Electron Paramagnetic Resonance and INDO Study of Carbon-13 Hyperfine Splitting Constants in Benzyl Radical and Toluene Radical Anion

Arthur M. Ihrig,[1] Paul Ronald Jones,*[1] Il Nam Jung,[1] Roger V. Lloyd,[2] James L. Marshall,[1] and David E. Wood*[2]

Contribution from the Department of Chemistry, North Texas State University, Denton, Texas 76203, and the University of Connecticut, Storrs, Connecticut 06268.

Received September 18, 1974

Abstract: The ^{13}C hyperfine splittings have been determined for the benzyl radical and the toluene radical anion each enriched in the 1 and 7 positions with carbon-13. The hfs in gauss are: benzyl, 1-^{13}C = (−) 14.45, 7-^{13}C = (+) 24.45; toluene radical anion, 1-^{13}C = (−) 4.26, 7-^{13}C = (−) 0.78. The proton and ^{13}C hfsc's have been calculated by means of the INDO method for both the symmetric (S) and antisymmetric (A) states of the toluene anion radical at their respective energy minimized geometries. By a least-squares fit of these calculated results to the experimental hfs, the wave function of the radical has been found to consist of approximately 20% S character and 80% A character at −95°. About half of this mixing results from vibronic interaction (11.3% S character) and the remainder is due to thermal population of excited states. The observed energy difference between the first two vibronic states is 225 cm^{-1}, in good agreement with previous work.

Studies of the fine details of the electron paramagnetic resonance (EPR) spectra of radicals and radical ions provide a great deal of electronic and geometric structural information useful to both the theoretical and synthetic chemist. In the case of the planar hydrocarbon radicals, the proton and ^{13}C hyperfine splitting constants (hfs) can be related to π-electron spin densities through the McConnell,[3] Colpa–Bolton,[4] or Giacometti–Nordio–Pavan[5] relations and the Karplus–Fraenkel[6] relation, respectively. Recently, all-valence-electron molecular orbital theories, and particularly Pople's INDO,[7] have come into widespread use for calculation of molecular properties including hfsc's of unpaired electron species. These calculations have resulted in a large number of predicted hfs for which there are no experimental results available. This is true even for many well-known radical species because the usual complexity and signal-to-noise ratio of EPR spectra make estimation of the ^{13}C hfsc's in natural abundance extremely difficult and unreliable. The solution to this problem is the preparation of specific carbon-13 labeled radicals. Thus when 1-^{13}C-toluene and 7-^{13}C-toluene were prepared for ^{13}C NMR studies,[8-10] we initiated an investigation of the benzyl radical and the toluene radical anion produced from these compounds. To our knowledge, the ^{13}C hfsc's for benzyl radical and for toluene radical anion labeled in the C-1 or C-7 position have not been reported. In addition, the ^{13}C label at the 1 position provides the only probe of spin density at this position in either radical.

The benzyl radical has been the subject of many theoretical and experimental investigations, including a recent study of the fully optimized INDO geometry.[11] The EPR spectrum of toluene radical anion is of special interest because its two lowest states are nearly degenerate.[12] Early EPR spectra had shown that the lowest antibonding orbital is antisymmetric with respect to reflection through the plane perpendicular to the molecule and passing through the 1,4 positions, the A state.[13,14] Tuttle observed a slight temperature dependence of the proton hfsc's and suggested a thermally accessible excited state for the toluene anion lying 1.5 to 2.0 kcal/mol above the ground state.[15] The discrepancies which exist between the theoretically calculated hfsc's and experimental values have been attributed to configuration interaction, vibronic coupling, and thermal equilibrium between the two lowest states.[16] Theoretical calculations of the vibronic coupling by Hobey indicated that the symmetric, S, state should be present in the ground state of toluene anion to an amount of about 8%.[17] Based on experimental results compared with theoretical calculations for both the S and A states de Boer calculated the separation of states to be 384 cm^{-1} or about 1.1 kcal/mol and set limits on the contribution of S to the ground state of 12 to 26%.[12] Purins and Karplus[18] found that an ASMO-CI treatment with full inclusion of vibronic mixing gave a ground state wave function containing 11.9% of the S state. Their approach was to fit their calculated π-orbital spin densities to those determined from the experimental proton hfsc's by adjusting the parameters in the MO calculation. We here present an alternative approach in which we assume that the hfsc's calculated by INDO for the energy minimized A and S states are correct and then determine the linear combination which best fits the experimental hfsc's.

Experimental Section

1-^{13}C-Toluene was synthesized according to the previously described procedure.[8] The sample used in this study was about 90% labeled, but during the synthesis the label was unavoidably scrambled in the following distribution: 87% C-1, 6% C-2, 6% C-3, 1% C-4, and 0% CH$_3$.[9]

7-^{13}C-Toluene was synthesized using the reported procedure.[10] The sample was about 90% labeled and the label was 99% at the methyl group.

Benzyl radical was prepared from the labeled compounds by cosublimation of ca. 10 mg of the appropriately substituted toluene with ca. 10 mg of adamantane-d_{16} at 140° in a sealed tube followed by crushing in air and 5 min X-irradiation with a 50 Kvp 32 ma tungsten-target tube. The unsubstituted benzyl radical was prepared by recrystallization of adamantane-d_{16} from toluene in the usual manner.[19] The EPR spectra were determined with a Varian V-4502 X-band spectrometer with second derivative presentation provided by a second field modulation frequency at 550 Hz.

