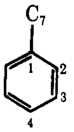
Carbon Magnetic Resonance Studies of Enriched Compounds. Carbon-13–Carbon-13 Coupling Constants of ^{13}C-7 Labeled Monosubstituted Benzene Derivatives

Sir:

Although much attention has been devoted to chemical-shift and carbon–hydrogen coupling phenomena in cmr,[1] only a few investigations involving $^{13}C-^{13}C$ coupling have been carried out. This lack of attention to J_{C-C} values is directly attributable to the low natural abundance ($\simeq 1\%$) of the ^{13}C isotope, statistically reducing the chances for the simultaneous presence of ^{13}C atoms at two given positions in a molecule. Nevertheless, some J_{C-C} values have been determined by enrichment[2-6] and by time averaging.[7,8]

Table I. Carbon-13 Parameters for Monosubstituted Benzenes



Hybridization of C_7 atom	^{13}C-7 substituent	Chemical shift, Hz[a] δ_1	δ_2	δ_3	δ_4	$^{13}C-^{13}C$ coupling constant, Hz J_{17}	J_{27}	J_{37}	J_{47}	J_{COC}
sp^3	$-CH_3$	-9.3	-0.6	0.0	3.1	44.19[b]	3.10	3.84	0.86	
	$-CH_2OH$	-13.0	1.4	0.0	1.2	47.72	3.45	3.95	0.73	
	$-CH_2Cl$	-9.3	-0.2	-0.3	0.0	47.78	3.69	4.23	0.69	
sp^2	$-CO_2^-Na^+$	-7.6[c]	-0.8[c]	0.0[c]	-2.8[c]	65.90	2.23	4.11	0.8	
	$-CO_2H$	-2.4	-1.6	0.1	-4.8	71.87	2.54	4.53	0.90	
	$-CO_2CH_3$	-2.1	-1.2	0.0	-4.4	74.79	2.38	4.56	0.90	2.63
	$-COCl$	-4.6	-2.9	-0.6	-7.0	74.35[b]	3.53	5.46	1.18	
sp	$-CN$	16.3	-3.6	-0.7	-4.4	80.40[b]	2.61	5.75	1.59	

[a] Referenced to 10% internal benzene standard. [b] These parameters have been previously determined to be, respectively, 44.2, 74.1, and 80.3 Hz (see ref 3). [c] No internal benzene; referenced to farthest upfield signal of sample (C_3).

Because of the enhanced resolution of recent nmr spectrometers and because of more attractively priced carbon-13 precursors, we felt it timely to begin a $^{13}C-^{13}C$ coupling study involving a sequence of compounds specifically labeled. For this sequence of compounds, a series of ^{13}C-7 labeled monsubstituted benzene derivatives was chosen as a relatively neglected system which could be synthesized economically.[9] Table I lists these compounds along with the determined cmr data. For each compound, the chemical shifts of all aromatic carbon atoms and all of the J_{C-C} values involving the C-7 atoms are presented. The J_{C-C} values were measured directly from the observable doublets of each natural-abundance carbon atom.[10]

The major difficulty in the compilation of Table I was that of correctly assigning the carbon signals. Although the assignments for C_1 and C_4 were easy,[11] those for C_2 and C_3 lay in doubt. The only useful assignments previously made for C_2 and C_3[12] were those for toluene[13] and benzonitrile[14] with the toluene assignments being in some doubt.[14] To verify the assignments for toluene and to establish the assignments for the carbonyl compounds, *m*-deuteriotoluene and *m*-deuteriobenzoic acid were synthesized[15] and the deuterium-bearing carbon atom was identified by the broadening and loss of intensity of the appropriate signal. It became apparent that the meta carbon–carbon coupling constant $^3J_{37}$ was larger than the ortho carbon–carbon coupling constant $^2J_{27}$. Thus, Table I was completed by always allowing $J_{37} > J_{27}$. Thus

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(1) For leading references, see J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965); J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, Elmsford, N. Y., 1966, pp 988–1031; F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 228; E. D. Becker, "High Resolution NMR," Academic Press, New York, N. Y., 1969, p 60–172.

