Carbon-13 NMR Spectra of Polybromoalkanes and Polychlorobromoalkanes. Structural Increments of Halogens in Polyhalogenated Groups

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The ¹³C NMR spectra of 48 polychlorobromoalkanes have been studied. Unlike the ¹³C signals of chlorine-containing groups (38-105 ppm), those of bromine-containing fragments, with the exception of CBr₂ (60-70 ppm), appear in a rather narrow range (25-50 ppm) and are shifted to higher field in relation to similar chlorine-containing groups. The spin-spin coupling constants in similar bromine- and chlorinecontaining groups practically coincide. Calculation of the chemical shifts for the polyhaloalkanes under study according to the additivity scheme, as previously observed for polychloroalkanes, renders values which are in considerable discord with experimental values (up to -32 ppm for CBr₃). These discrepancies may be compensated for by corrections for the binary interaction of halogen atoms by grouping the halogencontaining fragments according to the geminal, vicinal, 1,3-, 1,3,5- and 1,2,3-arrangement of halogen atoms, and by introducing an increment for the position of the halogen at the secondary atom. It is established that as compared to 1-monohaloalkanes: (a) in the case of the geminal arrangement of halogen atoms the α - and γ -effects diminish ($\Delta \alpha$ from -3.2 to -8 ppm; $\Delta \gamma$ =2.6 ppm), while the β -effect increases slightly (from 0 to 1.2 ppm); (b) in the case of a vicinal arrangement both the α - and β -effects diminish (by about -3.5 ppm) and the γ -effect remains constant, as if the vicinal system of the halogens was topologically insulated; (c) for the 1,3- and 1,3,5-arrangement of halogens their mutual influence is weak (about -0.5 ppm for each halogen atom in the α - and γ -positions); (d) the 1,2,3 system (serial arrangement of halogen atoms) is the sum of two vicinal fragments and hardly deviates from the additivity scheme; (e) the arrangement of a halogen at the secondary C atom enhances the α -effect ($\Delta \alpha$ =2.8 and 1.0 for methyl and methylene, respectively, in the case of Cl, and 3.5 and 3.7 ppm in the case of Br); the variation of the β -effect has a different sign in relation to CH₃ and CH₂ groups (+1.2 and -1.7 for Cl, and +2.5 and -1.0 for Br). More distant effects of halogens (δ and ε) were not considered. The determined increments ($\Delta \alpha$, $\Delta \beta$ and $\Delta \gamma$) for the α -, β - and γ -effects of chlorine and bromine atoms allow the prediction of the ¹³C chemical shifts in polyhaloalkanes with an accuracy up to ± 1.5 ppm. Some deviations of up to ± 5 ppm may be connected with the influence of a three particle interaction of halogen atoms, which was taken into account only in the case of a geminal arrangement of halogen atoms.

INTRODUCTION

The application of ¹³C NMR is becoming increasingly popular in organic chemistry, and in recent years the nature of the influence of heteroatomic substituents on the shielding of carbon nuclei has been investigated in numerous studies.^{1,2} The complexity of this effect, depending on various electronic and conformational changes in the molecule, has already been described³⁻⁵ and the accumulation and systematization of experimental data on the ¹³C NMR of compounds with heteroatomic substituents is of considerable interest.

The aim of the present study was to establish, from data on 48 polybromoalkanes and polybromochloroalkanes, the specific features of the ¹³C NMR spectra of bromine- and chlorine-containing fragments in an aliphatic chain and the comparison of the bromo moieties with similar chloro groups, the ¹³C NMR

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spectral parameters of which have been published previously.^{6,7} The presence of several heteroatomic substituents in a molecule is known to reduce considerably the predictive possibilities of theoretical and empirical additivity schemes of ¹³C chemical shifts.⁶⁻¹⁰

Additivity schemes for calculating the ¹³C chemical shifts operate with such concepts as α -, β -, γ -, δ - and ε -effects of the substituents.^{3,11,12} The α -effect of a halogen atom correlates approximately with the electronegativity of the atom. The difference in α -effects between halogens (31.2 for chlorine and 20.0 for bromine) is usually associated with the polarizability of C—Hal bonds and is frequently decisive in assignment of the signal when choosing between the C—Cl and C—Br fragments. The difference for β -and γ -effects of chlorine and bromine is considerably less. More distant influences (δ and ε) are small in absolute value and their contributions are comparable with the error in calculation.

The influence of α , β , γ and more distant effects is usually studied on alicyclic compounds with fixed

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		¹³ C chemical shifts								
		Molecular	(ppm from TMS)			• •	'J(CH) (Hz)			
Number	Compounds	formula	C-1	C-2	C-3	C-1	C-2	C-3		
1	CHCl ₂ CHClCH ₂ Br	C₃H₄BrCl₃	72.5	64.5	31.8	181	159	157		
2	CCl ₃ CH ₂ CH ₂ Br	C₃H₄BrCl₃	97.5	58.4	24.8	_	138	154		
3	CHCl ₂ CHBrCH ₂ Br	C₃H₄Br₂Cl₂	72.3	56.4	32.3	179	157	157		
4	CHBrCICH ₂ CHBrCl	C₃H₄Br₂Cl₂	55.2	56.5	55.2	175	139	175		
5	CBrCl ₂ CH ₂ CH ₂ Br	C₃H₄Br₂Cl₂	78.7	58.1	25.6	—	138	154		
6	CHBr ₂ CH ₂ CHBrCl	C₃H₄Br₃Cl	39.4	57.0	56.2	185	137	181		
7	CHBr ₂ CHBrCH ₂ Br	C₃H₄Br₄	45.9	57.4	34.2	179	159	157		
8	CBr ₃ CH ₂ CH ₂ Br	C₃H₄Br₄	36.6	61.0	27.1		136	154		
9	CH ₂ CICHBrCH ₂ CI	C₃H₅BrCl₂	44.8	48.2	44.8	153	156	153		
10	CHCl ₂ CH ₂ CH ₂ Br	C₃H₅BrCl₂	71.2	45.6	27.8	183	132	153		
11	CH ₂ BrCHBrCH ₂ Cl	C₃H₅Br₂Ci	33.4	48.6	46.4	154	154	156		
12	CHBrCICH ₂ CH ₂ Br	C₃H₅Br₂Cl	58.0	45.9	28.8	179	136	154		
13	CHBr ₂ CH ₂ CH ₂ CI	C₃H₅Br₂Cl	42.0	47.1	41.2	180	134	153		
14	CH ₂ BrCHBrCH ₂ Br	C₃H₅Br₃	35.4	48.9	35.4	155	154	155		
15	CH ₂ BrCBr ₂ CH ₃	C₃H₅Br₃	46.7	60.1	38.8	154	—	132		
16	CHBr ₂ CH ₂ CH ₂ Br	C₃H₅Br₃	43.2	46.9	29.9	175	135	155		
17	CHBr ₂ CHBrCH ₃	C₃H₅Br₃	49.1	51.0	23.7	182	154	134		
18	CH ₂ BrCH ₂ CH ₂ Br	C₃H ₆ Br₂	30.5	34.9	30.5	150	129	150		
19	CH ₂ BrCHBrCH ₃	C₃H ₆ Br₂	37.7	45.7	24.4	159	153	128		
20	CH ₃ CBr ₂ CH ₃	C₃H₀Br₂	43.2	60.2	43.2	133		133		
21	CH ₃ CCl ₂ CH ₃	C₃H ₆ Cl₂	39.2	85.9	39.2	132	_	132		
22	CH ₃ CHBrCH ₃	C ₃ H ₇ Br	28.6	44.5	28.6	132	166	132		

