocarbon **16h** (1.00 g, 6.4 mmol) in methylene chloride (5 ml) was added dropwise over 30 min to the acid mixture maintaining the temperature below 25 °C. The reaction mixture was stirred 2 h longer at 25 °C and then poured onto ice and extracted with methylene chloride (2 × 25 ml). The extract was washed to neutrality with 10% sodium bicarbonate and then dried over magnesium sulfate. The solvent was evaporated to yield a yellow oil (1.00 g). Vapor-phase chromatography (4 ft × 0.375 in., 20% SF 96 on Chromosorb W, 210 °C, 50 ml He min^{-1}) separated the isomers. Compound **16n** (mp 56–58 °C) comprised 60% of the mixture. The integrity of the structure was secured by the NMR spectrum: ($CDCl_3$) δ 7.95 (d of d, J = 8.3, 2.1 Hz, 1 H), 7.81 (d, J = 2.1 Hz, 1 H), 7.26 (d, J = 8.3 Hz, 1 H), 3.08 (t, J = 4.5 Hz, 1 H), 2.14 (t, J = 7.5 Hz, 1 H), 1.79 (d of d, J = 4.5, 12 Hz, 2 H), 1.69 (d, J = 7.5 Hz, 2 H), 0.7 (d, J = 12 Hz, 2 H).

Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.79; H, 5.64; N, 6.87.

2-Nitro-9,10-dimethyl-9,10[1′,2′]benzenoanthracene (20n). 9,10-Dimethylanthracene (3.17 g, 15.4 mmol) was dissolved in 1,2-dichloroethane. The solution was refluxed and stirred vigorously under nitrogen. Isoamyl nitrite (1.90 g, 16 mmol) was added followed by the dropwise addition over 15 min of a solution of 4-nitroanthranilic acid (2.80 g, 16.3 mmol) in dry diglyme (40 ml). The clear amber solution was refluxed 10 min longer. The flask was then fitted for distillation and the solvent was distilled until the head temperature reached 150 °C. Maleic anhydride (1.50 g, 15 mmol) was then added to the reaction mixture and the solution was refluxed for 15 min. The mixture was cooled to 5 °C and potassium hydroxide (2 g) in methanol:water (1:2, 30 ml) was added. The mixture was stirred for 10 min at 5 °C and then filtered. The crude product was washed with cold 80%

aqueous methanol (100 ml). The tan solid was then added to a solution of potassium hydroxide (5.6 g) in 75% aqueous methanol (200 ml) and stirred vigorously for 35 min. The light tan solid was then collected and washed with cold methanol (25 ml) and water (25 ml) and air dried to give **20n** (1.72 g, 34%, mp 241–242 °C; lit.[50] mp 240–241 °C).

Amines. Commercial samples of 4-methylbenzenamine (**2a**), 4-trifluoromethylbenzenamine (**3a**), and 4-ethylbenzenamine (**4a**) were distilled prior to spectroscopic work.

4-(1-Methylethyl)benzenamine (5a). The reduction was accomplished by Method C. Compound **5n** (2.0 g, 12 mmol) was dissolved in ethanol (50 ml). Platinum oxide (50 mg) was added and the mixture was shaken under 3 atm of hydrogen for 6 h. The catalyst was separated and the solvent was removed in vacuo to yield a yellow oil. Distillation of the oil afforded colorless **5a** (1.47 g, 90%, bp 108–110 °C (20 Torr); lit.[51] bp 225 °C): NMR ($CDCl_3$) δ 7.10 (d, J = 8.5 Hz, 2 H), 6.52 (d, J = 8.5 Hz, 2 H), 3.33 (s, 2 H), 2.80 (septet, J = 7 Hz, 1 H), 1.19 (d, J = 7 Hz, 6 H).

4-(1,1-Dimethylethyl)benzenamine (6a). Compound **6n** (9.0 g, 0.05 mol) was reduced by method C to yield after distillation a slightly yellow oil which solidified on cooling to give **6a** (7.3 g, 98%, bp 106–108 °C (6 Torr); mp 14–16 °C; lit.[52] mp 14.5–16 °C): NMR ($CDCl_3$) δ 7.21 (d, J = 8.5 Hz, 2 H), 6.61 (d, J = 8.5 Hz, 2 H), 3.45 (s, 2 H), 1.27 (s, 9 H).

