# Carbon-13 NMR Spectra of DDT, its Analogues and Related Compounds

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**Carbon-13 NMR spectra of mono- and disubstituted aromatic compounds including DDT, its analogues, homologues, derivatives and certain model compounds have been studied. The Savitsky scheme of carbon chemical shifts in disubstituted benzenes is applicable to these compounds. The data obtained show that in mono- and disubstituted aromatic compounds containing two different substituents in the α- and β-positions of the side chain, the substituted ring carbon atom shifts follow the additivity rule and can be calculated from substituent increments. Mutual effects of substituents in the ring and in the side chains are analysed. The chlorine atoms in α-position to the phenyl ring give rise to an additive α-effect of about 25 ppm, as in perchloroalkanes. The influence of a β-chlorine atom in the side chain on the substituted carbon atom in the ring is, however, only 3 ppm as against the usual value of about 10 ppm for the β-effect in alkyl chains. Moreover, the first β-chlorine substituent has no noticeable influence on the substituted ring carbon chemical shift: the effect of 3 ppm is transferred to the *para*-carbon atom almost without attenuation. The ring substituted carbon atom signal shifts caused by the γ-effect of chlorine in the side chain are similar to those observed in aliphatic chains. The *ortho*-chlorine substituents shift the side chain α-carbon atom signal by 3.6–5.2 ppm to high field compared to *para*-chlorophenyl compounds. This is similar to the chlorine γ-effect in aliphatic chains.**

## INTRODUCTION

During recent years, $^{13}$C NMR spectra of substituted benzenes have been the focus of ever increasing interest for chemists studying the relationships between molecular structure and the physical and chemical properties. The most important results obtained for monosubstituted benzenes have been summarized by Levy[1] and Stothers.[2] Much work has been done in search of correlations between aromatic carbon chemical shifts and such quantities as the Taft constants,[3] the $\sigma^+$ and $\sigma^-$ values,[4] MO charge densities[5] and substituent electronegativities[6] etc. In all these investigations, the utility of the $^{13}$C NMR method for the study of the electronic properties of aromatic compounds is emphasized.

An additive scheme has been suggested[7] for assigning ring carbon signals in *para*-disubstituted benzenes which was later extended to the *ortho*-disubstituted species.[8] The substituents studied included $CH_3$, Alk, $CH_3O$, $NO_2$, Cl and many others.[1,2,9,10]

The shifts of the side chain carbon atom signals caused by substituents in the ring are also of interest. An attempt to determine the correlation between the $\beta$-carbon atom shifts and the $\sigma^*$ constant values in $\beta,\beta$-dichlorostyrenes, $XC_6H_4CH{=}CCl_2$, where X is H, $CH_3$, Cl, CN, $NO_2$, proved a failure.[4] The authors[6] suggested a correlation scheme to calculate $\alpha$- and $\beta$-side chain carbon atom shifts in *para*- and *meta*-disubstituted benzenes.

This study deals with side chain substituent effects on the ring carbon atom shifts in monosubstituted benzenes. We have also tested the applicability of Savitsky's scheme[7] to chemical shift calculations in certain *para*- and *ortho*-disubstituted benzenes, DDT analogues and related compounds. The choice of substances to be studied was dictated by our interest in the $^{13}$C NMR spectra of DDT, its homologues, analogues and derivatives as a means of structure determination and identification, and investigation of conjugation phenomena in these compounds. Molecules containing substituents of opposite polar properties, e.g. C—OH and C—Cl, at adjacent side chain carbon atoms, show a particularly interesting spectral behaviour.

## EXPERIMENTAL

### Compounds

Compounds **14**, **22**, **23** and **33** were prepared by a technique similar to that described in Ref. 11. Compounds **8**, **13**, **26** and **27** were synthesized as recommended in Ref. 12. 1,1-Dichloro-2-phenylethane, (**8**): $n_D^{20}$ 1.5437, $d_4^{20}$ 1.2136. Found, %: C, 55.08; H, 4.63; Cl, 40.39. $C_8H_8Cl_2$. Calculated, %: C, 54.89; H, 4.61; Cl, 40.51. The syntheses of compounds **19**, **20**, **21**, **29** and **30** were described in Ref. 13. 1,1,1-Trichloro-3-phenylpropane (**16**) was made by condensation of 1,1,1,3-tetrachloropropane with benzene in the presence of $AlCl_3$, b.p. 110° (6 mm Hg), $n_D^{20}$ 1.5375, $d_4^{20}$ 1.2688. Found, % : C, 48.79; H, 4.22; Cl,

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47.01. $C_9H_9Cl_3$. Calculated, %: C, 48.36; H, 4.06; Cl, 47.89. The other compounds were commercial reagents. Their purity was checked by GLC and their structures were confirmed by proton NMR spectra.