 Table 1. Parameters of the ¹³C NMR spectra of polychlorobromopropanes, polybromopropanes, 2,2-dichloropropane and 2-bromopropane

geometry.¹³⁻²⁰ At present, it is still impossible to determine precisely the nature of each effect. Thus, α and β -effects are mainly attributed to the inductive, steric and anisotropic influence of substituents,^{13,15,17} and predominant in the γ -effect are the steric^{19,20} and polar^{4,17,21,22} factors, the latter especially noticeable in the case of substituents with a free electron pair.^{18,23}

Very bulky and easily polarizable halogen atoms (chlorine and bromine) may provide an interesting pattern of α -, β - and γ -effects under the conditions of the mutual influence of halogen-containing groups in an aliphatic molecule. It should be noted that as early as 1970 Lippmaa *et al.* observed variability in the increments of the additivity scheme for single chlorine and bromine atoms, depending on their position in the aliphatic chain and on the configuration of the molecule.^{24,25} The same phenomenon was later reported in the ¹³C NMR spectra of isomeric tetra-chloroheptanes²⁶ and polychloro polymers;^{27,28} in these studies attempts were made to provide corrections for the known increments.

Data presented in Tables 1–4, in our opinion, make it possible to consider the specific features of ¹³C spectra of compounds containing chlorine and bromine in various combinations and also to refine the additivity scheme, in our case, by introducing structural increments for halogens which take into account the position of the halogen in the chain and the mutual influence of various fragments containing halogens.

EXPERIMENTAL

Compounds

The compounds listed in Tables 1–4 were synthesized by known methods: **3**, **7**, **11**, **14**, **15**, **17** and **19** by addition of bromine to the α -double bond, in CCl₄ or CH₃COOH solutions;^{29a} **2**, **4**, **5**, **6**, **8**, **12**, **13**, **16**, **24**, **25**, **28**, **29**, **30**, **32–35**, **37**, **39**, **41**, **42**,^{29b–g} **27**^{29h} and **40**²⁹ⁱ by homolytic addition and telomerization of bromo and bromochloro polyhaloalkanes and α olefines in the presence of peroxide or coordinating initiators; **10**, **31**, **36** and **43–47** by replacement of chlorine by bromine,^{29j,k} compound **1** by radical addition of HBr to the terminal double bond²⁹¹ and compounds **20**, **21** and **48** by interaction of the appropriate ketone with PCl₅ or PCl₃Br₂.

Table 2. Parameters of the ¹³C NMR spectra of polychlorobromobutanes and 1,1-dibromobutane

		Molecular	¹ J(CH) (Hz)							
Number	Compounds	formula	C-1	C-2	C-3	C-4	C-1	C-2	C-3	C-4
23°	CHCl ₂ CCl(CH ₃)CH ₂ Br	C₄H ₆ BrCl ₃	77.2	71.8	25.1	39.6	181	_	132	159
24	CHBr ₂ CH ₂ CHCICH ₂ CI	C ₄ H ₆ Br ₂ Cl ₂	40.2	50.1	58.0	46.7	178	135	153	154
25	CHBr ₂ CH ₂ CHBrCH ₂ CI	C₄H ₆ Br ₃ Cl	42.4	50.2	49.8	47.1	179	130	159	154
26	CHBr ₂ CH ₂ CH ₂ CH ₃	C ₄ H ₈ Br ₂	45.4	47.3	21.4	12.8	176	128	126	126

^a C-3 = CH₃.