Toluene radical anions were prepared by reduction with potassium metal which was rinsed with pentane and triply sublimed in vacuo to finally produce a metal mirror coating on a high surface area Vigreux type tube. Reductions were accomplished at −100° in a 2:1 mixture of tetrahydrofuran-dimethoxyethane with a sample concentration of ca. 10^{-4} *M*. The procedure has been described previously.[20] The first derivative EPR spectra were recorded on a Varian V-4502-13 spectrometer with 100 kHz field modulation.

INDO energy minimization of the toluene radical anion was performed by the method previously described[11] starting from the standard hexagonal geometry.[7] The only restrictions on the bond lengths and angles were maintainance of C_{2v} symmetry for the

Table I. EPR Data for Benzyl Radical and Toluene Radical Anion

		Hyperfine splittings, G[a,b]					
Radical	Temp, °C	7-C*H*	2-H	3-H	4-H	1-^{13}C	7-^{13}C
Benzyl							
Exptl	RT	(−)15.68	(−)5.08	(+)1.70	(−)6.00	(−)14.45	(+)24.45
INDO[c]		−17.34	−7.18	4.19	−6.68	−13.15	32.22
Toluene							
Ref 14	−70	0.79	5.12	5.45	0.59		
This work	−82	(+)0.80	(−)5.12	(−)5.45	(−)0.50		
1-^{13}C	−95	(+)0.78	(−)5.18	(−)5.50	(−)0.50	(−)4.26	
7-^{13}C	−95	(+)0.79	(−)5.31	(−)5.58	(−)0.50		(−)0.78
INDO (A)[d]		−4.59	−7.23	−7.15	2.06	−7.35	1.87
INDO (S)[d]		21.87	−2.25	0.02	−9.16	12.77	−7.73
Calcd[e]		0.82	−6.21	−5.68	−0.23	−3.24	−0.09
Temp dep at −95° × 10^{-3} G/deg[f]		21.5	−4.05	−5.82	9.11	−16.3	7.79

[a] Benzyl: ±0.05 G. [b] Toluene anion: ±0.03 G. [c] Based on complete energy minimization by INDO at C_{2v} symmetry, ref 11. [d] Energy minimization by INDO, this work. [e] Calculated from eq 3; $\lambda_A^2 = 0.7956$, $A_S^2 = 0.2044$. [f] Calculated by eq 9.

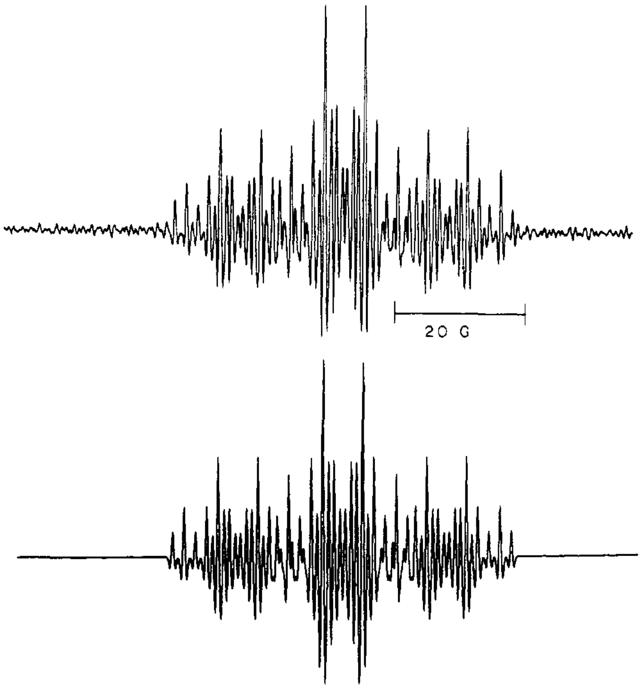

Figure 1. Second derivative EPR spectrum of benzyl radical in adamantane-d_{16} at room temperature compared with its computer simulation (lower).

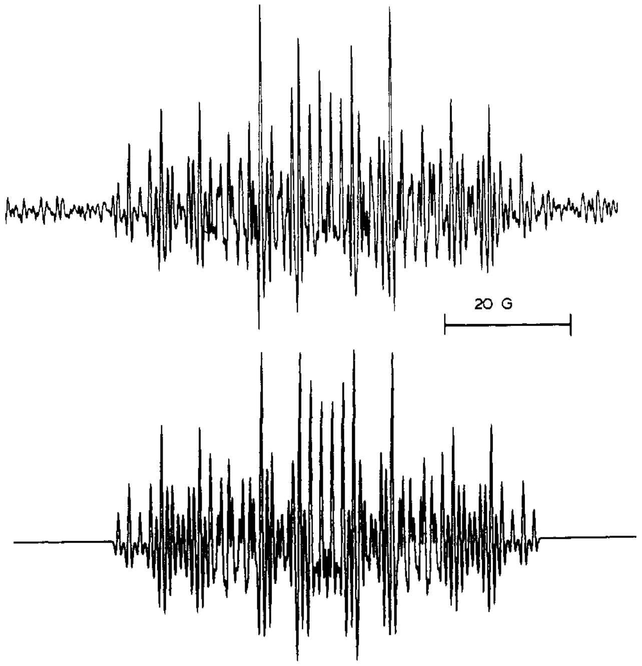

Figure 2. Second derivative EPR spectrum of 1-^{13}C-benzyl radical (90% enriched) in adamantane-d_{16} at room temperature compared with its computer simulation (lower).

