

NMR SPECTRAL PARAMETERS OF MONOSUBSTITUTED BENZENES:HALOBENZENES

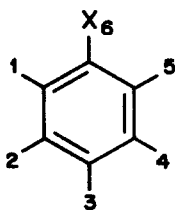
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The general trends of the variations of the proton-proton coupling constants of monosubstituted benzenes versus the electronegativity of the substituents have been briefly reported in an earlier paper (1). The determination of accurate nmr spectral parameters (chemical shifts and coupling constants) is of central importance in this type of study, since, in many instances, only minor variations of the parameters are observed by changing the nature of the substituent.

In this communication, we present the complete results obtained from the analyses of the nmr spectra of monohalogenated benzenes. Both the spectra of the neat liquids and of solutions in CCl_4 were recorded on a Varian A-60, DP-60, or HA-100 spectrometer and then analyzed with the aid of the LAOCN3 program (2,3), using either a 7090 IBM or a 1604-A CDC computer. The parameters obtained from the analyses are reported in Table I. The labelling of the protons and of other magnetic nuclei present in the molecule is as follows:



The data pertaining to chlorobenzene, both as a neat liquid and in CCl_4 solutions, refer to independent determinations on different samples using, as indicated in Table I, different full-scale sweep width for the recording of the spectra. All the spectral parameters of fluoroben-

TABLE I
NMR Spectral Parameters of Halobenzenes (C₆H₅X)^a

X	Solvent	Concn. W/W, %	Chemical Shifts			Coupling Constants											
			W(1)	W(2)	W(3)	J(1,2)	J(1,3)	J(1,4)	J(1,5)	J(2,3)	J(2,4)	J(1,6)	J(2,6)	J(3,6)			
-I	Neat		451.214	411.802	425.934	7.929	1.154	0.451	1.852	7.466	1.831						
-I	CCl ₄	10	458.233	421.754	434.726	7.934	1.142	0.465	1.877	7.472	1.754						
-Br	Neat		438.072	417.020	421.317	8.038	1.128	0.463	2.126	7.523	1.750						
-Br	CCl ₄	10	445.769	429.271	432.105	8.054	1.121	0.457	2.121	7.444	1.778						
-Cl	Neat		428.483	419.924	417.942	8.056	1.108	0.512	2.214	7.538	1.622						
-Cl ^b	Neat		428.492	419.957	418.057	8.037	1.145	0.476	2.281	7.485	1.672						
-Cl	CCl ₄	10	435.845	431.766	428.439	8.040	1.109	0.563	2.227	7.612	1.624						
-Cl ^b	CCl ₄	10	435.916	431.975	428.488	8.053	1.125	0.481	2.266	7.506	1.715						
-F	Neat		411.800	424.333	413.764	8.361	1.073	0.429	2.766	7.393	1.808	9.084	5.742	0.236			
-F	CF ₃ CCl ₃	85	413.388	426.025	415.318	8.362	1.053	0.401	2.754	7.428	1.803	9.018	5.686	0.306			
-F ^c	CF ₃ CCl ₃	85	688.827	710.000	692.106	8.341	1.040	0.417	2.749	7.445	1.810	9.114	5.676	0.342			
-F	CCl ₄	10	418.361	434.458	422.066	8.363	1.069	0.433	2.738	7.468	1.821	8.914	5.687	0.221			

^aAll data in cps.; chemical shifts are referred to TMS used as an internal standard. Unless otherwise stated, all proton spectra were recorded using a 50 cps. full sweep width at $\nu_0 = 60$ Mcps.

^bProton spectra recorded using a 25 cps. full sweep width.

^cProton spectra recorded at $\nu_0 = 100$ Mcps. The corresponding values (in cps.) of the chemical shifts converted to $\nu_0 = 60$ Mcps. are: W(1) = 413.296; W(2) = 426.000; W(3) = 415.264.

benzene as a neat liquid and in CCl_4 solution were obtained from the analyses of the proton spectra. However, in the case of the sample containing 15% of 1,1,1-trifluorotrchloroethane, both the proton and fluorine spectra were analyzed. The two sets of parameters reported in Table I for this sample were obtained from spectra recorded at two different magnetic field strengths (^1H : 60 and 100 Mcps.; ^{19}F : 56.4 and 94.1 Mcps.). In Table I the proton chemical shifts are referred to TMS used as an internal standard; all parameters are given in cps. The data are reported with three decimal places as obtained from the output of the computer; the calculated probable errors were always ≤ 0.05 cps. As a typical example of our analysis, we present in Figure 1 the experimental and calculated spectrum of iodobenzene as a neat liquid.*

The trends of the proton-proton coupling constants of halobenzenes versus the electronegativity of the substituent follow the general pattern previously described (1). The largest changes are observed for $J(1,2)$ and $J(1,5)$ which increase in the order: $\text{I} < \text{Br} < \text{Cl} < \text{F}$. Definite trends are also observed for some of the other coupling constants but in general the variations are quite small. Of particular interest is the magnitude of $J(3,6)$ in fluorobenzene; earlier analyses of the spectrum assigned a value equal to zero to this parameter (4,5,6,7). As expected, large variations of the proton chemical shifts are observed in passing from the neat liquids to dilute solutions in CCl_4 . The data resulting from the analyses of the latter spectra follow the trends already obtained by Spiesecke and Schneider (8) from the nmr spectra of deuterated samples. We believe, however, that our data are more accurate and better suited for the extrapolation of the chemical shifts at infinite dilution. A complete discussion of our analyses and the interpretation of the experimental results will be reported elsewhere.