		Molecular	Molecular ¹³ C chemical shifts (ppm from TMS)							¹ J(CH) (Hz)			
Number	Compounds	formula	C-1	C-2	C-3	C-4	C-5	C-1	C-2	C-3	C-4	C-5	
27	CCl ₃ CH ₂ CHBrCH ₂ CCl ₃	C₅H₅BrCl ₆	98.0	62.8	40.5	62.8	98.0	_	141	153	141		
28	CHBrCICH2CHBrCH2CHBrCI	C ₅ H ₇ Br ₃ Cl ₂	57.7	51.4	48.8	51.4	57.7						
			56.3	52.0	49.0	52.0	56.3	188	135	153	135	188	
			56.3	51.4	48.5	51.4	56.3						
29	CHBr ₂ CH ₂ CHClCH ₂ CHBrCl	C₅H ₇ Br₃Cl₂	40.5	51.8	57.5	51.3	55.2	176	125	151	125	176	
					57.9	50.8	56.6	170	135	101 130		170	
30	CHCl ₂ CH ₂ CHClCH ₂ CH ₂ Br	C₅H ₈ BrCl₃	70.0	51.1	57.1	41.2	29.3	-	—		-	—	
31	CCI ₃ CH ₂ CH ₂ CH ₂ CH ₂ Br	C₅H ₈ BrCl ₃	99.6	53.2	25.1	31.3	33.2	—	128	126	129	150	
32	CH ₂ BrCH ₂ CCl ₂ CH ₂ CH ₂ Br	C₅H ₈ Br₂Cl₂	24.6	50.7	90.8	50.7	24.6	147	132		132	147	
33	CHBrCICH ₂ CHCICH ₂ CH ₂ Br	$C_5H_8Br_2Cl_2$	57. 3	51.7	57.7	40.2	20.0	181	135	153	101	150	
			55. 8	52.1	58.1	40.3	20.0	181	135	154	131	153	
34	CHBrClCH ₂ CHBrCH ₂ CH ₂ Br	C₅H ₈ Br₃Cl	58.4	52.4	50.7	40.0	20.7	178	132	159	100	154	
			57.0	52.0	50.3	40.0	29.7	176	129	154	130	154	
35	CH ₂ BrCH ₂ CBr ₂ CH ₂ CH ₂ Br	C₅H ₈ Br₄	26.7	53.2	68.4	53.2	26.7	153	135	—	135	153	
36	CHCl ₂ CH ₂ CH ₂ CH ₂ CH ₂ Br	C₅H₀BrCl₂	73.4	42.5	24.6	31.6	33.2	182	136	127	132	153	
37	CHBr ₂ CH ₂ CH ₂ CH ₂ CH ₂ Br	C₅H ₉ Br₃	44.9	44.3	26.7	31.2	32.6	176	129	124	128	149	
38	CH ₂ BrCH ₂ CH ₂ CH ₂ CH ₂ Br	$C_5H_{10}Br_2$	33.3	31.9	26.8	31.9	33.3	150	128	127	128	150	

Table 3. Parameters of the ¹³C NMR spectra of polychlorobromopentanes and polybromopentanes

Table 4. Parameters of the ¹³C NMR spectra of polychlorobromo-hexanes and -heptanes and polybromoheptanes

		al shift	shifts (ppm from TMS)						¹ J(CH) (Hz)							
Number	Compounds	formula	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-1	C-2	C-3	C-4	C-5	C-6	C-7
39	CH ₃ CCl ₂ CH ₂ CH ₂ CH ₂ CH ₂ Br	C ₆ H ₁₁ BrCl ₂	37.0	9 0.0	48.3	24.0	31.6	32.7		131		128	127	126	151	
40	CCI ₃ CH ₂ CHBrCH ₂ CH ₂ CH ₂ CHCl ₂	C ₇ H₁₀BrCl₅	96.9	62.3	47.7	37.8	23.5	42.3	72.7		135	159	132	129	136	175
41	CHBr ₂ CH ₂ CHClCH ₂ CHClCH ₂ CHBrCl	C ₇ H ₁₀ Br ₃ Cl ₃	40.8	52.9	57.4	45.5	56.8	52.5	55.6	181	135	160	135	160	135	185
							56.4	50.0	57.0					153		190
42 *	CHBr ₂ CH ₂ CH(CH ₂ CI)CH ₂ CHBrCH ₂ CI	$C_7H_{11}Br_3Cl_2$	42.3	45.2	37.5	48.2	36.2	49.6	47.3	175	132	131	155	130	153	155
				45.9	36.9		38.2									
43	CCl ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ Br	C ₇ H ₁₂ BrCl ₃	99.8	54.7	26.0	27.2	32.2	32.2	33.1		129	128	126	124	128	153
44	CHCl ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ Br	C ₇ H ₁₃ BrCl₂	73.4	43.3	25.6	27.7	27.7	34.2	33.2	176	136	127	128	123	133	152
45	CBrCl ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	C ₇ H ₁₃ BrCl ₂	82.4	56.9	27.1	27.9	31.4	22.4	13.9	_		_		_	_	
46	CBr ₂ CICH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	C ₇ H₁₃Br₂Cl	63.3	58.4	27.7	28.2	31.3	22.3	14.0		135	126	127	121	126	126
47	CBr ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	C ₇ H₁₃Br₃	41.6	61.6	27.1	28.9	30.1	21.9	13.5		131	126	126	125	124	125
48	CH ₃ CH ₂ CH ₂ CBr ₂ CH ₂ CH ₂ CH ₃	C ₇ H ₁₄ Br₂	13.3	21.0	52.8	77.2	52.8	21.0	13.3	125	125	126		126	125	125

 $^{\circ}$ C-4 = CH₂CI.

NMR procedure

The natural abundance ¹³C NMR spectra were obtained on a Bruker HX-90 spectrometer (21 KGauss) operating in the pulsed FT mode at 22.635 MHz for both single and double resonance runs (with broad band proton decoupling at 90 MHz). All spectra were measured for 80% (by volume) mixtures of the neat compound with 20% CHCl₃ as internal reference $(\delta CHCl_3 = 77.17 \text{ ppm})$ at 30 °C. The mixtures were placed in coaxial sample inserts for a 10 mm diameter tube, containing D_2O . A pulse width of 15 μ s (~26°) was used and approximately 1000 scans were accumulated with 8K data points and a 6024.1 Hz spectral width. An exponential line broadening of 0.47 Hz was applied before the FT procedure. The standard measurement error was 0.1 ppm for the chemical shifts and 1 Hz for the coupling constants. The arrangement of compounds in Tables 1-4 corresponds to that in the Chemical Abstracts Formula Index.

RESULTS

Practically no data are available in the literature on the ¹³C NMR spectra of long-chain polybromo and chlorobromo aliphatic compounds. Spectral data on bromo aliphatic compounds mainly concern halomethanes^{3,11} and ethanes.³⁰ Several papers have been published on monobromo derivatives (with the halogen situated at the primary and secondary carbon atom)^{3,24,31} and α,ω -dibromoalkanes.³ Recently, a paper has appeared describing the ¹³C NMR spectra of chlorobromo aliphatic ketones.³²

Experimental data obtained in the present study (Tables 1–4) and literature data on ^{13}C NMR chemical shifts of chlorine- and bromine-containing groups in aliphatic compounds are shown in Fig. 1. As can be seen, unlike the chlorine-containing groups in which accumulation of geminal chlorine atoms shifts the signal of the corresponding C atom to low field (from a



Figure 1. ¹³C chemical shifts of bromine- and chlorinecontaining groups (data on halomethanes are not included). [Solid areas: X = Br, our data; open areas: X = Br, literature data (Ref. 24); hatched areas: X = CI, Refs 6 and 7. (a) In polybromoethanes; (b) in α -haloketones (Ref. 32).]

