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NMR SPECTRAL PARAMETERS OF ORTHO-DISUBSTITUTED BENZENES. INVESTIGATION OF THE ADDITIVITY OF SUBSTITUENT EFFECTS ON THE PROTON-PROTON COUPLING CONSTANTS.

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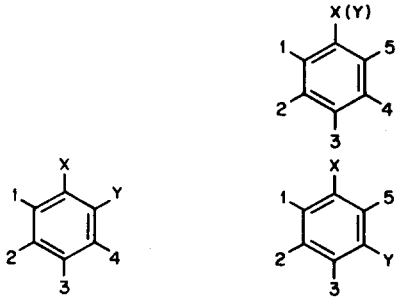
In recent communications (1,2,3) accurate nmr spectral parameters of several monosubstituted benzenes have been reported and the short range effects of the substituent on the proton-proton coupling constants has been repeatedly emphasized. The absence of correlations between chemical shifts and coupling constants (3) has been interpreted as evidence of the minor influence exerted by mesomeric effects on the magnitudes of the latter parameters. It follows that the variations of these proton-proton coupling constants are primarily determined by effects of the inductive type (1,3). On this basis, the effects of the substituents on the proton-proton coupling constants of disubstituted benzenes would be expected to show additive properties.

An additivity relation for the coupling constants between meta protons in para-disubstituted benzenes has already been proposed by Dischler (4), but the lack of data on monosubstituted benzenes (the knowledge of precise values of the coupling constants in benzene itself is not essential) prevented a thorough investigation of the consistency of that relation. If substituent effects are indeed additive, sets of equations can be established connecting the parameters of benzene (J_o, J_m, J_p) and those of the mono- (J^x_{ij}, J^y_{kl}) and disubstituted benzenes (J^{xy}_{mn}) as shown in Fig. 1 where the labelling of the aromatic protons used in this paper is also given. If experimental data on mono- and disubstituted benzenes are available, and the additivity scheme holds, insertion of these data in the right hand side of the equations of Fig. 1 should yield values of J_o, J_m, and J_p constant for the whole series of compounds. Constancy is

Figure 1



$J_o = J^x_{12} + J^y_{23} - J^{xy}_{12}$	$J_o = J^x_{12} + J^y_{23} - J^{xy}_{12}$	$J_o = J^x_{12} + J^y_{12} - J^{xy}_{12}$
$J_o = J^x_{23} + J^y_{23} - J^{xy}_{23}$	$J_o = J^x_{23} + J^y_{12} - J^{xy}_{23}$	
$J_o = J^x_{23} + J^y_{12} - J^{xy}_{34}$		
$J_m = J^x_{13} + J^y_{24} - J^{xy}_{13}$	$J_m = J^x_{13} + J^y_{13} - J^{xy}_{13}$	$J_m = J^x_{15} + J^y_{24} - J^{xy}_{15}$
$J_m = J^x_{24} + J^y_{13} - J^{xy}_{24}$	$J_m = J^x_{15} + J^y_{13} - J^{xy}_{15}$	$J_m = J^x_{24} + J^y_{15} - J^{xy}_{24}$
	$J_m = J^x_{13} + J^y_{15} - J^{xy}_{35}$	
$J_p = J^x_{14} + J^y_{14} - J^{xy}_{14}$	$J_p = J^x_{14} + J^y_{14} - J^{xy}_{25}$	$J_p = J^x_{14} + J^y_{14} - J^{xy}_{14}$

also required of the values of J_o determined from compounds with the same substituents in ortho and meta positions; and of the values of J_m determined from ortho, meta and para-disubstituted benzenes. This treatment of the data offers the opportunity of deducing spectral parameters of benzene as accurate as those obtained experimentally for the mono- and disubstituted compounds.

To check the above additivity schemes we have analyzed the nmr spectra of 13 ortho-disubstituted benzenes (7 as both neat liquids and 10% solutions in CCl_4); some of these compounds had been studied before (5,6), but an accuracy of the spectral parameters greater than that reported in the literature was needed for our purpose. The results of our analyses, which were performed with the same procedures and methods previously described (2,3), are summarized in Table I. The calculated probable error for each of the parameters was always smaller than 0.01 cps, but we prefer to adopt a more conservative estimate of $\pm$ 0.05 cps.

