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NMR SPECTRAL PARAMETERS OF MONOSUBSTITUTED BENZENES: NITROSOBENZENE, NITROBENZENE, ANILINE, N-METHYLANILINE, N,N-DIMETHYLANILINE, TRIMETHYLANILINIUM IODIDE, PHENOL, DIPHENYL ETHER, AND ANISOLE

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Accurate nmr spectral parameters of monosubstituted benzenes are still lacking in the chemical literature. An extensive study of the proton nmr spectra of this series of compounds has been recently completed in our laboratory, and some of the results obtained have been communicated in previous papers (1,2,3,4,5,6). Data on a few monosubstituted benzenes have also been published by other authors (7,8).

In this communication we present a complete set of data (chemical shifts and coupling constants) obtained from the analyses of the proton nmr spectra of the title compounds. All liquid substances were investigated both as neat liquids and as solutions in CCl_4; the solids as solutions in the solvents indicated in Table I. All spectra were recorded on a Varian A-60 spectrometer and then analyzed with the aid of the LAOCN3 program (1,9), using either an IBM 7090 or a CDC 1604-A computer. In each case the line frequencies used in the calculations were the averaged values of four measurements on two sets of spectra recorded with alternate directions of the magnetic field sweep. The parameters obtained from the analyses are reported in Table I where the labeling of the protons is as follows:

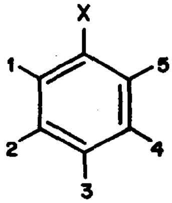

Table I

NMR Spectral Parameters of Monosubstituted Benzenes $(C_6H_5X)^a$: Nitrosobenzene, Nitrobenzene, Aniline, N-Methylaniline, N,N-Dimethylaniline, Trimethylanilinium Iodide, Phenol, Diphenyl Ether, and Anisole

-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)
-NO	CCl_4	10	468.797	452.849	456.627	7.907	1.276	0.555	1.974	7.414	1.362
$-NO_2$	Neat		486.378	449.125	458.882	8.346	1.153	0.517	2.468	7.474	1.483
$-NO_2$	CCl_4	10	491.447	451.202	459.178	8.361	1.176	0.550	2.396	7.468	1.484
$-NH_2$	Neat		381.270	420.550	398.355	8.037	1.129	0.474	2.460	7.341	1.663
$-NH_2$	CCl_4	10	387.424	420.500	397.114	8.018	1.105	0.468	2.530	7.389	1.595
$-NHCH_3$	Neat		380.214	424.807	398.332	8.195	1.104	0.413	2.513	7.326	1.684
$-NHCH_3$	CCl_4	10	386.025	422.547	394.692	8.199	1.086	0.444	2.532	7.337	1.654
$-N(CH_3)_2$	Neat		392.449	427.700	400.035	8.403	1.015	0.407	2.756	7.258	1.752
$-N(CH_3)_2$	CCl_4	10	395.371	425.076	395.884	8.402	1.009	0.434	2.756	7.288	1.759
$-N^+(CH_3)_3I^-$	CH_3OH^b	15	478.748	459.502	456.233	8.554	0.930	0.451	3.120	7.470	1.660
$-N^+(CH_3)_3I^-$	$CH_3OH^{b,c}$	15	478.897	459.618	456.314	8.554	0.915	0.483	3.048	7.461	1.693
-OH	C_6D_6	10	396.879	421.170	405.635	8.189	1.050	0.468	2.694	7.423	1.720
-OH	CCl_4	10	403.954	425.612	408.926	8.168	1.090	0.491	2.712	7.398	1.741
-Oφ	Neat		415.481	425.663	413.690	8.236	1.112	0.469	2.581	7.355	1.783
-Oφ	CCl_4	10	415.470	433.091	418.649	8.251	1.111	0.456	2.633	7.408	1.733
$-OCH_3$	Neat		407.066	427.926	409.367	8.343	1.052	0.450	2.754	7.332	1.775
$-OCH_3$	CCl_4	10	406.315	428.948	409.015	8.295	1.025	0.440	2.737	7.355	1.761

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[a] All data in cps.; ν_o= 60 Mcps. Chemical shifts are referred to TMS used as an internal standard unless otherwise specified.

[b] Chemical shifts measured from acetone and then referred to TMS.

[c] Proton spectrum recorded while irradiating the ^{14}N nucleus.