### NMR procedure

The natural abundance $^{13}C$ NMR spectra were recorded on a Bruker HX-90 instrument (21 kGauss), operating in the FT mode with noise modulation of the 90 MHz proton decoupling frequency, for the compounds in coaxial sample inserts for 10 mm diameter tubes containing $D_2O$. A pulse width of 15 $\mu$s (*c.* ~26°) was used, and ~1000 scans were accumulated with 8 K data points/6024.1 Hz spectral width. An exponential line broadening of 0.47 Hz was applied before the Fourier transform. The operating frequency was 22.635 MHz. The temperature was maintained at 28±2 °C in both the single and double resonance runs. The standard error of the spin–spin coupling constant measurements was ±1 Hz. The samples contained 10–30% $CHCl_3$ as internal reference (77.17 ppm from TMS). Independant experiments showed that the $CHCl_3$ chemical shift value depended only slightly on the chloroform concentration in the solutions of aromatic compounds. The $\delta_{CHCl_3}$ value was found to be 77.17±0.3 ppm in 4:1 and 1:4 $C_6H_6/CHCl_3$ mixtures. The deviation of ±0.3 ppm was taken as the standard error of the chemical shift measurements.

## RESULTS AND DISCUSSION

The $^{13}C$ NMR spectra of 33 aromatic compounds were measured and the substituent effects on the ring and side chain carbon chemical shifts were studied for Cl, Ar and OH as substituents. The data obtained are summarized in Tables 1–4.

### Monosubstituted benzenes

The $^{13}C$ chemical shifts of the monosubstituted benzenes studied are listed in Table 1. For comparison, literature data on the $^{13}C$ NMR chemical shifts of some other aromatic compounds are also included.

The assignment of the *ortho*- and *meta*-carbon shifts is the major difficulty. If the difference between the $\delta_{ortho}$ and $\delta_{meta}$ values is sufficiently large, the signal closer to the benzene signal, $\delta_{C_6H_6} = 128.5$ ppm, must be the *meta*-carbon signal.[2] If, however, the two signals fall close together and are thus almost equidistant from the benzene signal (**6**, **7**, **14** etc.), the assignment can be made from the consideration of their intensities in proton-decoupled spectra: because of a larger number of protons in its vicinity, as compared with the *ortho*-carbon atom, the *meta*-carbon atom is more likely to give rise to the stronger signal due to the Overhauser effect. For the same reason, the relaxation time, $T_1$, of the carbon in the *meta*-position may be relatively smaller, which should decrease the *ortho*-signal intensity still further. The intensity patterns observed in the spectra which were assigned unambiguously (**4**, **9**) confirm these considerations. This line intensity rule is not absolute, however, and depends upon competition between the dipole–dipole and other relaxation mechanisms, which is usually the case in small molecules.

The C-1 chemical shifts vary within a 13 ppm range in the compounds studied. Other ring carbon atoms show far smaller variations depending on the side chain substituents: *ortho*-, *meta*- and *para*-carbon