ring and tetrahedral bond angles for the methyl carbon. This procedure resulted in the calculation of the S state. The A state was obtained by starting the minimization from a distorted ring geometry wherein the 2-3 and 5-6 C-C bonds were slightly longer than the others. It is possible to perform such a minimization on one of the states without danger of flipping to the other because after the initial SCF cycle is completed the "old" density matrix is reused as the starting point in order to save time for the following calculations with new bond lengths or bond angles. The orthogonality of the two solutions in C_{2v} symmetry ensures that they will not mix. The *caveat* in using INDO as illustrated by these results is that one may unwittingly cause the program to converge on an excited state by an inappropriate choice of starting geometry (see ref 22).

Results

The use of adamantane-d_{16} as a matrix reduced the line width of the benzyl radical EPR spectrum to 0.47 G at room temperature from the value of 1.4 G in ordinary adamantane.[11] This results in better accuracy for the hfsc's and in better S/N ratio. Nevertheless, differences could not be detected in the proton hfsc's as a result of carbon-13 substitution, as was found to be the case for the toluene radical anion (vide infra). The experimental hfsc's for benzyl radical are compared to those calculated using the energy minimized geometry at C_{2v} symmetry by the INDO method[11] in Table I.

The EPR spectrum of benzyl radical in adamantane-d_{16} at room temperature is compared to its computer simulation in Figure 1. Figure 2 is the second derivative EPR spectrum of benzyl radical 90% ^{13}C enriched at the 1 position recorded in adamantane-d_{16} at room temperature. The computer simulation is the sum of the spectra of 1-^{13}C enriched radical and ordinary benzyl radical in the ratio 9:1. Figure 3 shows the second derivative EPR spectrum of benzyl radical 90% ^{13}C enriched at the methylene or 7 position, again recorded in adamantane-d_{16} at room temperature. The computer simulation is the sum of the spectra of 7-^{13}C-benzyl radical and ordinary benzyl radical in the ratio 9:1. The extra lines not present in the computer simulations are due mostly to methylcyclohexadienyl radicals produced by hydrogen and deuterium atom addition to the precursors[19] and in a lesser degree to the scrambling of the label in the 1-^{13}C-toluene precursor.

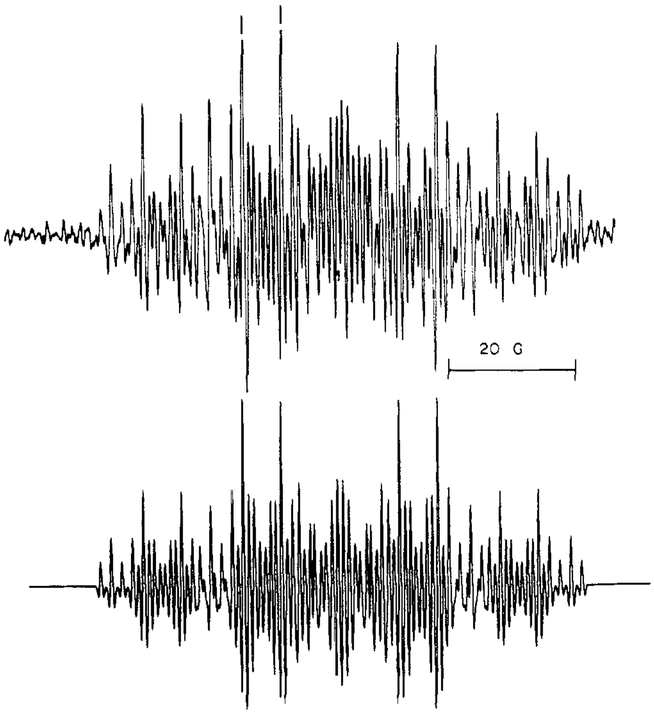

Figure 3. Second derivative EPR spectrum of 7-^{13}C-benzyl radical (90% enriched) in adamantane-d_{16} at room temperature compared with its computer simulation (lower).