4-Propylbenzenamine (7a). Compound **7n** (2.0 g, 12 mmol) was reduced by method C to yield after distillation a yellow oil **7a** (1.58 g, 96%, bp 110–113 °C (20 Torr); lit.[53] 112 °C bp (20 Torr)): NMR ($CDCl_3$) δ 6.78 (d, J = 8.5 Hz, 2 H), 6.38 (d, J = 8.5 Hz, 2 H), 3.37 (s, 2 H), 2.42 (t, J = 7.5 Hz, 2 H), 1.55 (m, 2 H), 0.89 (t, J = 7.5 Hz, 3 H). The product was stored at 0 °C.

4-(2-Methylpropyl)benzenamine (8a). Compound **8n** (2.0 g, 11 mmol) was reduced by method C to yield after distillation colorless **8a** (1.5 g, 92%, bp 108–111 °C (13 Torr); lit.[54] bp 112 °C (14 Torr)): NMR ($CDCl_3$) δ 6.88 (d, J = 8.5 Hz, 2 H), 6.53 (d, J = 8.5 Hz, 2 H), 3.34 (s, 2 H), 2.33 (d, J = 7 Hz, 2 H), 1.77 (nonet, J = 7 Hz, 1 H), 0.87 (d, J = 7 Hz, 6 H).

4-(2,2-Dimethylpropyl)benzenamine (9a). Compound **9n** (2.0 g, 10 mmol) was reduced by method C to yield light yellow crystals. Recrystallization from pentane gave light yellow plates of **9a** (1.52 g, 93%, mp 56–58 °C; lit.[55] mp 56.0– 56.5 °C): NMR δ 6.88 (d, J = 8.5 Hz, 2 H), 6.53 (d, J = 8.5 Hz, 2 H), 3.32 (s, 2 H), 2.36 (s, 2 H), 0.87 (s, 9 H).

4-(1,1-Diethylpropyl)benzenamine (10a). Compound **10n** (2.0 g, 9 mmol) was reduced by method C to yield yellow crystals. Recrystallization from petroleum ether gave light yellow crystals of **10a** (1.58 g, 92%, mp 55–58 °C; lit.[56] mp 61 °C): NMR ($CDCl_3$) δ 7.06 (d, J = 8.3 Hz, 2 H), 6.57 (d, J = 8.3 Hz, 2 H), 3.46 (s, 2 H), 1.61 (q, J = 7.2 Hz, 6 H), 0.63 (t, J = 7.2 Hz, 9 H).

4-(1-Tricyclo[3.3.1.$3^{3,7}$]decyl)benzenamine (11a). Compound **11n** (0.5 g, 1.9 mmol) was reduced by method C to yield a yellow solid which after recrystallization from hexane gave light yellow crystals of **11a** (0.41 g, 93%, mp 102–104 °C; lit.[49] mp 105 °C): NMR ($CDCl_3$) δ 7.15 (d, J = 8.5 Hz, 2 H), 6.61 (d, J = 8.5 Hz, 2 H), 3.45 (s, 2 H), 2.00 (m, 3 H), 1.79 (m, 6 H), 1.67 (m, 6 H).

4-Cyclopropylbenzenamine (12a). Compound **12n** (2.5 g, 15 mmol) was reduced by method C to give after distillation slightly yellow **12a** (1.8 g, 90%): NMR (CCl_4) δ 6.72 (d, J = 8.2 Hz, 2 H), 6.39 (d, J = 8.2 Hz, 2 H), 5.11 (s, 2 H), 1.50–2.00 (m, 1 H), 0.42–0.90 (m, 4 H). The compound was converted to the acetyl derivative in the usual way (mp 118–120 °C; lit.[30] mp 120–121 °C).

1α,2α,3α-4-(2,3-Dimethylcyclopropyl)benzenamine (13a). Compound **13n** (13.1 mg, 0.068 mmol) was reduced by method C to yield after distillation a yellow oil **13a** (9.5 mg, 86%): NMR ($CDCl_3$) δ 7.00 (d, J = 8.5 Hz, 2 H), 6.61 (d, J = 8.5 Hz, 2 H), 3.46 (s, 2 H), 1.88 (t, J = 7 Hz, 1 H), 1.07 (m, 2 H), 0.87 (m, 6 H). Mass spectrum: *m/e* calcd for $C_{11}H_{15}N$, 161.1204; found, 161.1210.