**Table 1. $^{13}C$ chemical shifts in monosubstituted benzenes $C_6H_5X$**

| Compound | Substituent X | $\delta_C$ ppm from TMS | | | | $\Delta_X^i$ ppm from $C_6H_6$[a] | | | | $\delta_C$ ppm from TMS | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C-1 | o- | m- | p- | C-1 | o- | m- | p- | C-7 | C-8 | C-9 | |
| 1 | $CH_3$ | 137.8 | 129.2 | 128.7 | 125.6 | 9.3 | 0.7 | 0.2 | −2.9 | 22.0 | — | — | 9(715) |
| 2 | $CH_2Cl$ | 137.7 | 128.7 | 128.3 | 128.7 | 9.2 | 0.2 | −0.2 | 0.2 | 46.1 | — | — | 9(276) |
| 3 | $CHCl_2$ | 140.4 | 126.1 | 128.6 | 129.7 | 11.9 | −2.4 | 0.1 | 1.2 | 71.9 | — | — | 9(275) |
| 4 | $CCl_3$ | 143.9 | 125.3 | 128.1 | 130.1 | 15.4 | −3.2 | −0.4 | 1.6 | 97.9 | — | — | — |
| 5 | $CH_2OH$ | 141.0 | 127.3 | 127.3 | 127.3 | 12.5 | −1.2 | −1.2 | −1.2 | | — | — | 3 |
| 6 | $CH_2CH_3$ | 143.4 | 127.2 | 127.8 | 125.2 | 14.9 | −1.3 | −0.7 | −3.3 | 29.1 | 15.8 | — | 9(43) |
| 7 | $CH_2CH_2Cl$ | 137.7 | 128.1 | 128.4 | 126.3 | 9.2 | −0.4 | −0.1 | −2.2 | 38.6 | 44.5 | — | — |
| 8 | $CH_2CHCl_2$ | 135.1 | 127.6 | 129.7 | 128.5 | 6.6 | 1.2 | −0.9 | 0.0 | 49.6 | 73.0 | — | — |
| 9 | $CH_2CCl_3$ | 132.9 | 131.3 | 128.1 | 128.0 | 4.4 | 2.9 | −0.4 | −0.5 | 59.5 | 99.0 | — | — |
| 10 | $(C_6H_5)CHCH_3$ | 146.0 | 127.3 | 128.1 | 125.7 | 17.5 | −1.2 | −0.4 | −2.8 | 44.5 | 21.7 | — | — |
| 11 | $ClCHCH_3$ | 142.4 | 126.1 | 128.2 | 127.8 | 13.9 | −2.4 | −0.3 | −0.7 | 58.4 | 26.1 | — | — |
| 12 | $CH(OH)CH_3$ | 146.1 | 125.5 | 128.3 | 127.1 | 17.6 | −3.0 | −0.2 | −1.4 | 69.9 | 25.1 | — | 9(228) |
| 13 | $CH(OH)CHCl_2$ | 137.4 | 126.9 | 128.2 | 128.6 | 8.9 | −1.6 | −0.3 | 0.1 | 78.4 | 76.0 | — | — |
| 14 | $CH(OH)CCl_3$ | 135.2 | 129.2 | 127.7 | 126.5 | 6.7 | 0.7 | −0.8 | −2.0 | 84.3 | 103.0 | — | — |
| 15 | $CH_2CH_2CH_3$ | 142.6 | 128.3 | 128.6 | 125.8 | 14.1 | −0.2 | 0.1 | −2.7 | 38.3 | 24.8 | 13.8 | 9(754) |
| 16 | $CH_2CH_2CCl_3$ | 138.6 | 128.4 | 128.6 | 126.5 | 10.1 | −0.1 | 0.1 | −2.0 | 32.7 | 56.6 | 99.2 | — |
| 17 | $CHClCH_2CCl_3$[b] | 140.1 | 127.1 | 128.6 | 127.1 | 11.6 | −1.4 | 0.1 | −1.4 | 58.0 | 62.5 | 96.1 | — |
| 18 | $(CH_2)_3CH_3$[c] | 142.7 | 128.3 | 128.3 | 125.7 | 14.2 | −0.2 | −0.2 | −2.8 | 35.8 | 33.9 | 22.5 | 10(380) |
| 19 | $CH_2CCl_2CH_2CCl_3$[d] | 132.9 | 131.2 | 127.6 | 127.6 | 4.4 | 2.7 | −0.9 | −0.9 | 52.4 | 86.8 | 65.4 | — |

[a] $\Delta_X^i = \delta_C^i - 128.5$, where the index *i* refers to the particular aromatic carbon atom position (substituted, *ortho*-, *meta*- or *para*-atom).

[b] *J*(CH)*ortho* = 159 Hz; *J*(CH)*meta* = 163 Hz; *J*(C-7, H) = 150 Hz; *J*(C-8, H) = 137 Hz.

[c] $\delta_{CH_3} = 13.9$ ppm.

[d] $\delta_{CCl_3} = 93.7$ ppm.

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atom shifts vary within 6.1, 2.4 and 4.9 ppm ranges, respectively.

The spectra of compounds **2–4** and **11** supply data on shifts due to the accumulation of the chlorine substituents at the side chain $\alpha$-carbon atom. Surprisingly, the first $\alpha$-chlorine substituent affects the substituted and the ring *meta*-carbon shielding only slightly, but shifts the *ortho*-carbon signal by about 1 ppm and has a still stronger influence (up to 3 ppm) on the *para*-carbon chemical shift. In general, the latter varies only within rather narrow limits,[15] cf., for example, $C_6H_5CH_3$ and $C_6H_5CH_2Cl$ (**1** and **2**) and $C_6H_5CH_2CH_3$ and $C_6H_5CHClCH_3$ (**6** and **11**). Similar effects were observed earlier with the $\alpha$-bromomethyl group as substituent.[14] The introduction of further $\alpha$-chlorine substituents (**3, 4**), however, gives rise to a 3 ppm shift of the substituted ring carbon signal, whereas the *para*-carbon chemical shift remains almost unaffected.