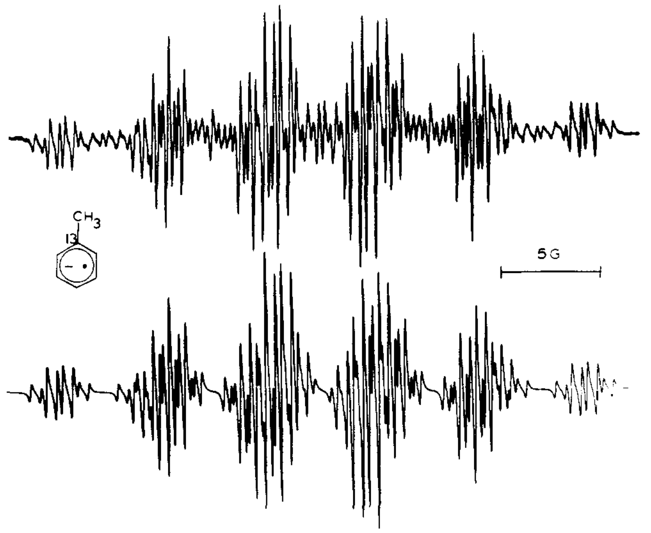

Figure 4. First derivative EPR spectrum of 1-^{13}C-toluene radical anion (90% enriched) at −95° compared with its computer simulation (lower).

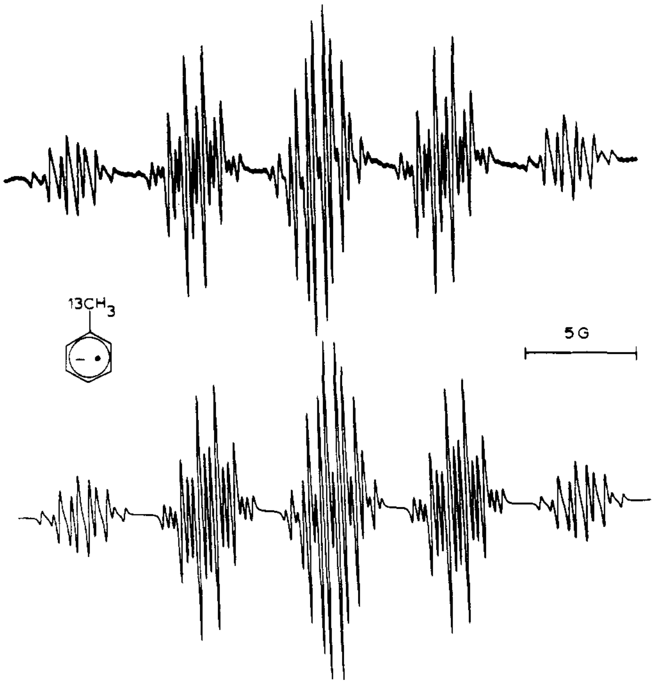

Figure 5. First derivative EPR spectrum of 7-^{13}C-toluene radical anion (90% enriched) at −95° compared with its computer simulation (lower).

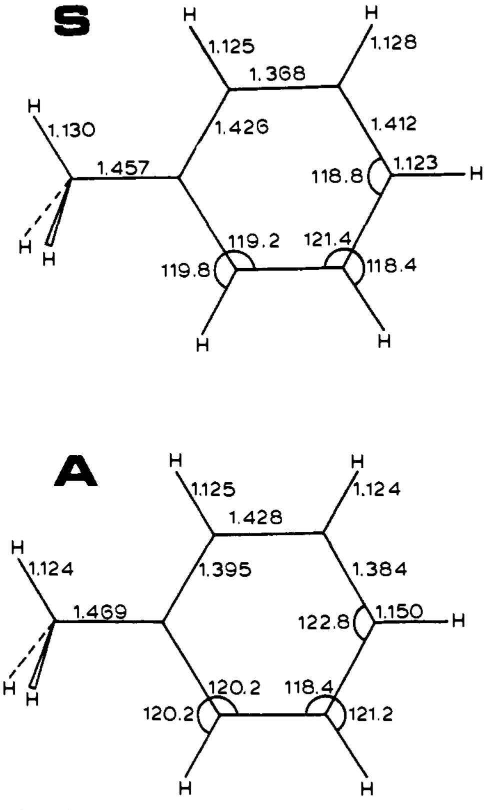

Figure 6. INDO energy minimized geometries for the antisymmetric state, A, and the symmetric state, S, of the toluene radical anion.

The EPR spectra of 1-^{13}C-toluene radical anion and 7-^{13}C-toluene radical anion recorded at −95° with their computer simulations are shown in Figures 4 and 5, respectively. The experimental values of the hfsc's for the toluene radical anions at −95° are listed in Table I. There are some differences in the proton hfsc's of the two ^{13}C substituted radicals even at the same temperature as can be seen in the table. In addition, the hfsc's are rather temperature dependent, particularly the ^{13}C hfsc's for 1-^{13}C-toluene which decreased from 4.7 G at −102° to 4.26 G at −95°. Unfortunately, line broadening at higher temperatures prevented accurate measurements of this effect over a wider temperature range. INDO energy minimized geometries for the S state and the A state of toluene radical anion are shown in Figure 6. The preferred orientation of the methyl group is with one hydrogen in the plane of the ring, but the sixfold barrier to rotation is less than 40 cal/mol for both states. The INDO hfsc's listed in Table I are the averages of the values calculated at 10° intervals of methyl group rotation listed in Table II.