(2) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962); P. M. Graham and C. E. Holloway, *Can. J. Chem.*, **41**, 2114 (1963).

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(8) F. J. Weigert and J. D. Roberts, *ibid.*, **89**, 5962 (1967); J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *ibid.*, **92**, 7107 (1970).

(9) The synthetic sequence involved a series of classical reactions originating with the reaction of phenylmagnesium bromide with 90% ^{13}C-enriched carbon dioxide (Monsanto Research Corporation, Mound Laboratory, Miamisburg, Ohio). The complete experimental procedure is available upon correspondence with the authors.

(10) The cmr spectra, all proton irradiated, were recorded by a single scan on a JEOL PS-100 nmr spectrometer, except for benzonitrile whose $J_{C_1-C_7}$ AB pattern was time averaged by a Fabri-tek 1071 computer. The J_{C-C} values are all considered to be accurate within 0.15 Hz.

(11) The C_1 atom was easily identified because the directly bonded coupling was always so large and because lack of an adjacent proton led to the weakest signal—with no directly bonded hydrogen atom, a carbon atom cannot experience an Overhauser effect [E. G. Paul and D. M. Grant, *J. Amer. Chem. Soc.*, **86**, 2977, 2984 (1964)]. The C_4 atom was next identified as being the next weakest signal (twice as many C_2 or C_3 carbons existed as C_4 atoms).

(12) For all monosubstituted carbonyl compounds previously studied, identical chemical shifts were given for C_2 and C_3: K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **43**, 479 (1965); **45**, 233 (1966); H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(13) T. D. Alger, D. M. Grant, and E. G. Paul, *J. Amer. Chem. Soc.*, **88**, 5397 (1966).

(14) Using the *Q* correlation developed by W. B. Smith [for a description of this correlation for aromatic proton chemical shifts, see W. B. Smith, A. M. Ihrig, and J. L. Roark, *J. Phys. Chem.*, **74**, 812 (1970)], the chemical-shift assignments appear to be rigorously established for benzonitrile but not so for toluene (W. B. Smith, private communiction).

(15) *m*-Deuteriotoluene was synthesized by treating *m*-tolylmagnesium bromide with deuterium oxide. *m*-Deuteriobenzoic acid was then synthesized by oxidizing *m*-deuteriotoluene with aqueous potassium permanganate.

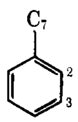
assigned, the chemical-shift assignments of Table I were consistent in that the C_3 chemical shift—the shift expected to be least affected by the substituent—was always closest to that for benzene (except for benzyl chloride, where the chemical shifts for C_2 and C_3 were almost the same).

The most obvious trend from Table I is the correlation between the magnitude of J_{17} and the hybridization of C_7. Increasing the s character of C_7 causes J_{17} to increase from 44.19 Hz in the sp^2–sp^3 system of toluene to 80.40 Hz in the sp^2–sp system of benzonitrile. This trend is quite consistent with previously proposed empirical expressions[3] which have been used to predict bond hybridization in strained systems.[8]

Another trend involving the C-1 carbon atom is the increase in J_{17} as the electronegativity of the C-7 substituent increases, for both the carbonyl and the sp^3 cases. However, this substituent effect is several times larger for the carbonyl series (*e.g.*, as -OH changes to -Cl, J_{17} changes by 0.06 and 2.48 Hz for the sp^3 and sp^2 cases, respectively). This observation is consistent with earlier work, where it was shown that $^1J_{\text{C-C}}$ values for acetyl compounds[4] vary to over 50%, whereas this variation for *tert*-butyl compounds[7] is much more modest. Perhaps this large difference between carbonyl and sp^3 systems is due to the polarizability of the carbonyl group.

As expected, the magnitude of the J values in Table I is attenuated dramatically beyond the first bond. For these long-range $J_{\text{C-C}}$ values, again hybridization and substituent trends are observed. As the s character of C-7 increases, again the magnitude of $J_{\text{C-C}}$ increases for J_{37} and J_{47} (but remains the same, or decreases slightly, for J_{27}). As the substituent becomes more electronegative, again the magnitude of $J_{\text{C-C}}$ increases for both the sp^2 and sp^3 cases for all the long-range values J_{27}, J_{37}, and J_{47} (except for the sp^3 J_{47} values, where the trend may be reversed). As in the case of J_{17} values, the substituent effect for the long-range J values is much more pronounced for the sp^2 case than for the sp^3 case.