The chemical shift patterns observed in $\alpha$- and $\beta$-substituted phenylethanes **7–14**, as compared with the substituted toluenes **1–5**, can be summarized as follows: $\alpha$-substituents in ethylbenzene, such as $C_6H_5$ or OH, have a deshielding action on the substituted C-1 atom (about 3 ppm from ethylbenzene). With aliphatic systems, $\beta$-effects caused by heteroatoms are known to differ only insignificantly from the $\beta$-effects produced by $C_6H_5$ and carbon substituents;[15] in the latter case their magnitude (about 10 ppm) is, however, much larger than that of the substituted carbon signal shifts induced by side chain $\beta$-substituents in the compounds studied in this work (about 3 ppm).

The accumulation of $\beta$-chlorine substituents has an influence, opposite to that observed in the series of $\alpha$-$CH_nCl_{3-n}$ substituted compounds, viz. $\delta_{C\text{-}1}$ shifts to higher field by 10 ppm from ethylbenzene (cf. **6–9**). The additional shielding of C-1 is analogous to the values of the $\gamma$-effect in chloroaliphatic compounds.

We have found that in the presence of two different substituents in the phenylethane side chain, their combined influence on the C-1 shielding is fairly additive. The corresponding increments for three monosubstituted phenylethanes, $C_6H_5CHYCH_nZ$, are given in Table 2. Calculations of $\delta_{C\text{-}1}$ values in disubstituted phenylethanes, $C_6H_5CHYCH_nZ$, e.g. for **13** and **14**, by the equation

$$\delta_{C\text{-}1} = 143.4 + \Delta^{Z} + \Delta^{Y} \qquad (1)$$

yield $\delta_{C\text{-}1}$ values of 137.8 and 135.6 ppm against the experimental values of 137.4 and 135.2 ppm, respectively. The substituent effects on the *ortho*-, *meta*- and *para*-carbon atom chemical shifts do not follow the additivity rule.

In the series $C_6H_5CHYCH_3$, for example **6**, **10** and **12**, and except for the case of Y = Cl, $\delta_{C\text{-}7}$ varies within a 40 ppm range depending on Y and decreases in the series OH > $C_6H_5$ > H, in the same direction as the substituent $\sigma^*$ values (1.39, 0.66 and 0.02, respectively).[16] Of the carbon atoms adjacent to C-7, viz. C-1 and C-8, the latter shows the higher sensitivity to Y (the C-8 signals shift by 6–9 ppm and C-1 by 3 ppm on going from **6** to **10** and **12**). It thus follows that, within the same molecule, the alkyl carbon atom experiences stronger $\beta$-effects than the substituted phenyl ring carbon atom.

**Table 2.** $^{13}C$ **chemical shifts in monosubstituted phenylethanes** $C_6H_5CHYCH_nZ$

| No. | Compound | C-1 | *n* | Y | Z | Δ (from $C_6H_5C_2H_5$) |
|---|---|---|---|---|---|---|
| **6** | $C_6H_5CH_2CH_3$ | 143.4 | 3 | — | — | — |
| **8** | $C_6H_5CH_2CHCl_2$ | 135.1 | 1 | — | 2Cl | −8.3 |
| **9** | $C_6H_5CH_2CCl_3$ | 132.9 | 0 | — | 3Cl | −10.5 |
| **12** | $C_6H_5CH(OH)CH_3$ | 146.1 | 3 | OH | — | 2.7 |

It should be noted that the presence of two geminal phenyl groups in a molecule has practically no influence on the *ortho*-, *meta*- and *para*-carbon chemical shifts in either of the rings (cf. **6** and **10**). As mentioned above, only the C-1 signals are affected and undergo an approximately 3 ppm downfield shift.

Increase of the side chain length in a series of the type $Ph(CH_2)_nCX_3$, where X is H or Cl, results in non-monotonic variation of $\delta_{C\text{-}1}$ (see **1**, **6**, **15**, **18** or **4**, **9**, **16**), which attain extreme maximal or minimal values at $n = 1$, depending on whether X is H or Cl. A similar carbon chemical shift alternation is observed in alkyl chains containing $\alpha$-, $\beta$- or $\gamma$-substituents.