Discussion

Benzyl Radical. The agreement of the ^{13}C hfsc's calculated by INDO with the experimental results (Table I) is entirely satisfactory for 1-^{13}C but is less so for 7-^{13}C. Also the

Table II.[a] Effect of Methyl-Group Orientation on Hfsc's for Toluene Radical Anion by INDO

θ	CH_3-a	CH_3-b	CH_3-c	2-H	3-H	4-H	5-H	6-H	1-^{13}C	7-^{13}C
					Symmetric State					
0	0.42	32.51	32.51	−1.99	−0.24	−9.15	0.26	−2.52	12.77	−7.74
10	1.67	38.43	25.34	−2.03	−0.20	−9.16	0.23	−2.48	12.77	−7.74
20	5.29	42.32	17.84	−2.12	−0.11	−9.16	0.14	−2.39	12.77	−7.73
30	10.90	43.68	10.90	−2.25	0.02	−9.16	0.02	−2.25	12.78	−7.73
40	17.87	42.30	5.28	−2.38	0.14	−9.16	−0.10	−2.12	12.77	−7.73
50	25.38	38.40	1.67	−2.48	0.22	−9.16	−0.20	−2.03	12.77	−7.74
					Antisymmetric State					
0	−0.86	−6.32	−6.32	−6.44	−7.61	2.04	−6.64	−7.99	−7.29	1.84
10	−1.08	−7.39	−5.13	−6.55	−7.56	2.05	−6.70	−7.90	−7.32	1.85
20	−1.73	−8.22	−3.93	−6.87	−7.38	2.07	−6.91	−7.62	−7.38	1.88
30	−2.74	−8.54	−2.74	−7.24	−7.16	2.08	−7.16	−7.24	−7.41	1.89
40	−3.94	−8.23	−1.73	−7.63	−6.91	2.07	−7.39	−6.86	−7.38	1.88
50	−5.14	−7.41	−1.08	−7.88	−6.72	2.05	−7.54	−6.57	−7.32	1.85

[a] For the definitions of the angle θ and the numbering system used see Figure 7.

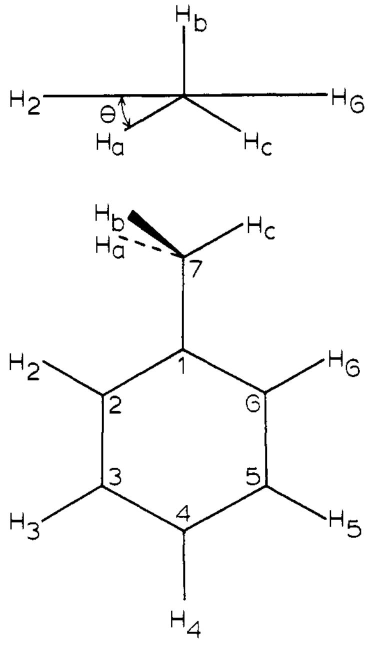

Figure 7. Numbering scheme for data in tables and explanation for angle θ.

INDO π-orbital spin-orbital densities are invariably larger in absolute value than those calculated from the experimental hfsc's via the McConnell[3] and Karplus-Fraenkel[6] relations (Table III). The internal consistency between the π-orbital spin densities calculated from proton and ^{13}C hfsc's is excellent for the 7 position but not as satisfactory for the 1 position, probably because of the small difference which must be taken between two relatively large numbers in solving the Karplus-Fraenkel relation for this case.

Toluene Radical Anion. As was noted in the introduction, the experimental EPR spectrum of toluene radical anion results from an admixture of the nearly degenerate A and S states. The vibronic coupling which mixes these two purely electronic states with certain vibrational modes of the ring to result in a manifold of vibronic states is critically dependent on the initial energy separation of A and S and the appropriate ring vibrational frequencies.[17,21] At temperatures above absolute zero the first excited vibronic state will begin to be populated, which will result in even more S contribution to the EPR spectrum. The decrease in the absolute value of the 1-^{13}C hfsc's with increasing temperature is completely consistent with this expectation. The values of the ^{13}C hfsc's reported herein coupled with optimized geometry INDO results can be used to provide an estimate of the mixing and separation of these states.

Table III. π-Orbital Spin Densities in Benzyl Radical

	Position				
	1	2	3	4	7
Exptl[a]	(−)0.0531[b] (−)0.0377[c]	0.1881	(−)0.0630	0.222	0.5807 0.5826[c]
INDO[d]	−0.1840	0.2576	−0.1489	0.2529	0.7138

[a] From proton hfsc's via McConnell relation, $Q = -27.0$ G, ref 3. [b] By difference assuming $\Sigma_{\rho\pi} = 1$. [c] From ^{13}C hfsc's and other spin densities via Karplus–Fraenkel relation, ref 6. [d] Based on complete energy minimization by INDO at C_{2v} symmetry, ref 11.