¹³C chemical shift of 38 ppm for CH_2Cl to 105 ppm for CCl_3), the signals of bromine-containing groups fall in a rather narrow spectral range from 25 to 50 ppm (apart from the exceptions discussed below).

Thus, the signals of CBr₃ found by us lie in the region from 36.6 to 41.6 ppm; those of CHBr₂ from 39.4 to 50.2; of CH₂Br from 24.6 to 39.6 and those of CHBr from 40.5 to 57.4 ppm, depending on the environment. Exceptions to this rule are the CBr₂ group (60.2–77.2 ppm) and the low field signals of carbon atoms which, in addition to bromine, carry other electronegative substituents, e.g. the CO group (α bromine containing ketones, $\delta^{13}C = 60-70$ ppm) or a chlorine atom (CClBr₂ and CCl₂Br groups, 60-80 ppm, Tables 1 and 4). It can also be seen that for similar groups the signals of bromine-containing groups are situated at higher field than those of chlorine-containing groups. Consideration of signal multiplicity, together with the ${}^{1}J(CH)$ coupling constants, usually allows an unambiguous assignment to be made for both bromine- and chlorine-containing fragments.

DISCUSSION

The polybromoalkanes and chlorobromoalkanes studied in this work and the chloro-,³ bromo-^{24,31} and polychloro-^{6,7,33} alkanes studied previously can be classified according to the type of halogen-containing group. The influences on the ¹³C chemical shifts of halogen atoms which are typical of geminal, vicinal, 1,3-, 1,3,5- and 1,2,3-arrangements of halogens will be considered here. A halogen substituted at a secon-

dary C atom is considered as a separate feature. Such an approach allows the deviation from additivity of ¹³C chemical shifts to be followed on the accumulation of halogen atoms in the molecule, and the determination of additional increments to the generally accepted additivity scheme³ by comparing the chemical shifts in the halogen-containing compound and the appropriate saturated hydrocarbon.^{3,34} Effects more distant than γ - were not taken into account since their values do not exceed 1–1.5 ppm per halogen atom, and α -, β -, γ - and other increments of the additivity schemes reported in the literature vary by approximately the same figure, while increments with opposite signs are reported for the δ -effect.^{3,12}

The di- and trihalomethyl group

The effect on the ¹³C chemical shift of an increasing number of halogens (Cl and Br) in the methyl group of the corresponding alkane is shown in Figs 2–4. Increments of the additivity scheme³ used in all our calculations are listed in the footnote to Table 5. Evidently, interaction of geminal halogen atoms occurs in the polyhalomethyl group, as a result of which the shielding of C- α is higher than when assuming additivity, i.e. $\delta_{exp} < \delta_{calc}$. Previously, deviations from the additivity



Figure 2. Dependence of the α -effect of halogen atoms ($\Delta\delta C - \alpha$) on their total electronegativity (PE); curves I–IV, for various numbers of halogen atoms at C- α : curve (a) in the trihalomethyl group; curve (b) see text. $\Delta\delta(C - \alpha) = \delta({}^{13}CH_nHal_{3-n}) - \delta({}^{13}CH_3)$ ppm.



Figure 3. Dependence of the β -effect of halogen atoms ($\Delta\delta C$ - β) on their total electronegativity (PE); curves I–IV, for various numbers of halogen atoms at C- β : curve (a) in the trihalomethyl group; curve (b) see text. $\Delta\delta(C$ - β) = $\delta(CH_nHal_{3-n}^{-13}CH_2) - \delta(CH_3^{-13}CH_2)$ ppm.



Figure 4. Dependence of the γ -effect of halogen atoms ($\Delta\delta C$ - γ) on their total electronegativity (PE); curves I–IV, for various numbers of halogen atoms at C- γ : curve (a) in the trihalomethyl group; curve (b) see text. $\Delta\delta(C-\gamma) = \delta(CH_{n}Ha_{3-n}(CH_{2}^{-13}CH_{2})-\delta(CH_{3}CH_{2}^{-13}CH_{2})$ ppm.

of chemical shifts were demonstrated for polyhalomethanes^{35,36} and it was proposed to introduce into the additivity scheme terms corresponding to binary³⁵ and triple³⁶ interactions of nonbonded halogen atoms.

Upon replacement of Br by Cl in the trihalomethyl group the α -effect increases linearly with the overall

electronegativity (PE) of the halogen atoms [Fig. 2, curve (a)]. [PE, Pauling³⁷ electronegativity; PE(Cl) =3.0, PE(Br) = 2.8.] In the case of hydrogen substitution by a halogen the α -effect depends non-linearly on PE. Although the overall α -effect increases when passing from mono- to dihalomethyl groups, the transition from di- to trihalomethyl groups depends on the halogen introduced: on introduction of chlorine the α -effect increases almost linearly (curve I), in the case of bromine it either increases insignificantly [on going from CHCl₂ to CCl₂Br (curve II)] or decreases [when going from CHBr₂ to CBr₃ (curve III)]. The latter is apparently connected with the negative contribution of the geminal interaction of halogen atoms, which is particularly strong in the case of the Br-Br interaction.

