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ADDITIVE PROTON-PROTON COUPLING EFFECTS IN DISUBSTITUTED BENZENES

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The determination of substituent effects on the NMR parameters in benzene derivatives is a matter of obvious theoretical interest and practical utility. A number of recent papers have dealt with chemical shifts in substituted benzenes, and it has been found that, within reasonable limits, these shifts follow a simple additivity relation (1-4). Analogous results for coupling parameters are much more limited. For example, Dischler recently found that meta couplings in a series of unsymmetrical para-disubstituted benzenes follow an additive relation (5). Inquiries into additivity of coupling parameters of substituted benzenes have been hampered in part by the unavailability of the coupling values for benzene itself and by difficulties inherent in the analysis of the spectral patterns of the monosubstituted benzenes. Recently these problems have been overcome by analysis of the benzene ^{13}C-H spectrum (6) and by complete analysis of the PMR spectra of a number of monosubstituted benzenes (7-10).

In an effort to ascertain the extent of transferability and additivity of substituent effects on the proton couplings, we have analyzed a series of thirty-two disubstituted benzenes, primarily the dihalogen derivatives (ortho, meta and para) but also including NO_2 and OCH_3. In most cases the samples were studied as 10% solutions in TMS (see footnote to Table I). In the case of the symmetrical para-disubstituted compounds, ^{13}C-H satellite spectra were required to provide the couplings and these were obtained from neat liquid or molten samples. As far as can be ascertained the effects of solvent or concentration on the couplings are negligible. The spectra were analyzed by iterative computer methods and the probable errors in the final couplings are not over ~0.05 Hz.

The substituent effects determined for the monosubstituted benzenes are given in Table I. Corresponding couplings in these compounds can be obtained by adding the appropriate benzene coupling values to those listed in the table. All of these values are based on analyses carried out in this laboratory. Table II gives the experimental coupling values for the disubstituted benzenes studied, as well as the calculated values (shown in parentheses) as determined using the results of Table I. All of the experimental values in Table II were determined here, and full details will be reported elsewhere. The agreement between the two sets of values in Table II is considered reasonably good. The largest deviations from additivity are ~0.25 Hz and the average deviation is on the order of the total uncertainty in the substituent effects (Table I).

On the basis of the present results it would appear that, with appropriate caution, the substituent effects in Table I and the assumption of additivity can be usefully applied in the interpretation and analysis of NMR spectra. The origin and significance of the observed additive property as well as its generality must await more extended studies, involving more substituents and derivatives.

TABLE I

Substituent Coupling Effects in Monosubstituted Benzenes[a]

J_{ij}	F[b]	Cl[c]	Br[c]	I[c]	NO_2[d]	OCH_3[d]
23	+0.81	+0.61	+0.53	+0.39	+0.77	+0.79
24	-0.34	-0.23	-0.27	-0.25	-0.20	-0.32
25	-0.24	-0.16	-0.20	-0.19	-0.16	-0.22
26	+1.21	+0.87	+0.71	+0.51	+1.02	+1.33
34	-0.04	+0.03	-0.05	-0.04	-0.07	-0.16
35	+0.39	+0.34	+0.36	+0.37	+0.08	+0.38

[a] All solutions are 10% in TMS; in Hz. Para coupling in benzene taken as 0.66 Hz rather than 0.69 Hz previously reported; $J_o = 7.54$ Hz and $J_m = 1.37$ Hz.

[b] Ref. 9

[c] Ref. 8

[d] Ref. 10

TABLE II

Observed and Additivity Calculated H-H Coupling Constants for Disubstituted Benzenes. Calculated Values are in Parentheses.[a]

