Carbon-13 Nuclear Magnetic Resonance Spectra of Polychloro- and Polybromobenzenes

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^{13}C N.m.r. spectra of a variety of polychloro- and polybromo-benzenes were determined and the chemical shifts were compared with the calculated values. The agreement between the observed and calculated values was best when the estimate based on the additivity relation is corrected for the buttress effect.

The simple additivity of substituent chemical shifts (SCS) values, conventionally defined as the chemical shift differences between monosubstituted benzenes and benzene, has an adequate level of predictive accuracy for polysubstituted benzenes.[1] Differences from the estimated values tend to be significant in cases where two substituents are sterically or electronically interacting. Thus, for *o*-dihalogenobenzenes, differences are in the order of a few p.p.m. at C-1,2 though these do not disturb the assignment based on the additivity relation.[2] Several attempts have been made to take account of the mutual steric interaction of substituents by introducing additional (second order or pairwise) terms,[3] or employing an appropriate standard.[4] We were interested in cases where more than two substituents occupy successive positions in the benzene ring (*e.g.* 1,2,3- or 1,2,3,4-), and attempted to establish whether 'additional' (*i.e.*, in addition to 1,2-interactions) crowdedness in these compounds will further affect the substituent effect observed for *o*-dihalogenobenzenes. For this purpose, the ^{13}C n.m.r. spectra of nine chlorobenzenes (**1a**)—(**9a**) and nine bromobenzenes (**1b**)—(**9b**) were determined and their chemical shifts were analysed in terms of steric effects.

Experimental

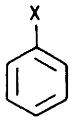
The preparation and characterization of tri-, tetra-, penta-, and hexa-chloro- and -bromo-benzenes (**3**)—(**9**) have been reported.[5]

Natural-abundance ^{13}C n.m.r. spectra of (**1**)—(**9**) and benzene at ambient temperature in CDCl$_3$ solution containing tetramethylsilane as internal reference were recorded on JEOL FX-60 and FX-90Q spectrometers operating at 15.0 and 22.5 MHz, respectively, in the Fourier transform mode. Except for (**8**) and (**9**), where a saturated solution is employed, the concentration of solutions is uniformly kept at *ca.* 20% (w/w).

Typically, 8 K data points were used, with a spectral width of 2 500 Hz, giving a digital resolution of 0.03 p.p.m. The pulse repetition time was 2.5 s, except for (**9**) where it was 6 s, and the pulse width was equivalent to 30—45°.

Results and Discussion

The assignment of signals was carried out in a conventional way, *i.e.* with the aid of spectra recorded with off-resonance decoupling, with gated-decoupling (without n.O.e.) or without decoupling. In certain cases the additivity relation of SCS (assuming conventionally defined SCS are applicable to all cases; see below) is sufficient for an unambiguous assignment. The results are summarized in Tables 1 and 2.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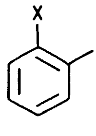
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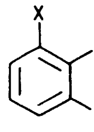
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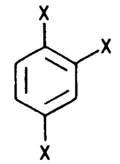
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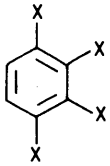
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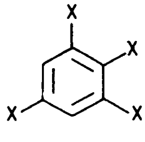
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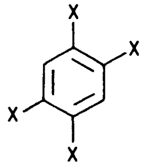
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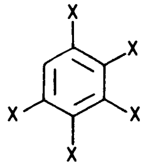
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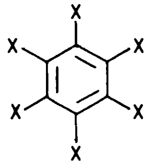
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a ; X = Cl
b ; X = Br

Chlorobenzenes.—The first row of Table 1 for chlorobenzenes (**1a**)—(**9a**) gives the observed chemical shifts. In the second row for (**2a**)—(**9a**), the calculated chemical shifts estimated under the assumption that the simple additivity of SCS for monosubstituted benzenes are also applicable to polysubstituted benzenes (method A). The differences from the observed values are large at the chlorinated carbon nuclei, and these are in the range 1.5—3.0 p.p.m. The differences may be corrected by the use of appropriate correction parameters, for which we selected $Z = \delta(\mathrm{obs}) - \delta(\mathrm{calc.})$ for (**2a** or **b**). Z Values are given in Table 3 together with SCS for monosubstituted benzenes. Though many authors have published SCS values,[6] we have determined SCS for our compounds in the light of the moderate sensitivity of them to solvents, concentrations, and instruments. Z_0 should be used for any C-1 and C-2 in a 1,2-dichlorobenzene moiety regardless of the number and position of other chlorine substituent(s). In a similar manner, Z_m and Z_p are used for C-3 and C-6, and C-4 and C-5, respectively.