It is known that in aliphatic and alicyclic halo compounds the β -effect of halogen atoms increases weakly on passing from Cl to I (in accordance with increasing atomic number and size of halogen but with decreasing electronegativity).^{16,18,39} In our case, the β -effect of halogen atoms in the CHal₃ group [Fig. 3 (curve a)] depends almost linearly on their overall electronegativity and, as expected, decreases with an increase of PE upon substitution of Cl for Br. Upon replacement of hydrogen by a halogen, not only is the

Structure type causing the increments		Type of interaction	Increment designation	Incre Δα	Increments (ppm) ^b Δα Δβ		
I	CHal ₂ CHal ₃	Double	gem (Cl, Cl) gem (Cl, Br) gem (Br, Br)	-3.2 -5.3 -8.0	0 +0.2 +1.2	+2.6 +2.6 +2.6	
	(Geminal arrangement Triple (of halogen atoms)		gem (Cl, Cl, Cl) gem (Cl, Cl, Br) gem (Cl, Br, Br) gem (Br, Br, Br)	+2.4 -1.5 -4.0 -8.7	+0.3 +1.9 +2.1 +3.6	-0.4 -0.8 -1.6 -3.2	
		Contribution of CHal ₃ group as a whole	(CCl ₃) (CCl ₂ Br) (CClBr ₂) (CBr ₃)	-7.2 -15.3 -22.6 -32.7	+0.3 +2.5 +3.7 +7.2	+7.4 +7.0 +6.2 +4.6	
H	CCHHalC° CC(Hal)₂C	Secondary C atom bonded to CH ₃ .	sec (Cl, CH ₃) sec (Br, CH ₃)	+2.8 +3.5	+1.2 +2.5	+1.5 +1.3	
	(Halogen at secondary carbon atom)	Secondary C atom bonded to a CH_2 or CH group	sec (CI, CH_2 or CH) sec (Br, CH_2 or CH)	+1.0 +3.7	−1.7 −1.0	+1.5 +1.3	
111	CHalCHal-	For primary carbon atom shift	vic (Cl, C _p) vic (Br, C _p)	-2.7 -3.3	-3.2 -4.0	0 0	
	(Vicinal arrangement of halogen atoms)	For secondary carbon atom shift	vic (Cl, C _s) vic (Br, C _s)	-2.4 -4.0	-4.3 -5.6	0 0	
IV	-CHal-CH ₂ -CHal (1,3 Arrangement of halogen atoms)	1,3 Interaction	1,3 (Cl) 1,3 (Br)	-0.5 -0.5	-0.5 -0.5	-0.5 -0.5	

Table 5. Structural increments of halogens for ¹³C chemical shifts in polyhalo hydrocarbons^a

^a For monohaloalkanes:³ α (Cl) = 31.2; β (Cl) = 10.5; γ (Cl) = -4.6; α (Br) = 20.0; β (Br) = 10.6; γ (Br) = -3.1.

^b Each increment is an addition to the corresponding halogen effect (α , β or γ in the commonly accepted additivity scheme.³ It is multiplied by the number of double geminal interactions and by the number of halogen atoms of the given type, determined by the structural fragment indicated in the Table.

^c Increments of part II are additively repeated both for each halogen atom and for each CH_3 , CH_2 or CH group adjacent to the halogen-substituted carbon atom (see example in text). Increments are not used when the adjacent carbon atom has only halogen atoms and no protons.

linearity of the β -effect variation distorted (curves I–IV), but the overall β -effect increases with PE, indicating a qualitative change in the C atom shielding when one halogen is substituted for another.

The γ -effect of halogens in the halomethyl group varies non-linearly on substitution of Br by Cl and of hydrogen by a halogen (Fig. 4), which points to the complex nature of the γ -effect. Upon replacement of Br by Cl in the CHal₃ group the γ -effect decreases in absolute value from CBr₃ to CClBr₂, and then increases practically linearly with PE [(Fig. 4 (curve a)]. Upon replacement of hydrogen by a halogen in the dibromomethyl group the absolute value of the overall γ -effect grows (curves III, IV) and falls in the case of the dichloromethyl group (curves I and II).

The complex dependence of the ¹³C chemical shifts on the α -, β - and γ -effects of halogen atoms in the polyhalomethyl group can be described by Eqn (1), which is similar to that proposed in Ref. 36 for polyhalomethanes:

$$\delta(\mathbf{C}) = \delta_{\mathbf{H}} + \sum_{i} p_{i}a_{i} + \sum_{i,j} p_{i,j}\Delta_{ij} + \sum_{i,j,k} p_{ijk}\Delta_{ijk} \qquad (1)$$

where $\delta_{\rm H}$ is the chemical shift of the given carbon atom in the corresponding *n*-alkane (in the absence of experimental data it may be calculated from the known additivity schemes^{3,12}); *i* is a halogen (bromine or chlorine); *p_i* the number of halogen atoms of a given type (Cl, Br); *a_i*, their α -, β - or γ -effects; *p_{ij}* and *p_{ijk}*, the number of possible double and triple interactions; Δ_{ij} and Δ_{ijk} , corrections for double and triple geminal interactions, respectively. In the absence of a trihalomethyl group in the molecule the third sum is reduced to zero.

Using both our own and the literature data and plots 2–4, we determined the structural increments to the chemical shifts of α -, β - and γ -C-atoms for double and triple geminal interactions of halogens, including the CHClBr group which is absent from the experimental data [Table 5 (part I) and Figs 2–4 (curves b)].

From the plots of $\alpha(PE)$, $\beta(PE)$ and $\gamma(PE)$ at PE(Cl, Br) = 5.8 we found corresponding increments for the geminal double Cl-Br interaction which are practically equal to half the sum of the increments of the influence of the homogeneous pairs (Cl--Cl and Br-Br). This observation allows the prediction of the value of the double heterogeneous geminal interactions of halogens when increments for homogeneous geminal pairs are known. As can be seen from Table 5 (part I), all double corrections decrease the absolute values of positive α - and negative γ -effects and slightly increase the positive β -effect. The nature of the pair affects the $\Delta \alpha_{ii}$ increments most, and does not affect the $\Delta \gamma_{ij}$ increments at all. This may be associated with the fact that $\Delta \alpha_{ii}$ and, to some extent, $\Delta\beta_{ii}$ reflect the differences between halogen pairs (Cl-Cl, Cl-Br and Br-Br), whereas $\Delta \gamma_{ii}$ characterizes their common properties. It is noteworthy that triple geminal corrections, $\Delta \alpha_{iik}$ and $\Delta \beta_{iik}$, have the same sign as the double corrections (with the exception of $\Delta \alpha_{\text{CICICI}}$), while $\Delta \gamma_{ijk}$ and $\Delta \gamma_{ij}$ have opposite signs, and the former decreases from $\Delta \gamma_{\text{CICICI}}$ to $\Delta \gamma_{BrBrBr}$ according to the $-0.4 \cdot 2^n$ law, (where *n* is the number of bromine atoms in the triplet of interacting geminal halogens), which is reflected in the non-linearity of curve (a) in Fig. 4.