Application of the equations given in Figure 1 to the experimental data presented in

TABLE I

NMR Spectral Parameters of ortho-Disubstituted Benzenes (C_6H_4XY)[a]

-X	-Y	Solvent[b]	Chemical Shifts				Coupling Constants									
			W(1)	W(2)	W(3)	W(4)	J(1,2)	J(1,3)	J(1,4)	J(2,3)	J(2,4)	J(3,4)	J(1,X)	J(2,X)	J(3,X)	J(4,X)
-F	-Br	Neat	415.329	424.672	409.423	441.027	8.273	1.462	0.242	7.460	1.664	8.014	8.887	4.914	-0.589	6.944
-F	-Br	CCl_4	422.633	432.274	416.918	449.010	8.333	1.467	0.250	7.525	1.656	7.993	8.574	4.894	-0.614	6.842
-F	-I	Neat	413.007	427.469	403.234	453.832	8.202	1.419	0.222	7.426	1.653	7.930	8.178	5.112	-0.231	6.402
-F	-I	CCl_4	419.493	434.388	409.591	461.270	8.177	1.422	0.256	7.452	1.611	7.890	7.988	5.061	-0.254	6.230
-Cl	-Cl	Neat	432.091	416.493	416.493	432.091	8.064	1.583	0.321	7.486	1.583	8.064				
-Cl	-Cl	CCl_4	441.932	426.582	426.582	441.932	8.040	1.537	0.315	7.449	1.537	8.040				
-Cl	-Br	Neat	432.696	419.805	412.203	442.694	8.006	1.526	0.312	7.438	1.548	8.046				
-Cl	-Br	CCl_4	442.113	429.386	421.647	452.198	8.007	1.604	0.318	7.432	1.554	8.086				
-Cl	-OH	Neat	428.047	400.401	417.869	418.454	8.051	1.594	0.290	7.398	1.581	8.176				
-Cl	-OH	CCl_4	432.762	405.329	424.083	416.917	7.988	1.584	0.305	7.396	1.519	8.188				
-Cl	$-NO_2$	CCl_4	451.174	450.119	444.389	468.394	8.106	1.336	0.336	7.403	1.543	8.153				
-Br	-Br	Neat	443.608	415.741	415.741	443.608	7.995	1.547	0.265	7.411	1.547	7.995				
-Br	-Br	CCl_4	452.622	424.747	424.747	452.622	7.972	1.504	0.302	7.467	1.504	7.972				
-Br	-I	Neat	444.672	419.767	467.481	459.295	7.966	1.544	0.267	7.375	1.607	7.928				
-Br	-I	CCl_4	453.095	427.487	414.802	467.593	7.981	1.533	0.292	7.367	1.623	7.935				
-I	-I	CCl_4	468.543	417.537	417.537	468.543	8.021	1.488	0.299	7.314	1.488	8.021				
$-NO_2$	$-NO_2$	Me_2CO	489.453	480.345	480.345	489.453	8.123	1.319	0.341	7.731	1.319	8.123				
-OH	-OH	Me_2CO	400.661	409.469	409.469	400.661	7.978	1.552	0.260	7.344	1.552	7.978				
-OH	$-NO_2$	CCl_4	425.816	451.716	416.190	482.852	8.497	1.321	0.392	7.156	1.665	8.543		±0.400		
$-C(CH_3)_3$	$-C(CH_3)_3$	CCl_4	418.348	446.796	446.796	418.348	8.105	1.591	0.273	7.002	1.591	8.105				

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

[b] Concentration of the solutions: 10% w/w.

this communication and previous reports * (2,3) furnished results in good agreement with the additivity scheme in all cases except four (X,Y: #-$C(CH_3)_3$, -$C(CH_3)_3$#-OH, -NO_2#-NO_2, -NO_2#-Cl, NO_2#) whose anomalous behavior will be considered later. The treatment of this data furnished 48 values of J_o, 32 values of J_m and 16 values of J_p whose averages, standard and maximum (in bracket) deviations we have reported in Table II, (entry 1). Also included in Table II are the results of a similar treatment of data in the literature: on 6 meta-disubstituted derivatives quoted in a recent review (5) and elsewhere (7), yielding 12, 13, and 6 calculated values of J_o, J_m, and J_p respectively, (entry 2); on the 27 para-disubstituted derivatives analyzed by Dischler (4) yielding 27, 54, and 27 values of J_o, J_m and J_p respectively, (entry 3); on 43 para -disubstituted derivatives quoted in Bothner-By's review (5), yielding 43, 58 ** and 43 values of J_o, J_m and J_p respectively, (entry 4). Finally we have reported in Table II the values of J_o, J_m and J_p determined experimentally in two ways (8,9), (entries 5 and 6) or derived from a different statistical treatment of the parameters of monosubstituted benzenes*** (10), (entry 7).