Compound	J_{23}	J_{24}	J_{25}	J_{26}	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}
1Br-2Br	--	--	--	--	8.00 (8.02)	1.52 (1.46)	0.30 (0.32)	7.48 (7.44)	1.52 (1.46)	8.00 (8.02)
1Br-3Br	--	1.85 (1.81)	0.29 (0.32)	1.85 (1.81)	--	--	--	8.03 (8.02)	0.95 (0.83)	8.03 (8.02)
1Br-4Br	8.41 (8.60)	--	0.46 (0.32)	2.38 (2.44)	--	2.38 (2.44)	0.46 (0.32)	--	--	8.41 (8.60)
1Br-2Cl	--	--	--	--	8.02 (1.10)	1.61 (1.50)	0.30 (0.33)	7.46 (7.52)	1.49 (1.44)	8.06 (8.10)
1Br-3Cl	--	1.96 (1.97)	0.36 (0.33)	1.87 (1.85)	--	--	--	8.06 (8.09)	0.95 (0.87)	8.06 (8.10)
1Br-4Cl	8.54 (8.68)	--	0.33 (0.33)	2.47 (2.42)	--	2.49 (2.60)	0.33 (0.33)	--	--	8.54 (8.68)
1Br-2F	--	--	--	--	8.25 (8.31)	1.48 (1.42)	0.29 (0.26)	7.50 (7.38)	1.61 (1.54)	8.02 (7.96)
1Br-3F	--	2.51 (2.38)	0.24 (0.26)	1.76 (1.77)	--	--	--	8.28 (8.31)	0.90 (0.79)	8.06 (7.96)
1Br-4F	8.79 (8.89)	--	0.26 (0.26)	2.55 (2.52)	--	3.16 (3.01)	0.26 (0.26)	--	--	8.79 (8.89)
1Br-2I	--	--	--	--	7.97 (7.88)	1.58 (1.46)	0.28 (0.30)	7.38 (7.45)	1.49 (1.47)	8.00 (8.03)
1Br-3I	--	1.60 (1.61)	0.25 (0.30)	1.88 (1.83)	--	--	--	7.93 (7.89)	0.96 (0.85)	8.05 (8.03)
1Br-4I	8.39 (8.46)	--	0.30 (0.30)	2.40 (2.45)	--	2.35 (2.24)	0.30 (0.30)	--	--	8.39 (8.46)
1Br-2MeO	--	--	--	--	7.83 (7.91)	1.61 (1.55)	0.25 (0.28)	7.42 (7.31)	1.42 (1.41)	8.25 (8.26)
1Br-4MeO	8.74 (8.86)	--	0.27 (0.24)	3.09 (3.06)	--	2.55 (2.46)	0.27 (0.24)	--	--	8.74 (8.86)
1Cl-2Cl	--	--	--	--	8.06 (8.18)	1.54 (1.48)	0.31 (0.34)	7.48 (7.60)	1.54 (1.48)	8.06 (8.18)
1Cl-3Cl	--	1.97 (2.01)	0.36 (0.34)	1.97 (2.01)	--	--	--	8.10 (8.18)	0.89 (0.91)	8.10 (8.18)
1Cl-4Cl	8.55 (8.76)	--	0.39 (0.34)	2.58 (2.58)	--	2.58 (2.58)	0.39 (0.34)	--	--	8.55 (8.76)
1Cl-2F	--	--	--	--	8.26 (8.33)	1.46 (1.40)	0.32 (0.27)	7.54 (7.46)	1.64 (1.58)	8.01 (8.04)

TABLE II (Cont'd.)

Compound	J_{23}	J_{24}	J_{25}	J_{26}	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}
1Cl-3F	--	2.45 (2.42)	0.39 (0.27)	2.01 (1.93)	--	--	--	8.42 (8.39)	0.89 (0.83)	8.02 (8.04)
1Cl-4F	8.81 (8.97)	--	0.32 (0.27)	2.70 (2.68)	--	3.11 (2.99)	0.32 (0.27)	--	--	8.81 (8.97)
1Cl-2I	--	--	--	--	7.96 (7.96)	1.55 (1.46)	0.30 (0.31)	7.40 (7.53)	1.53 (1.51)	8.01 (8.11)
1Cl-3I	--	1.62 (1.65)	0.30 (0.31)	2.04 (1.99)	--	--	--	7.94 (7.96)	0.96 (0.89)	8.06 (8.11)
1Cl-4I	8.41 (8.54)	--	0.33 (0.31)	2.54 (2.61)	--	2.22 (2.22)	0.33 (0.31)	--	--	8.41 (8.54)
1Cl-3NO$_2$	--	2.06 (2.16)	0.40 (0.34)	2.09 (2.04)	--	--	--	8.26 (8.28)	0.99 (0.94)	8.04 (8.08)
1F-3F	--	2.45 (2.34)	0.33 (0.20)	2.45 (2.34)	--	--	--	8.39 (8.25)	0.79 (0.75)	8.39 (8.25)
1F-2I	--	--	--	--	8.24 (8.32)	1.42 (1.43)	0.26 (0.24)	7.41 (7.39)	1.64 (1.56)	7.89 (7.82)
1F-3I	--	2.50 (2.40)	0.30 (0.24)	1.57 (1.57)	--	--	--	8.38 (8.32)	0.95 (0.81)	7.88 (7.82)
1F-4I	8.69 (8.75)	--	0.29 (0.24)	2.31 (2.32)	--	3.10 (3.02)	0.29 (0.24)	--	--	8.69 (8.75)
1I-2I	--	--	--	--	7.92 (7.89)	1.56 (1.49)	0.30 (0.28)	7.35 (7.46)	1.56 (1.49)	7.92 (7.89)
1I-3I	--	1.62 (1.63)	0.28 (0.28)	1.62 (1.63)	--	--	--	7.93 (7.93)	0.99 (0.96)	7.93 (7.93)
1I-4I	8.26 (8.32)	--	0.33 (0.28)	2.21 (2.25)	--	2.21 (2.25)	0.33 (0.28)	--	--	8.26 (8.32)
1OMe-2NO$_2$	--	--	--	--	8.06 (8.15)	1.75 (1.55)	0.31 (0.28)	7.41 (7.31)	1.16 (0.97)	8.52 (8.26)

[a] All coupling values in Hz.

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