For practical calculations of ¹³C chemical shifts in the chlorobromo compounds, it is more convenient to use increments for the trihalomethyl group as a whole, and these are listed at the end of part I of Table 5 and are obtained from the last two summation terms of Eqn (1).

Halogen at the secondary carbon atom (the $\overset{1}{C}$ -- $\overset{2}{C}$ Hal-- $\overset{3}{C}$ - system)

The different reactivity of halogen atoms (chlorine and bromine) in 1-, 2- and the more remote positions in the carbon chain is well known. Thus, in $S_N 2$ reactions which are most typical of the influence of spatial and polar factors on the reaction site⁴⁰ (e.g. in the Finkelstein reaction; halogen exchange RHal+Hal^{*-} \rightarrow RHal^{*} + Hal⁻), the relative rate of chlorine replacement by iodine (KI in acetone, 50 °C) is higher for the halogen at the primary C-atom than that at the secondary C-atom, and remains practically constant for the various secondary C-atoms within the carbon chain.^{41,42}

Since ¹³C chemical shifts also depend on polar and spatial factors, it would be expected that the ¹³C increments for halogen atoms in the CH₂X, CH₃CHXCH₂- and $-CH_2CHXCH_2-$ (X = Cl, Br) groups should reflect the halogen position in the carbon chain.

Both literature data²⁴ and our observations indicate that additivity increments for a halogen at a secondary carbon atom differ from the increments at a primary carbon atom. Thus, for the α -effect of bromine at primary and secondary C atoms Lippmaa et al.24 give values of 19.9 and 24.7 ppm, respectively. In our case, deviations from additivity are especially noticeable for compounds with the CH_3CHX -group 17 and 22. On the basis of the analysis of the ¹³C NMR spectra of 12 compounds with one or two halogen atoms at the secondary C-atom, we determined the α -, β - and γ -structural increments (Δ_{sec}) introduced by the halogen at the secondary C-atom into the chemical shift of this and neighbouring carbon atoms. The following compounds were used: 20 and 22 (Table 1); **39** and **48** (Table 4); $(CH_3)_2CHCl$ and $CH_3CCl_2C_2$ - H_5 ;⁷ CH₃CHXC₆ $H_{13} - n$, C₂ H_5 CHXC₅ $H_{11} - n$ (X = Cl, Br) and $C_3H_7CHClC_4H_9 - n.^{24}$

$$\alpha_{sec} = \alpha_{add} + \Delta \alpha_{sec}$$

$$\beta_{sec} = \beta_{add} + \Delta \beta_{sec}$$

$$\gamma_{sec} = \gamma_{add} + \Delta \gamma_{sec}$$
(2)

Here α_{add} , β_{add} and γ_{add} are increments of the end halogen atom used in the additive schemes and Δ_{sec} are the structural increments for the halogen at the secondary carbon.

It was found that the α -effect of halogen at the secondary C-atom increases and depends markedly on the position of the halogen-bearing carbon in the chain. In the case of chlorine, the highest α -effect is

observed for a halogen-bearing carbon with two methyl groups, i.e. in 2-chloropropane³ and 2,2dichloropropane (21), and decreases upon replacement of the methyl group by an alkyl chain. Substitution of propyl for ethyl, on the other hand, does not affect the α -effect, as was shown for mono-halooctanes.²⁴ For bromine the pattern is rather different: substitution of an alkyl chain for a methyl group has almost no influence on the α -effect, while data on the CBr₂ group suggest that substitution of an alkyl chain for a methyl group somewhat increases the α -effect, as opposed to the case of chlorine. The average values of the structural increments of halogen at a secondary C-atom are listed in Table 5 (part II), where each halogen atom and the type of group on either side are taken into account additively. However, if the adjacent carbon atoms (C-1 and C-3) do not carry protons (only halogens), the chemical shift of the halogen-bearing carbon atom under consideration (C-2) does not incorporate $\Delta \alpha_{sec}$, and $\Delta \beta_{sec}$ is not taken into account in calculations of the chemical shifts of C-1 and C-3 (the contribution of C-2), i.e. $\Delta \alpha, \beta = 0$ in these cases.

The β -effect of the halogen atom at a secondary C atom exceeds the value for the halogen in the CH₂Hal group (10.5 ppm for Cl and 10.6 ppm for Br) only in the CH₃CHX fragment, i.e. in relation to the methyl group. In the -CH₂CHXCH₂- group the β -effect of the halogen on the adjacent C-atom decreases, and further lengthening of the chain has practically no influence on the β -effect.

The γ -effect of a halogen at a secondary carbon atom is weaker than at a primary carbon. Two specific features should be noted. First, the structural increments for bromine and chlorine nearly coincide, as in the case of geminally arranged halogens (see above). Second, similarly to α - and β -effects, this does not change upon substitution of a longer alkyl chain for an ethyl group.

The vicinal arrangement of halogens

The vicinal arrangement of halogens is characterized by mutual deactivation of halogens in the reactions of electrophilic substitution and dehydrohalogenation.⁴⁰ This allows the singling out of vicinality as a characteristic topological property of halogens and the introduction of an increment for the vicinal arrangement of halogens into the additivity scheme of ¹³C NMR chemical shifts. Keller and co-workers²⁷ made an attempt to take into account the effect of the vicinal arrangement of chlorine atoms on the chemical shifts of carbon nuclei of the vicinal system in a polymer chain. It was found that in the case of a vicinal arrangement of chlorine atoms, the chemical shift of the chlorine-bearing C-atom decreases by 7 ppm as compared with the value predicted by the additivity scheme.²⁸

In the present work we investigated vicinal systems containing chlorine and bromine atoms in eight compounds. The following compounds were used: **15**, **17** and **19** (Table 1); $CH_2ClCCl_2CH_3$;⁷ $CCl_3CCl_2(CH_2)_2$ -CH₂Cl and $CCl_3CHCl(CH_2)_2CH_2Cl$;⁶ $CH_2ClCHCl$ -

(CH₂)₃CHCl₂ (VIII) and CH₂ClCHCl(CH₂)₄CHCl₂ (VII).²⁶ Both carbon atoms C-1 and C-2 bearing a halogen were found to be more shielded than expected from the additivity scheme. This phenomenon is similar to the excessive shielding of the C-2 atom in the end polyhalomethyl group; however, in the case of vicinal halogens the α - and β -effects for each halogen bearing a C-atom are apparently mixed due to the interaction of the electron pairs of vicinal halogen atoms. Consideration of the structural increments obtained above allows the derivation of a systematic component of excessive shielding of the C-1 and C-2 atoms in the system -Hal(C-1)—(C-2)Hal-.