1α,2β,3β-4-(2,3-Dimethylcyclopropyl)benzenamine (14a). Compound **14n** (12.0 mg, 0.063 mmol) was reduced by method C to yield **14a** (8.2 mg, 81%): NMR ($CDCl_3$) δ 6.82 (d, J = 8.5 Hz, 2 H), 6.59 (d, J = 8.5 Hz, 2 H), 3.42 (s, 2 H), 1.13 (m, 6 H), 1.08 (m, 1 H), 1.01 (m, 2 H). Mass spectrum: *m/e* calcd for $C_{11}H_{15}N$, 161.1204; found, 161.1204.

2′,3′-Dihydrospiro[cyclopropane-1,1′-inden-5-amine] (15a). The related nitrobenzene (**15n**) (1.00 g, 5.3 mmol) was reduced by method C to yield **15a** as a red oil (0.72 g, 85%): NMR ($CDCl_3$) δ 6.50 (m, 1 H), 6.41 (m, 2 H), 3.41 (s, 2 H), 2.92 (t, J = 7 Hz, 2 H), 2.05 (t, J = 7 Hz, 2 H), 0.80 (s, 4 H). A portion of the oil was acetylated with acetic anhydride (mp 129–131 °C; lit.[31] mp 131.5–133 °C).

1a,2,3,7b-Tetrahydro-1,3-methano-1*H*-cyclopropa[*a*]naphthalen-5-amine (16a). The related nitrobenzene (**16n**) (29.1 mg, 0.145 mmol) was dissolved in ethanol (10 ml). Platinum oxide (5 mg) was added and the mixture was hydrogenated at atmospheric pressure. Filtration followed by removal of the solvent yielded light yellow crystals of **16a** (24.3 mg, 98%, mp 32–34 °C): NMR ($CDCl_3$) δ 6.83 (d, J = 8 Hz, 1 H), 6.50 (d of d, J = 2.7, 8 Hz, 1 H), 6.38 (d, J = 2.7 Hz, 1 H), 3.93 (s, 2 H), 2.88 (t, J = 4.5 Hz, 1 H), 2.00 (t, J = 7.5 Hz, 1 H), 1.74 (d of d, J = 4.5, 12 Hz, 2 H), 1.53 (d, J = 7.5 Hz, 2 H), 0.88 (d, J = 12 Hz, 2 H). Mass spectrum: *m/e* calcd for $C_{12}H_{13}N$, 171.1048; found, 171.1049.

1,2,3,4-Tetrahydronaphthalen-6-amine (17a). Compound **17n** (2.0 g, 11 mmol) was reduced by method C to yield colorless crystals of 6-amino-1,2,3,4-tetrahydronaphthalene (1.48 g, 90%, mp 36–38 °C; lit.[57] mp 38.5–39.5 °C): NMR ($CDCl_3$) δ 6.81 (d, J = 8 Hz, 1 H), 6.39 (d of d, J = 8, 2.3 Hz, 1 H), 6.33 (d, J = 2.3 Hz, 1 H), 3.42 (s, 2 H), 2.64 (m, 4 H), 1.74 (m, 4 H).

1,1,3,3-Tetramethyl-2,3-dihydro-1*H*-inden-5-amine (18a). Compound **18n** (2.0 g, 9.1 mmol) was reduced by method C to yield **18a** (1.62 g, 94%): NMR ($CDCl_3$) δ 6.88 (d, J = 8.5 Hz, 1 H), 6.51 (d of d, J = 2.5, 8.5 Hz, 1 H), 6.42 (d, J = 2.5 Hz, 1 H), 3.46 (s, 2 H), 1.86 (s, 2 H), 1.25 (s, 12 H). A portion of the product was treated with acetic anhydride to yield the acetamide (mp 129–131 °C; lit.[58] mp 128.5–129 °C).

1,2,3,4-Tetrahydro-1,4-ethanonaphthalen-6-amine (19a). Compound **19n** (1.50 g, 7.4 mmol) was reduced by method C to yield a yellow oil which solidified on storage at −10 °C. The yellow crystals of **19a** (1.21 g, 95%, mp 45–46 °C) darkened somewhat on exposure to air: NMR ($CDCl_3$) δ 6.87 (d, J = 8 Hz, 1 H), 6.48 (d, J = 2.3 Hz, 1 H), 6.43 (d of d, J = 8, 2.3 Hz, 1 H), 3.46 (s, 2 H), 2.80 (s, 1 H), 2.77 (s, 1 H), 1.64 (m, 4 H), 1.32 (m, 4 H). The amine was converted to the hydrochloride for analysis. Anal. Calcd for $C_{12}H_{16}NCl$: C, 68.72; H, 7.69. Found: C, 68.64; H, 7.65.