For polyhalogenobenzenes, there are at least two ways of correcting δ(calc.) (method A) with Z values. In method **B**, only

Table 1. Observed[a] and calculated[b] ^{13}C chemical shifts (p.p.m. from Me_4Si) of chlorobenzenes

Compound		C-1	C-2	C-3	C-4	C-5	C-6
(1a)	obs.	*134.30*	128.61	129.69	126.39		
(2a)	obs.	*132.51*		130.45	127.69		
	calc. (A)[c]	134.41 (+1.90)		129.80 (−0.65)	127.58 (−0.11)		
(3a)	obs.	*134.28*	*131.52*		128.64	127.47	
	calc. (A)	135.60 (+1.32)	134.52 (+3.00)		127.69 (−0.95)	128.77 (+1.30)	
	calc. (B)[d]	133.70 (−0.58)	132.62 (+1.10)		128.34 (−0.30)	128.88 (+1.41)	
	calc. (C)[e]	134.35 (+0.07)	130.72 (−0.80)		128.45 (−0.19)	128.99 (+1.52)	
(4a)	obs.	*131.03*	*133.74*	130.14	*132.94*	127.79	130.91
	calc. (A)	132.30 (+1.27)	135.60 (+1.86)	129.91 (−0.23)	133.38 (+0.44)	127.69 (−0.10)	130.99 (−0.08)
	calc. (B)	130.40 (−0.63)	133.70 (−0.04)	130.56 (+0.42)	133.49 (+0.55)	127.80 (−0.01)	131.64 (+0.73)
(5a)	obs.	*132.53*	*133.10*			128.31	
	calc. (A)	133.49 (+0.96)	135.71 (+2.61)			128.88 (+0.57)	
	calc. (B)	131.59 (−0.94)	133.81 (+0.71)			129.53 (+1.22)	
	calc. (C)	132.35 (−0.18)	132.56 (−0.54)			129.75 (+1.44)	
(6a)	obs.	*134.73*	*130.30*		128.56	*132.66*	
	calc. (A)	136.79 (+2.06)	132.41 (+2.11)		127.80 (−0.76)	134.57 (+1.91)	
	calc. (B)	134.89 (+0.16)	130.51 (+0.21)		128.45 (−0.11)	134.68 (+2.02)	
	calc. (C)	135.54 (+0.81)	128.61 (−1.69)		128.56 (0)	134.79 (+2.13)	
(7a)	obs.	*131.60*		132.20			
	calc. (A)	133.49 (+1.89)		131.10 (−0.10)			
	calc. (B)	131.59 (−0.01)		131.75 (+0.55)			
	calc. (C)	131.70 (+0.10)		132.40 (+1.20)			
(8a)	obs.	*132.25*	*131.60*	*134.36*			128.84
	calc. (A)	134.68 (+2.43)	133.60 (+2.00)	136.90 (+2.54)			128.99 (+0.15)
	calc. (B)	132.78 (+0.53)	131.70 (+0.10)	135.00 (+0.64)			129.64 (+0.80)
	calc. (C)	133.65 (+1.40)	130.56 (−1.04)	133.86 (−0.50)			130.52 (+1.68)
(9a)	obs.	*132.34*					
	calc. (A)	134.79 (+2.45)					
	calc. (B)	132.89 (+0.55)					
	calc. (C)	132.51 (+0.17)					
Benzene	obs.	128.50					

[a] The italicized values are for halogenated carbons. [b] Values in parentheses are δ(calc.) − δ(obs.). [c] Calculated by method A (see text). [d] Calculated by method B (see text). [e] Calculated by method C (see text).

Table 2. Observed[a] and calculated[b] ^{13}C chemical shifts (p.p.m. from Me_4Si) of bromobenzenes

Compound		C-1	C-2	C-3	C-4	C-5	C-6
(1b)	obs.	*122.43*	131.37	129.91	126.71		
(2b)	obs.	*124.55*		133.38	128.23		
	calc. (A)[c]	125.30 (+0.75)		132.78 (−0.60)	128.12 (−0.11)		
(3b)	obs.	*126.08*	*127.54*		132.37	129.00	
	calc. (A)	126.71 (+0.63)	128.17 (+0.63)		130.99 (−1.38)	129.53 (+0.53)	
	calc. (B)[d]	125.96 (−0.12)	127.42 (−0.12)	131.59 (−0.78)		129.64 (+0.64)	
	calc. (C)[e]	126.56 (+0.48)	126.67 (−0.87)		131.70 (−0.67)	129.75 (+0.75)	
(4b)	obs.	*123.65*	*125.72*	135.95	*121.25*	131.56	134.48
	calc. (A)	123.51 (−0.14)	126.71 (+0.99)	135.66 (−0.29)	122.05 (+0.80)	130.99 (−0.57)	134.19 (−0.29)
	calc. (B)	122.76 (−0.89)	125.96 (+0.24)	136.25 (+0.30)	122.16 (+0.91)	131.10 (−0.46)	134.79 (+0.31)
(5b)	obs.	*124.71*	*129.00*			132.66	
	calc. (A)	124.92 (+0.21)	129.56 (+0.56)			132.40 (−0.26)	
	calc. (B)	124.17 (−0.54)	128.81 (−0.19)			133.00 (+0.34)	
	calc. (C)	124.88 (+0.17)	128.66 (−0.34)			133.22 (+0.56)	
(6b)	obs.	*126.53*	*126.73*		134.81	*121.34*	
	calc. (A)	128.12 (+1.59)	126.38 (−0.35)		133.86 (−0.95)	123.46 (+2.12)	
	calc. (B)	127.37 (+0.84)	125.63 (−1.20)		134.46 (−0.35)	123.57 (+2.23)	
	calc. (C)	127.97 (+1.44)	124.88 (−1.85)		134.57 (−0.24)	123.68 (+2.34)	
(7b)	obs.	*124.26*		137.12			
	calc. (A)	124.92 (+0.66)		137.06 (−0.06)			
	calc. (B)	124.17 (−0.09)		137.66 (+0.54)			
	calc. (C)	124.28 (+0.02)		138.26 (+1.14)			
(8b)	obs.	*124.71*	*127.83*	*129.90*			135.50
	calc. (A)	126.33 (+1.62)	127.99 (−0.04)	130.99 (+1.09)			135.27 (−0.23)
	calc. (B)	125.58 (+0.87)	127.04 (−0.79)	130.24 (+0.34)			135.87 (+0.37)
	calc. (C)	126.40 (+1.69)	127.00 (−0.83)	130.69 (+0.79)			136.69 (+1.19)
(9b)	obs.	*128.52*					
	calc. (A)	129.20 (+0.68)					
	calc. (B)	128.45 (−0.07)					
	calc. (C)	129.12 (+0.60)					
Benzene	obs.	128.50					