Since in a vicinal system each halogen atom simultaneously acts as an α - and a β -substituent, it is logical to give a two-parameter form to the value reflecting the contribution of vicinal interaction of halogens in order to distinguish the α - and β influences of a halogen on the chemical shift of each carbon.

The structural increments of carbon atoms in a system with vicinal halogens, obtained separately for the primary (C_p) and secondary (C_s) carbon atoms, are listed in Table 5 (part (III). Negative signs of the increment indicate that, as in the case of the geminal arrangement, vicinal interaction of halogens weakens their α - and β -effects on the halogen-bearing carbons. The value of the increment presumably depends on the halogen (chlorine or bromine) and its position (at a primary or secondary carbon atom). The chemical shifts of C-3 (the carbon atom adjacent to the vicinal system), determined according to the additivity scheme and taking into account our increments for the geminal and secondary halogens, display only small random deviations from the experimental values $(\pm 1.4 \text{ ppm})$. This means that the influence of a vicinal interaction does not exceed the bounds of the vicinal system. The considerable deviation for compound VIII²⁶ of -2.8 ppm is evidently connected with the δ -effect of chlorine atoms in the CHCl₂ group on C-3, which we did not take into account. The homologue VII²⁶ does not show such a deviation.

As an illustration we present below the calculation of the ¹³C chemical shifts in 1,2,2-tribromopropane (**15**) using all the structural increments derived above. The results (δ_n) are compared with the experimental data (δ_{exp}) , and the values obtained using the generally accepted additivity scheme (δ_{add}) .

Example 1: $\overset{1}{C}H_{2}Br - \overset{2}{C}Br_{2} - \overset{3}{C}H_{3}$ [parent alkane $CH_{3}CH_{2}CH_{3}$, $\delta(CH_{3}) = 15.6$, $\delta(CH_{2}) = 16.1$ ppm]

$$\delta_n(\mathbf{C}_i) = \delta_{\mathrm{add}}(\mathbf{C}_i) + \Delta \delta_{\mathrm{str}}(\mathbf{C}_i) \ i = 1, 2, 3$$

 $\Delta \delta_{\rm str}(C_i)$ is the pair-interaction term in Eqn (1).

(1)
$$\delta_{add}(C-1) = \delta(CH_3) + \alpha(Br) + 2\beta(Br)$$

= 15.6 + 20.0 + 2 × 10.6 = 56.8 ppm
 $\Delta \delta_{str}(C-1) = \Delta \beta_{gem}(Br-Br) + 2\Delta \beta_{sec}(Br, CH_2)$
+ $\Delta \alpha_{vic}(Br, C_p) + 2\Delta \beta_{vic}(Br, C_p)$
= 1.2 - 2 × 1.0 - 3.3 - 2 × 4.0
= -12.1 ppm

From the $\Delta\beta_{sec}$ increments the one related to the

Number	Compounds	No. ^b	exp.	C-1 add.	n	exp.	C-2 add.	n.	exp.
1	CHBr ₂ CH ₂ CHBrCH ₂ Cl	(25)	42.4	50.1	41.9	50.2	52.2	50.9	49.8
2	CHBr ₂ CH ₂ CHCICH ₂ Cl	(24)	40.2	48.6	40.6	50.1	52.1	50.1	58.0
3	CH2BrCCI(CH3)CHCI2	(23)	39.6	45.4	39.8	71.8	87.8	76.0	25.1
4	CCI ₃ CH ₂ CHBrCH ₂ CCI ₃	(27)	98.0	104.0	96 .1	62.8	64.1	61.4	40.5
5	CHBr ₂ CH ₂ CHCICH ₂ CHCICH ₂ CHCIBr	(41)	40.8	49.1	41.1	52.9	54.3	52.3	57.4
6	CCI ₃ CH ₂ CHBrCH ₂ CH ₂ CH ₂ CHCl ²	(40)	96.9	104.2	96.3	62.3	64.7	64.0	47.7
7	CHBr ₂ CH ₂ CH(CH ₂ CI)CH ₂ CHBrCH ₂ CI	(42)	42.3	50.9	42.9	45.2	46.1	47.3	37.5
						45.9			36.9
8	CCI3CCI2CCI3	(8) ³³	101.4	116.4	102.1	103.0	141.5	108.3	101.4
9	CCI ₃ CCI ₂ CCI ₂ CCI ₃	(12) ³³	102.9	118.6	99.5	103.5	126.1	104.3	103.5
10	CHCI ₂ CCI ₂ CH ₂ CHCICH ₃	(19) ⁷	78.1	96.9	78.5	91.8	100.8	88.2	51.9

Table 6. Calculation of ¹³C chemical shifts for polyhalohydrocarbons⁴

^a add.: Calculation according to the additivity scheme (see Ref. 3); n: calculation using the new increments (see Table 5). ^b In Tables 1–4 or references.

^c Chemical shifts in diastereomers.