It should be noted that when the geometry optimization for toluene radical anion was initiated using INDO "standard geometry", the program converged on the "wrong" state, the S state for the radical. The slight modifications of the initial geometry indicated in the experimental section resulted in convergence on the experimentally correct state, the A state.[22] Moreover the calculation predicted the energy minimized S state to be about 8 kcal/mol *lower* in energy than the energy minimized A state. In spite of this there is abundant evidence that the INDO approximation gives reasonable expectation values for hyperfine coupling constants.[23] We will therefore take the INDO calulated hyperfine coupling constants for both the antisymmetric and symmetric state as reasonable expectation values for toluene anion if it were purely in the A or S state. These values are listed in Table I. It is interesting that HMO and ASMO-CI calculations also give the incorrect relative ordering of the A and S states unless the parameters are adjusted, although the EHT method gives the correct order without parameter changes.[18,24] Single point ab initio calculations at the STO-3G level[25] for the A and S geometries predicted by INDO (Figure 6) yield the correct ordering with an energy difference of 2.75 kcal/mol.[26] However, since these geometries are prejudiced by the INDO calculations we will empirically measure the amount of mixing and then back calculate to obtain the initial electronic energy separation. A systematic examination by ab initio calculations of substituent effects on the removal of the benzene anion degeneracy will be reported at a later date.

Regarding the wave function for toluene radical anion, ψ, as a linear combination of the wave functions for the antisymmetric and symmetric states, ϕ_A and ϕ_S, respectively

$$\psi = \lambda_A\phi_A + \lambda_S\phi_S \qquad (1)$$

where λ_A and λ_S are the mixing coefficients for the two states, the effective expectation value of the isotropic hyperfine coupling constant, a_{eff} for the *i*th nucleus is given as

$$a_{i,\text{eff}} = \langle\psi|\xi|\psi\rangle = \lambda_A^2\langle\phi_A|\xi|\phi_A\rangle + \lambda_S^2\langle\phi_S|\xi|\phi_S\rangle + \lambda_A\lambda_S\langle\phi_A|\xi|\phi_S\rangle \qquad (2)$$

Because ϕ_A and ϕ_S are orthogonal the integral $\langle\phi_A|\xi|\phi_S\rangle$ vanishes. Taking $\langle\phi_A|\xi|\phi_A\rangle$ and $\langle\phi_S|\xi|\phi_S\rangle$ as the expectation values, a_{iA} and a_{iS}, for the pure antisymmetric and symmetric states obtained from the INDO calculations we obtain the relation:

$$a_{i,\text{eff}} = \lambda_A^2 a_{iA} + \lambda_S^2 a_{iS} \tag{3}$$

The requirement of normalization, $\lambda_A^2 + \lambda_S^2 = 1$ yields the result:

$$a_{i,\text{eff}} - a_{iS} = (a_{iA} - a_{iS})\lambda_A^2 \tag{4}$$

A linear least-squares fit of $a_{i,\text{eff}}$ to all the experimental proton and ^{13}C hfsc's (measured at −95°) using eq 4 gives $\lambda_A^2 = 0.7956$. This yields

$$\psi = 0.8920\phi_A + 0.4521\phi_S$$

as the wave function for toluene anion at −95°. The values of the hyperfine coupling constants calculated using eq 3 are compared with the experimental values in Table I. The standard deviation between experimental and calculated hfsc's is 0.67 G.

Based on this correlation the total contribution of the S state to the hfsc's of the toluene radical anion at −95° is about 20% due to both vibronic coupling and thermal equilibrium.[27] The vibronic coupling arises from the interaction of the A state ring vibrational manifold with that of the S state, resulting in a new vibronic manifold each state of which contains both S and A character. This mixing is more pronounced as the original electronic energy splitting, 2d, between the S state and A state becomes smaller, and it is a particularly important effect for the case of the monoalkylbenzene radical anions wherein this splitting is less than the ring vibrational frequencies. Hobey[17] has calculated the first two vibronic states and their resulting energy differences, ΔW, for monoalkylbenzene radical anion with 2d ranging from 123 to 1416 cm^{-1}. Hobey's result for the spin densities in the first two vibronic states (eq 9.1, ref 17) can be rewritten in terms of hfsc

$$\begin{aligned} a_i &= \langle n_a|n_a\rangle a_{iA} + \langle n_b|n_b\rangle a_{iS} \\ a_i' &= \langle n_a'|n_a'\rangle a_{iA} + \langle n_b'|n_b'\rangle a_{iS} \end{aligned} \tag{5}$$

where the unprimed and primed quantities refer to the ground and first excited vibronic states, respectively. The $\langle n_a|n_a\rangle$ and $\langle n_b|n_b\rangle$ are the mixing coefficients for the pure electronic A and S states, respectively. Assuming that only these first two vibronic states are appreciably populated and that rapid thermal interchange occurs between them, the effective hfsc's for nucleus i at temperature T is

$$a_{i,\text{eff}} = [a_i + a_i' \exp(-\Delta W/KT)]/[1 + \exp(-\Delta W/KT)] \tag{6}$$

Rearrangement of this equation and comparison with eq 3 shows that

$$\lambda_A^2 = [\langle n_a|n_a\rangle + \langle n_a'|n_a'\rangle \exp(-\Delta W/KT)]/[1 + \exp(-\Delta W/KT)]$$

and

$$\lambda_S^2 = [\langle n_b|n_b\rangle + \langle n_b'|n_b'\rangle \exp(-\Delta W/KT)]/[1 + \exp(-\Delta W/KT)] \tag{7}$$