9,10-Dimethyl-9,10[1′,2′]benzenoanthracen-2-amine (20a). The nitrotriptycene, **20n** (0.5 g, 1.5 mmol), was dissolved in glacial acetic acid (15 ml). The solution was stirred and heated to reflux. A hot solution of stannous chloride dihydrate (1.73 g, 7.7 mmol) in concentrated hydrochloric acid (3 ml) was added dropwise over 5 min to the solution of nitro compound. The resulting mixture was refluxed 5 h, poured into water, made basic with 10% potassium hydroxide solution, and extracted with chloroform (2 × 50 ml). The extract was washed once with 10% potassium hydroxide solution (25 ml) and twice with water (50 ml) and dried over anhydrous magnesium sulfate. Filtration followed by evaporation of the solvent in vacuo yielded colorless crystals of **20a** (0.34 g, 76%, mp 297–300 °C (sealed tube)): NMR ($CDCl_3$) δ 7.39 (m, 4 H), 7.15 (d, J = 7.8 Hz, 1 H), 7.08 (m, 4 H), 6.76 (d, J = 2.1 Hz, 1 H), 6.31 (d of d, J = 2.1, 7.8 Hz, 1 H), 3.48 (s, 2 H), 2.31 (s, 3 H), 2.30 (s, 3 H); IR (KBr) 3440, 3370 (m, N–H), 2940 (s, C–H), 1610 (s, N–H), 750 cm^{-1} (s, C–H). Anal. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.44; H, 6.09; N, 4.60.

Contact Shift Measurements. The techniques used to determine the contact chemical shifts were adapted from the procedures of Morishima and his associates.[59] All the amines were distilled or recrystallized prior to use. Nickel acetylacetonate was dried in vacuo at 55 °C for 3 days. Aliquots of a solution of the nickel salt, 0.250 M, were added to a solution of the amine, 2 M, in deuteriochloroform. The concentration of the nickel reagent was adjusted when the amine concentration was limited by solubility or availability. Tetramethylsilane was used as an internal reference in all the magnetic resonance experiments. The proton and carbon NMR spectra were recorded following each incremental addition of the nickel reagent, Figure 1. The proton spectra were recorded at either 60 or 270 MHz at 30 ± 5 °C. The carbon spectra were recorded at 22.6 MHz at 38 ± 2 °C.

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(42) The $\langle\cos^2\theta_H\rangle$ values were determined graphically from the empirical relationship between $(\sigma_\beta^H/\sigma_0^H)$ and $\langle\cos^2\theta_H\rangle$ defined by the rigid molecules, **17a**–**20a**. This relationship is based on the equation

$$(\sigma_\beta^H/\sigma_0^H) = \frac{\rho_p^\pi(B_0^H + B_2^H\langle\cos^2\theta_H\rangle)}{\rho_0^\pi Q}$$

where Q is the McConnell constant, ref 33.

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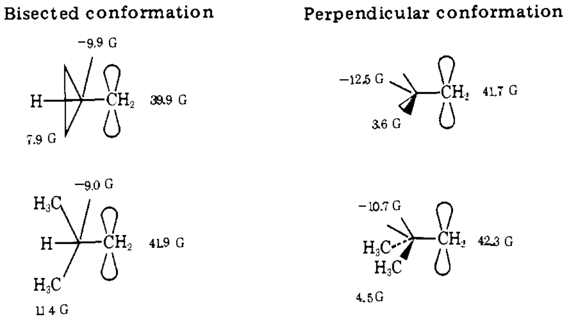

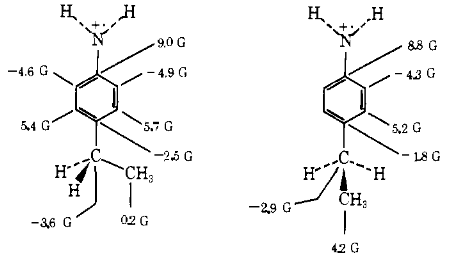

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