[a–e] As Table 1.

Table 3. ^{13}C Substituent chemical shifts (SCS) and correction parameters (Z) for chloro- and bromo-benzenes[a]

X		*ipso*	*ortho*	*meta*	*para*
Cl	SCS	+5.80	+0.11	+1.19	−2.11
	Z		−1.90	+0.65	+0.11
Br	SCS	−6.07	+2.87	+1.41	−1.79
	Z		−0.75	+0.60	+0.11

[a] For definition see text.

Table 4. Average deviation from the observed chemical shifts (p.p.m.)*

	Cl	Br
Method A	1.62	0.76
Method B	0.66	0.58
Method C	0.86	0.89

* $(\Sigma|\delta(\text{calc.}) - \delta(\text{obs.})|)/18$: the results for (**4**) are excluded.

the nearest CCl–CCl pair is taken into account while in method C the effect of the CCl–CCl pairs is corrected. Thus, three methods are exemplified for calculating the δ value of C-1 of (**3a**). Z_o corresponds to the correction for C(1)Cl–C(2)Cl. In

$$\text{method A: } \delta(\text{calc.})\ (\text{A}) = 128.50 + \Sigma\text{SCS} = 135.60 \tag{1}$$

$$\text{method B: } \delta(\text{calc.})\ (\text{B}) = 135.60 + Z_o = 133.70 \tag{2}$$

method C, the effect of another pair, C(2)Cl–C(3)Cl, is also corrected, for which Z_m is required. Hence, we have equation (3).

$$\text{method C: } \delta(\text{calc.})\ (\text{C}) = 135.60 + Z_o + Z_m = 134.35 \tag{3}$$

To generalize the methodology, the three methods are summarized in equations (4)—(6). In the third row for (**3a**)—(**9a**)

$$\text{method A: } \delta(\text{calc.})\ (\text{A}) = 128.50 + \Sigma\text{SCS} \tag{4}$$

$$\text{method B: } \delta(\text{calc.})\ (\text{B}) = 128.50 + \Sigma\text{SCS} + \Sigma(\text{nearest}) \tag{5}$$

$$\text{method C: } \delta(\text{calc.})\ (\text{C}) = 128.50 + \Sigma\text{SCS} + \Sigma Z \tag{6}$$

in Table 1, calculated chemical shifts by method B are listed. Evidently, the improvement is substantial and the differences are in most cases <1 p.p.m. Chemical shifts estimated by method C are listed in the fourth row for each compound in Table 1. By definition, method C is not applicable to (**4a**).

Initially we expected that method C would give the best predicted values. This is the case for (**3a**)—(**5a**), but not for (**6a**) and (**8a**). The average deviations (the absolute values) from the observed values for each method are tabulated in Table 4. The result seems to indicate that the magnitude of the buttress effect is not necessarily proportional to the number of chlorine atoms occupying successive positions of the benzene ring, and multiple use of Z values will finally result in an excessive correction for the steric effect.

Bromobenzenes.—In Table 2, the results obtained for bromobenzenes (**1b**)—(**9b**) by procedures similar to those described in the previous section are also listed. Compared with those for (**2a**), the difference Z_o obtained from (**2b**) is much smaller though Z_m and Z_p are much the same for the two series. Consequently, estimation of chemical shifts for (**3b**)—(**9b**) by method A gave values close to the observed, and the differences are in most cases below 1 p.p.m. Use of method B moderately improved the prediction particularly in cases where differences with method A are large [*e.g.*, C-1 of (**6b**)—(**9b**)]. As in the case with chlorobenzenes, use of method C gave in general poorer predicted values.

In conclusion it is likely that the buttress effect on ^{13}C chemical shifts of polychloro- or polybromo-benzenes is not proportional to the number of halogen atoms occupying successive positions of the benzene ring, and that method B is the most convenient method of predicting chemical shifts of (**3**)—(**9**).

Acknowledgements

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