Values of λ_A^2 at −95° were calculated from eq 7 for the six values of ΔW treated by Hobey (Table IV, ref 17).[28] The λ_A^2 were plotted against both their ΔW and 2d values and then the value of λ_A^2 found from our least-squares fit to the experimental data was plotted on the graphs to find "observed" ΔW and 2d values for toluene radical anion of 225 and 330 cm^{-1}, respectively. The corresponding values found by Purins and Karplus[18] via ASMO-CI calculations are 284 and 365 cm^{-1}. Linear interpolation yields the following results for the vibronic mixing coefficients

$$\begin{aligned} a_i &= 0.8867a_{iA} + 0.1133a_{iS} \\ a_i' &= 0.2255a_{iA} + 0.7745a_{iS} \end{aligned} \tag{8}$$

Thus this work predicts that the ground vibronic state contains 11.3% of the S electronic state, which is nearly identical with the 11.9% found by the treatment of Purins and Karplus.[18]

Turning the calculations around now that we have the splitting ΔW for toluene radical anion, we can calculate the temperature dependence of the hyperfine splittings via the $\partial/\partial T$ of eq 6. These values are tabulated for −95° in Table I.

$$\partial a_{i,\text{eff}}/\partial T = [(a_i' - a_i)\Delta W \exp(-\Delta W/KT)]/[1 + \exp(-\Delta W/KT)]^2 KT^2 \tag{9}$$

Our experimentally measured temperature dependence for the 1-^{13}C hfsc of -16×10^{-3} G/deg is rather fortuitously the same as our calculated value. Comparing our calculated values for the temperature dependence to the slopes of the plots of the CH$_3$, para plus CH$_3$, and ortho plus meta proton hfsc's reported by De Boer and Colpa[12] for toluene radical anion we find that the calculated values are too high, by an order of magnitude in some cases; however, the sign of the slope is correct in each case. It should be noted that the experimental temperature dependencies are the change in absolute values of the respective hfsc's and that the signs of the values reported in Table I follow this convention also.

Although the initial electronic separation, the spacing of the lowest two vibronic states, and the amount of the S electronic state found in this study are very nearly identical with those found by Purins and Karplus,[18] the latter's calculated hfsc's are much closer to the experimental values. This is to be expected since the present work utilizes only one adjustable parameter, λ_A^2, whereas Purins and Karplus adjusted their MO parameterization specifically to obtain a good fit to the hfsc's. It is likely that a similar adjustment to the INDO parameterization would result in a correspondingly good fit.

The INDO calculations overemphasize the interaction of the HOMO with the antibonding methyl-group orbitals in the same manner as do the HMO calculations with the usual parameterization[24] thus resulting in too large a delocalization of the spin onto the methyl group. This phenomenon may also explain the incorrect ordering of the states by INDO since the delocalization is a stabilizing influence and the S state has a much larger interaction with the methyl group than the A state. In addition, the INDO calculations show an interesting asymmetric interaction of the methyl group with the ring. This effect can be seen from Table II wherein the hfs of the ring-proton nearest to the out-of-plane protons and the ring proton *para* to it become more negative while their counterpart's hfs become more positive. This effect arises from the unequal hyperconjugative interaction of the methyl group with the ortho carbon orbitals when $\theta \neq 30°$. This results in the mixing in of S and A electronic states which do not have their planes of symmetry through the 1,4 positions thereby complicating the situation: however, this effect does appear to be small.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Robert A. Welch Foundation, Research Corporation, and the North Texas State University Faculty Research Fund for support of this work.

References and Notes

(1) North Texas State University.
(2) University of Connecticut.