* The sharp single peak of the experimental spectrum, which is not matched in the calculated spectrum is due to benzene, which was used as a second internal standard in this particular sample.

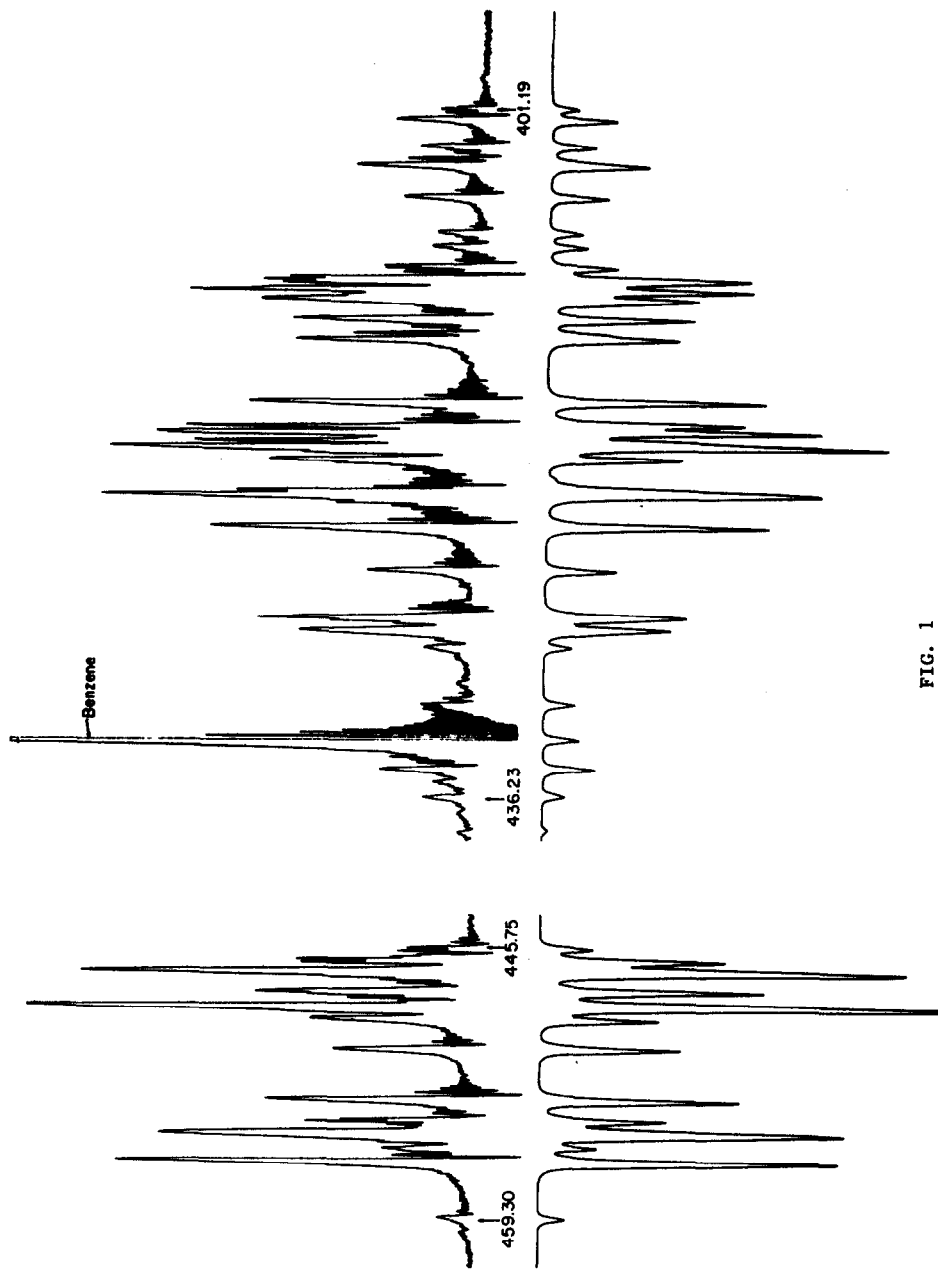


FIG. 1

Experimental and calculated nmr spectrum of iodobenzene.

Frequencies, in cps., referred to TMS; $\nu_0 = 60$ Mcps.

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