CH₂ group is chosen, and it is doubled because of two bromine atoms in the β -position to C-1. Both the vicinal increments, $\Delta \alpha$ and $\Delta \beta$, are taken for a primary carbon because of the terminal CH₂Br group.

$$\delta_{n}(C-1) = 56.8 - 12.1 = 44.7 \text{ ppm}; \ \delta_{exp}(C-1) = 46.7 \text{ ppm}$$
(2) $\delta_{add}(C-2) = \delta(CH_{2}) + 2\alpha(Br) + \beta(Br)$
 $= 16.1 + 2 \times 20.0 + 10.6 = 66.7 \text{ ppm}$
 $\Delta \delta_{str}(C-2) = \Delta \alpha_{gem}(Br - Br) + 2\Delta \alpha_{sec}(Br, CH_{2})$
 $+ 2\Delta \alpha_{sec}(Br, CH_{3}) + 2\Delta \alpha_{vic}(Br, C_{s})$
 $+ \Delta \beta_{vic}(Br, C_{s})$
 $= -8.0 + 2 \times 3.7 + 2 \times 3.5 - 8.0 - 5.6$

Here the secondary C-2 atom has adjacent CH₂ and CH₃ groups, and so the increments
$$\Delta \alpha_{sec}$$
 (Br, CH₂) and $\Delta \beta_{sec}$ (Br, CH₃) are used, both doubled for two bromines at C-2. Vicinal increments $\Delta \alpha$ and $\Delta \beta$ are taken for a secondary carbon and $\Delta \alpha$ is also doubled.

= -7.2 ppm

$$\begin{split} \delta_n(C-2) &= 66.7 - 7.2 = 59.5 \text{ ppm}; \ \delta_{exp}(C-2) = 60.1 \text{ ppm} \\ (3) \quad \delta_{add}(C-3) &= \delta(CH_3) + 2\beta(Br) + \gamma(Br) \\ &= 15.6 + 2 \times 10.6 - 3.1 = 33.7 \text{ ppm} \\ \Delta \delta_{str}(C-3) &= \Delta \beta_{gem}(Br - Br) + 2\Delta \beta_{sec}(Br, CH_3) \\ &= 1.2 + 2 \times 2.5 = 6.2 \text{ ppm} \\ \delta_n(C-3) &= 33.7 + 6.2 = 39.9 \text{ ppm}; \ \delta_{exp}(C-3) \\ &= 38.8 \text{ ppm} \end{split}$$

It should be noted that geminal structural increments relate to a pair of halogens and so are used only once for each pair.

Separate considerations of the influence of a vicinal arrangement of halogen atoms on the chemical shifts of primary and secondary carbon atoms of the vicinal system make it possible to extend the obtained results to vicinal systems containing only secondary carbon atoms. In this case only the Δ_{vic} (Hal, C_{sec}) increments are used in the calculations.

If a higher accuracy than 3 ppm is not required in the ¹³C chemical shift calculations, the vicinal arrange-

ment of halogen atoms can be represented by a single value $\Delta \alpha_{vic} = \Delta \beta_{vic} = -3.5$ ppm per halogen atom. For isomers, as in the case of compounds **17** and **15**, a more detailed table of increments should be used.

1,3 and 1,3,5-Arrangement of halogen atoms

1,3 and 1,3,5-Arrangements of halogen atoms (15 and 9 compounds respectively) do not introduce significant distortions into the additivity scheme (taking into account all the previous increments). The following compounds were used for the 1,3-arrangement: 2, 4, 5, 6, 8, 10, 12, 13, 16 and 18 (Table 1); CH₂ClCH₂CH₂Cl;³ CHCl₂CH₂CHCl₂ and CH₂ClCH₂CHCl₂;⁷ CH₂-ClCH₂CCl₃;⁶ CH₂ClCH₂CH₂Br (No. 369, Ref. 45; in this case the values of the chemical shifts of carbons 2 and 3 were interchanged). The following compounds were used for the 1,3,5-arrangement: 28-30, 32, 33, 35 and 38; CH₂ClCH₂CCl₂CH₂CH₂Cl and CH₂-CICH₂CCl₂CH₂CHCl₂.⁷ All deviations of the experimental values from the calculated chemical shifts for all carbon nuclei have a negative systematic component of -0.5 ppm per halogen, caused by the 1,3environment of the given carbon atom. It is natural to take this value, which is equal for the α -, β - and γ -positions of the halogen in relation to the given C-atom, as a measure of the influence of the 1,3interaction of halogens on the ¹³C chemical shifts in the given system [Table 5 (part IV)].

Experience shows that the 1,3,5-system can be considered as a sum of two independent 1,3-systems, with the same correction.

Serial 1,2,3-arrangement of halogens

In compounds with a serial 1,2,3-arrangement of halogen atoms (ten compounds) consideration of all the structural increments introduced above gives good agreement with experiment. (The following compounds were used: 1, 3, 7, 9, 11, 14; CH₂-CICHCICH₂Cl and CH₂CICCl₂CH₂Cl;⁷ CCl₃-CHCICH₂Cl and CCl₃CHCICCl₃.⁶) This suggests that

C-3			C-4			C-5			C-6			C-7	
add.	n	exp.	add.	n	exp.	add.	n	exp.	add.	n	exp.	add.	n
49.3	49.5	47.1	55.0	47.3									
60.5	56.9	46.7	54.9	47.3									
22.3	26.1	77.2	93.9	79.3									
26.5	44.7	62.8	64.1	61.4	98.0	104.0	96.1						
52.4	55.8	45.5	50.0	45.6	56.8°	50.9	54.5	52.5°	54.2	51.2	55.6°	60.3	55.0
					56.4			50.0			57.0		
38.2	51.0	37.8	39.6	38.6	23.5	19.7	23.6	42.3	43.6	43.6	72.7	76.1	72.9
35.5	39.4	48.2	50.0	50.0	36.2	40.4	39.4	49.6	50.7	49.8	47.3	55.7	48.5
					38.2								
116.4	102.1												
126.1	104.3	102. 9	118.6	99.5									
56.4	52.4	52.9	44.0	51.9	26.6	24.0	25.2						
					· · · · ·								

a serial arrangement of halogens in polyhalo-alkanes can be considered as a sum of independent vicinal fragments with one common middle carbon atom in which 1,3-interaction of halogens is absent. Examples of chemical shift calculations for polyhalohydrocarbons not used in the derivation of the structural increments are listed in Table 6. Some significant deviations $\delta_{exp} - \delta_n$ occurring in the case of many halogen atoms in a vicinal system may be connected with the influence of vicinal triple interactions, which we did not take into account.

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