TABLE II

Experimental and Calculated Values of the Proton-Proton Coupling Constants of Benzene (in cps.)

Entry	J_o	J_m	J_p	References
1	7.52 ± 0.07 [0.15]	1.31 ± 0.08 [0.20]	0.65 ± 0.02 [0.06]	this work
2	7.55 ± 0.05 [0.15]	1.40 ± 0.06 [0.20]	0.57 ± 0.06 [0.20]	5,7
3	7.54 ± 0.12 [0.27]	1.39 ± 0.21 [0.41]	0.69 ± 0.11 [0.28]	4
4	7.56 ± 0.13 [0.28]	1.39 ± 0.12 [0.37]	0.64 ± 0.08 [0.18]	5
5	7.50	1.40	0.50	8
6	7.56 ± 0.04	1.38 ± 0.04	0.69 ± 0.04	9
7	7.50 ± 0.05	1.35 ± 0.05	0.66 ± 0.05	10

In all cases the agreement between experimental and calculated average values of J_o, J_m and J_p is excellent. Standard and maximum deviations lie within the expected limits of accuracy for the values derived from ortho and meta compounds as well; larger deviations are found for the values derived from the para compounds reflecting the uncertainty (± 0.1 cps) in the determination of the corresponding meta coupling constants ****. The values of J_o are, however, quite reliable for this series of compounds. Large departures from additivity, due to mesomeric interactions of the two substituents, should have been particularly noticeable in this series of compounds yielding an averaged value of J_o smaller than in benzene. All the

results presented in Table II seem, therefore, to verify that the substituent effect on the proton-proton coupling constants are indeed additive and can be calculated, within the limits of accuracy of the data, from simple group contributions.

We must, however, point out that our experimental results on the ortho-disubstituted benzenes, show that the additivity rule fails in cases of strongly interacting ortho substituents. In Table III are reported the values of J_o calculated for the four compounds whose parameters deviate strongly from the additivity rule.

TABLE III

Calculated Values of J_o from ortho-di-t-Butylbenzene, ortho-Nitrophenol, ortho-Dinitrobenzene, and ortho-Nitrochlorobenzene

X	Y	J_o as calculated from:		
		J_{12}^{xy}	J_{23}^{xy}	J_{34}^{xy}
$-C(CH_3)_3$	$-C(CH_3)_3$	7.255	7.796	7.255
-OH	$-NO_2$	7.139	7.710	7.216
$-NO_2$	$-NO_2$	7.706	7.205	7.706
-Cl	$-NO_2$	7.406	7.624	7.767

We think that these anomalies can be rationalized in terms of variations of bond length and bond angles of the aromatic ring caused by the repulsions of the bulky $-C(CH_3)_3$ groups in ortho-di-t-butylbenzene and by the closure of a six membered ring, through hydrogen bonding, in nitrophenol. Evidence for the occurrence of the chelate is the measured long range coupling constant between the -OH and the aromatic proton in position 2. Such a coupling is not observed in phenol. Smaller variations of J_o, but with trends similar to that reported for the first two compounds of Table III are also detected in the data derived from the parameters of ortho-diiodobenzene. The variation of J_o observed in the case of ortho-dinitrobenzene shows a reverse trend and seems to indicate geometrical distortion of the aromatic ring opposite to the ones occurring in the first two compounds. If our interpretation is correct, careful detection of deviations from the additivity rule may prove to be more illuminating than the mere application of the additive scheme itself.

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* The spectral parameters of t-butylbenzene (10% w/w in CCl_4) have not been reported before; they are (in cps. at ν_o = 60 Mcps.): W(1)= 436.804; W(2)= 430.390; W(3)=422.700; J(1,2)= 7.961; J(1,3)= 1.164; J(1,4)= 0.570; J(1,5)= 2.180; J(2,3)= 7.399; J(2,4)= 1.554.

** J_m was not calculated for those cases in which only averaged or identical values of the meta coupling constants were given.

*** These values, obtained from least squares correlations of the coupling constants among themselves, are more accurate than those reported in Reference 1.

**** Many of these spectra of the AA'BB' type are deceptively simple, so that $J_{AA'}$ and $J_{BB'}$ are poorly determined. Furthermore, the values of these two parameters can be easily misassigned.

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