(3) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1955).
(4) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).
(5) G. Giacometti, P. L. Nordio, and M. W. Pavan, *Theor. Chim. Acta*, **1**, 404 (1963).
(6) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).
(7) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.
(8) J. L. Marshall, A. M. Ihrig, and D. E. Miller, *J. Mol. Spectrosc.*, **43**, 323 (1972).
(9) J. L. Marshall, D. E. Miller, and A. M. Ihrig, *Tetrahedron Lett.*, 4391 (1973).
(10) A. M. Ihrig and J. L. Marshall, *J. Am. Chem. Soc.*, **94**, 1756 (1972).
(11) R. V. Lloyd and D. E. Wood, *J. Am. Chem. Soc.*, **96**, 659 (1974), and references therein.
(12) E. De Boer and J. P. Colpa, *J. Phys. Chem.*, **71**, 21 (1967).
(13) T. R. Tuttle and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 5342 (1958).
(14) J. R. Bolton and A. Carrington, *Mol. Phys.*, **4**, 497 (1961).
(15) T. R. Tuttle, *J. Am. Chem. Soc.*, **84**, 1492 (1962).
(16) J. R. Bolton, A. Carrington, A. Forman, and L. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).
(17) W. D. Hobey, *J. Chem Phys.*, **43**, 2187 (1965).
(18) D. Purins and M. Karplus, *J. Chem. Phys.*, **50**, 214 (1969).
(19) R. V. Loyd and D. E. Wood, *Mol. Phys.*, **20**, 735) 1971); see also S. DiGregorio, M. B. Yim, and D. E. Wood, *J. Am. Chem. Soc.*, **95**, 8455 (1973).
(20) P. R. Jones and R. West, *J. Am. Chem. Soc.*, **90**, 6978 (1968).
(21) J. S. Alper and R. Silbey, *J. Chem. Phys.*, **51**, 3129 (1969); **52**, 569 (1970).
(22) The INDO program[7] employs an EHT calculation as an initial guess for the molecular orbitals which are then populated according to their energies. These populated orbitals are strongly lowered in energy relative to the unoccupied orbitals by the SCF procedure. Subsequent calculations at new geometries during the minimization utilize the previous density matrix. Therefore, once a particular electronic state has been chosen its energy surface in parameter space (bond lengths and angles) can be calculated by our program although there exists a state of lower energy. The following conditions must, however, be met: (a) the energy of the excited state being calculated must not be too greatly above the ground state or the lowering effect of the SCF procedure will be overcome; (b) the symmetry of the excited state must be sufficiently different from that of the ground state so that significant mixing will not occur. Condition (a) is easily satisfied for species with near electronic degeneracies such as the substituted benzene anions and cations. Condition (b) is obviously met for the A and S states of the benzene ion problem; however, distortions which remove the planes of symmetry can result in convergence to the ground state (e.g., the methyl group is not a large enough perturbation, but putting one of the ring carbons out of the plane by 0.1 Å is). We have modified our INDO program to allow selection of the initial population so that the "trick" method described in the experimental section is no longer necessary. In any case the INDO results reported herein for toluene radical anion correspond to the same S and A states known from HMO, EHT, and ASMO-CI calculations.
(23) See, for example: G. R. Underwood and V. L. Vogel, *J. Am. Chem. Soc.*, **93**, 1058 (1971), and references therein; or ref 7. We have also observed excellent correlation between CNDO calculated π-orbital spin densities and hyperfine coupling constants for silyl-substituted aniline radical cations: M. J. Drews, P. S. Wong, and P. R. Jones, *J. Am. Chem. Soc.*, **94**, 9122 (1972), and P. R. Jones and I. N. Jung, unpublished results.
(24) D. Purins and M. Karplus, *J. Am. Chem. Soc.*, **90**, 6275 (1968).
(25) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(26) A. R. Rossi and D. E. Wood, unpublished results.
(27) The INDO method yields nonzero s-orbital spin densities for planar π radicals through the inclusion of one-center electron exchange terms.[7] To this extent it accomplishes the same result as the σ–π configuration interaction usually used to explain this phenemonon: A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance", Harper and Row, New York, N.Y., 1967, p 81.
(28) The simple iterative method of Hobey (ref 17) gives results comparable to the complete treatment of Purins and Karplus (ref 18) according to Alper and Silbey (ref 21).

Quantitative Carbon-13 Fourier Transform Nuclear Magnetic Resonance. Limitations of Spin Relaxation Reagents

George C. Levy* and Ulf Edlund

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306.

Received January 25, 1975

Abstract: There are several problems associated with the use of paramagnetic relaxation reagents such as chromium (tris)acetylacetonate (Cr(acac)$_3$) to quantify ^{13}C NMR spectral data. In medium and large sized organic molecules ^{13}C–^{1}H NOE suppression will be incomplete and variable owing to the fact that efficient ^{13}C–^{1}H dipole-dipole relaxation is able to successfully compete with electron-nuclear relaxation to the Cr(acac)$_3$. For these molecules the use of Cr(acac)$_3$ actually can degrade the performance of the experiment. These conclusions are illustrated with a complete spin-lattice relaxation study at 67.9 MHz on cholesteryl chloride as a representative organic compound. Another finding of this study is that at the high field employed (63 kG) the chemical shift anisotropy (CSA) mechanism accounts for 60% of the spin-lattice relaxation of the nonprotonated olefinic carbon, C-5. The calculated anisotropy of the C-5 chemical shift tensor is somewhat higher than previously observed for sp^2 carbons not attached to heteroatoms, 340 ppm.

Theory

Paramagnetic relaxation additives such as chromium tris(acetylacetonate) (Cr(acac)$_3$) are being utilized increasingly to shorten long spin-lattice relaxation times and to eliminate the nuclear Overhauser effect (NOE) in proton decoupled ^{13}C NMR studies.[1,2] These reagents have also been found to be valuable in spectral analyses complementing or replacing lanthanide chemical shift reagents[3] and in NMR of other nuclei like silicon-29 and nitrogen-15 where the negative magnetogyric ratios could cause signals to vanish (negative NOE ≈ -1).[4]

The most widely reported application of these paramagnetic relaxation reagents (PARR), however, has been to quantify spectral results in ^{13}C FT NMR.[2] The main purpose of this paper is to show that the use of PARR materials in these analyses *should be strongly restricted* because NOE's may not be effectively suppressed in the general case.

Early studies evaluated NOE quenching and enhanced spin-lattice relaxation for nonprotonated carbons or for other carbons in small molecules where rapid molecular tumbling makes the normal ^{13}C–^{1}H dipole-dipole relaxation process, R_1^{DD}, inefficient. In these restricted cases a relaxation contribution of ca. 0.3 sec to T_1^{obsd} ($\approx$3 sec^{-1} to the relaxation rate, R_1^{obsd}) from a 0.1 M solution of Cr(acac)$_3$ is able to effectively suppress all NOE's and essentially equalize all T_1's for protonated and nonprotonated