The observation that the three-bonded coupling constant J_{37} is larger than the two-bonded coupling constant J_{27} is most striking. In view of this remarkable observation, ^{13}C-7 *p*-nitrotoluene was synthesized to verify the coupling pattern. For this molecule, whose chemical-shift assignments have been rigorously established,[16] again J_{37} was larger than J_{27} (3.88 and 3.47 Hz, respectively). The observation that $J_{37} > J_{27}$ in the present system, **1**, is quite analogous to the geometrically identical J_{CH} system in benzene (**2**) where $J_{\text{H}_1\text{-C}_3} > J_{\text{H}_1\text{-C}_2}$ (7.4 Hz > 1.0 Hz),[17] but is in contrast to the geometrically identical J_{CF} system in fluorobenzene (**3**)



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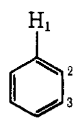

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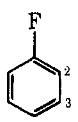

3

where $J_{\text{F-C}_3} < J_{\text{F-C}_2}$ (7.7 Hz < 21.0 Hz).[18]

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Ligand-to-Metal Intramolecular Electron Transfer in the Reduction of *p*-Nitrobenzoatopentaamminecobalt(III) Ion[1]

Sir:

The hydrated electron, e_{aq}^-, generated in the radiolysis of aqueous solutions, reacts with coordination complexes of cobalt(III) with specific rates very near to the diffusion-controlled limit[2] quantitatively generating Co^{2+}.[3] However, in all the cases reported, no transient species have been detected by pulse radiolysis from the reaction of e_{aq}^- with simple pentaammine complexes.[4-6] These negative results imply either that the electron initially attacks the ligands followed by very rapid intramolecular electron transfer to the metal center or that attack is *via* tunnelling directly into the orbitals of the tripositive metal. We wish to report that the reaction of e_{aq}^- and the reducing radicals $\cdot CO_2^-$ and $(CH_3)_2\dot{C}OH$ with $p\text{-}O_2NC_6H_4CO_2Co^{III}(NH_3)_5^{2+}$ (PNBPA) generates a transient intermediate (PNBPA⁻) in which the transferred electron is localized on the coordinated *p*-nitrobenzoato ligand; $PNBPA^-$ decays *via* ligand-to-metal intramolecular electron transfer to form Co^{2+}.[7]

The radiolysis of aqueous solutions generates e_{aq}^-, OH, and H radicals with G values (number of molecules produced per 100 eV of energy absorbed) of 2.8, 2.8, and 0.6, respectively.[8] In a N_2O-saturated solution (2.5×10^{-2} M), e_{aq}^- is efficiently scavenged

$$e_{aq}^- + N_2O \longrightarrow OH + N_2 + OH^-$$
$$k = 5.6 \times 10^9\ M^{-1}\ \text{sec}^{-1}$$

The reducing radicals $\cdot CO_2^-$ and $(CH_3)_2\dot{C}OH$ can be generated conveniently

$$OH/H + HCO_2^- \longrightarrow \cdot CO_2^- + H_2O/H_2$$
$$k = 2.5 \times 10^9/2.5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$$
$$OH/H + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + H_2O/H_2$$
$$k = 1.3 \times 10^9/5.0 \times 10^7\ M^{-1}\ \text{sec}^{-1}$$

N_2O-saturated neutral aqueous solutions of PNBPA (as the ClO_4^- salt)[9] in the presence of 0.1 M formate

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(1) Supported in part by NSF Grant GP 11213 and by NIH Grant GM 13557.

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(7) $Co(NH_3)_5^{3+}$ is also reduced to Co^{2+} by $\cdot CO_2^-$ and $(CH_3)_2\dot{C}OH$, as well as by e_{aq}^-: E. P. Vanek and M. Z. Hoffman, manuscript in preparation.

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