All parameters are given in cps, and the chemical shifts are referred to TMS which, unless otherwise specified, was always used as an internal standard. The calculated probable error for each of the parameters was always smaller than 0.01 cps; accordingly in Table I, all data are reported to three decimal places as directly obtained from the computer output. We prefer, however, with a more conservative estimate, to consider our data reliable to within ± 0.05 cps. Two sets of parameters are given for the spectrum of the same solution of trimethylanilinium iodide in methanol. In this spectrum the lines corresponding to the resonance of the ortho protons appear broadened by the coupling of these protons to the ^{14}N nucleus. The two sets of data reported in Table I were obtained: a) by using in the analysis all the line frequencies corresponding to the resonances of the para and meta protons and only a few lines - the sharpest ones - pertaining to the resonance of the ortho protons, b) by recording the proton spectrum while irradiating the ^{14}N nucleus. Very minor broadening appears also in the regions corresponding to the resonances of the ortho protons in the spectra of N-methylaniline, N,N-dimethylaniline and anisole, but this does not interfere with an accurate determination of the spectral parameters. For all the compounds listed in Table I, the differences between corresponding coupling constants determined from the spectra of the neat liquids and 10% (w/w) solutions in CCl_4 are smaller than the estimated limit of accuracy of the measurements, and, therefore, the dilution effect, if any, on these parameters should be smaller than 0.05 cps.

In the monosubstituted benzenes considered in this paper, the substituents are bonded to the phenyl ring through either a nitrogen or an oxygen atom. Within each series, however, significant differences are observed in the values of J(1,2) and J(1,5) which are the coupling constants most sensitive to the nature of the substituent (5). In the nitrogen series, the smallest values of these parameters are found in nitrosobenzene and the largest ones in trimethylanilinium iodide. The values of J(1,2) and J(1,5) in the latter compound represent absolute maxima in the sense that they are the largest values of these coupling constants so far found in any monosubstituted benzene. Particularly interesting are the regular increasing trends of these parameters upon progressive methylation of the amino group. Identical trends are also evident in passing from phenol to anisole. Definite trends are also found for some of the other coupling constants within each series, but, in general, the variations are quite small.

The chemical shifts of several compounds studied in this work have been previously reported by Spiesecke and Schneider (10) who analyzed the proton nmr spectra of partially deuterated samples as 5% solutions in C_6H_{12}. Notwithstanding the differences of solvents and concentrations, their data are in substantial agreement with our values obtained from the analyses of 10% solutions in CCl_4. The effects of the substituents on the chemical shifts of the protons of the phenyl ring have already been described in the literature (10) and rationalized on the basis of migration of charge (π electrons) from the substituent to the aromatic ring or vice versa (mesomeric effect). The chemical shifts of the *ortho* and *para* protons of all the compounds listed in Table I, with the exception of the trimethylanilinium iodide, follow qualitatively the trends predicted by the mesomeric effect, although anisotropic (10) and/or van der Waals' effects (11) may contribute significantly to the shifts of the *ortho* protons. No satisfactory interpretation of the variations (usually small) of the chemical shifts of the *meta* protons *versus* the nature of the substituent is available (10) at the present time. The fact, however, that the resonances of these protons occur at higher or lower field than in benzene, according as the substituent is of the I^+ or I^- type, suggests that an inductive polarization of the π electrons, concurrent with the classical mesomeric effect, may be responsible for the observed shifts of the *meta* protons. The latter mechanism should be predominant in the case of a typical I^- substituent as $-N^+(CH_3)_3$ and would explain the large down field shifts of all the aromatic protons in the trimethylanilinium ion.

The absence of any correlation between chemical shifts and coupling constants is evident from the data reported in Table I. If the variations of the chemical shifts are mainly determined by redistribution of charges in the π system, the above observation indicates that some other mechanism must be primarily responsible for the variations observed in the coupling constants. The association of maximal and minimal (5) values of the most sensitive coupling constants [$J(1,2)$ and $J(1,3)$] with two typical I^- and I^+ substituents [$-Li$, $N^+(CH_3)_3$], as well as the overall good correlation between coupling constants and the Pauling electronegativity of the first atom of the substituent bonded to the phenyl ring (5), point toward the conclusion that the variations of the coupling constants are associated with a perturbation introduced by the substituent in the σ molecular framework, highly localized around the position to which the substituent is bonded. A study of the nmr spectra of *ortho* disubstituted benzenes supports the previous conclusion in the sense that the coupling constants of these compounds can be, to a very good approximation, calculated from the data on the corresponding monosubstituted benzenes by simple additivity relationships and contribution of groups. The same technique also reproduces fairly well much of the data appearing in the literature on *para* disubstituted benzenes. It must be pointed out, however, that in some of the ortho disubstituted benzenes investigated by us, steric effects may cause discrepancies as large as 0.3 cps between calculated and observed parameters. A communication on this subject will follow in this Journal.

A full discussion of the analyses of the spectra and a more detailed interpretation of the experimental results presented in this communication will be reported elsewhere.

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