## Disubstituted benzenes

***para*-Disubstituted benzenes.** The chemical shift values of 11 *para*-disubstituted benzenes are summarized in Table 3. Examples **20–23** and **28–30** show that the experimental $\delta_C$ values of the ring carbon atoms coincide with those calculated using Savitsky's scheme[7] to within ±1 ppm. Nitro derivatives **21** and **30** are the only exceptions; their C-1 and C-4 chemical shifts differ from the calculated values by about 2 ppm. In addition, the carbon chemical shifts of other nitro derivatives do not conform to the additivity rule.[8]

Comparison of $\delta_C^{\text{arom}}$, calculated by Savitsky's scheme, with the experimental values has made it possible to assign aromatic ring carbon signals in compounds **20** to **23** and **28** to **30**. (Owing to a misprint, an erroneous assignment of compounds **19**, **29** and **30** is cited in Ref. 13.)

The absence of data on the shift increments for R = $CH(Ar)CCl_3$ and $CH(Ar)CHCl_2$, where Ar stands for *o*-$ClC_6H_4$ or *p*-$ClC_6H_4$, however, bars application of the additivity scheme to compounds **24–27**. The ring carbon atom signals in those compounds have been assigned from the following considerations. The results obtained show that the position of the chlorine in one of the aromatic rings in compounds of the type $(ClC_6H_4)_2CHCCl_2X$, where X is H or Cl, does not affect the carbon chemical shifts of the other ring (cf. **24** and **25**, **26** and **27**). We have also shown that the presence of two geminal phenyl rings in a molecule does not shift the *para*-carbon atom signals from those in the corresponding monophenyl derivatives (cf. **6** and **10**). We have, therefore, suggested that the *p*-$ClC_6H_4CH_2CCl_2X$ $\delta_{C\text{-}4}$ values should be close to those of $(p\text{-}ClC_6H_4)_2CHCCl_2X$. Savitsky's scheme gives $\delta_{C\text{-}4}$ of 134.2 ppm with X = Cl and 134.7 ppm with X = H for *p*-$ClC_6H_4CH_2CCl_2X$. Therefore, we have assigned the signals at 134.2, 134.1, 133.5 and 133.5 ppm to C-4 in **24–27**, containing two substituted ring carbons

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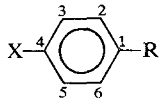
**Table 3.** $^{13}C$ **chemical shifts in *para*-disubstituted benzenes**



| Compound | Substituent R | Substituent X | $\delta$(ppm) $\frac{found}{calcd}$ C-1 | C-2<br>C-6 | C-3<br>C-5 | C-4 | C-7 | C-8 | $^{1}J$(CH)(Hz) C-2 | C-3 | C-7 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **20** | $\overset{7}{C}H_2\overset{8}{C}Cl_3$ | $CH_3$[a] | $\frac{130.1}{129.7}$ | $\frac{131.2}{131.6}$ | $\frac{128.7}{128.8}$ | $\frac{137.8}{137.3}$ | 59.3 | 99.3 | — | — | — |
| **21** | $CH_2CCl_3$ | $NO_2$ | $\frac{139.9}{138.6}$ | $\frac{132.5}{132.2}$ | $\frac{123.2}{122.8}$ | $\frac{146.5}{147.6}$ | 58.9 | 100.0 | — | — | — |
| **22** | $CH(OH)CCl_3$ | $OCH_3$[b] | $\frac{127.2}{127.3}$ | $\frac{130.3}{130.2}$ | $\frac{113.1}{113.3}$ | $\frac{159.9}{158.9}$ | 83.9 | 103.4 | 156 | 160 | 151 |
| **23** | $CH(OH)CCl_3$ | $NO_2$ | $\frac{142.0}{141.2}$ | $\frac{130.3}{130.0}$ | $\frac{122.6}{122.4}$ | $\frac{148.2}{146.1}$ | 83.1 | 101.9 | 167 DT[f] | 169 DD[f] | 150 |
| **24** | $CH(p\text{-}ClC_6H_4)CCl_3$ (DDT) | Cl | 136.2 | 131.3 | 128.5 | 134.2 | 69.8 | 100.9 | 162 DT[f] | 176 DD[f] | 154 |
| **25** | $CH(o\text{-}ClC_6H_4)CCl_3$ | Cl | 135.8 | 132.1 | 128.2 | 134.1 | 64.6 | 100.8 | — | — | — |
| **26** | $CH(p\text{-}ClC_6H_4)CHCl_2$ (DDD) | Cl | 137.5 | 129.8 | 128.8 | 133.5 | 60.8 | 73.9 | 159 DT[f] | 166 DD[f] | 132 |
| **27** | $CH(o\text{-}ClC_6H_4)CHCl_2$ | Cl | 137.2 | 130.2 | 128.7 | 133.5 | 57.2 | 73.7 | — | — | 129 |
| **28** | $CH_2CH_2CCl_3$[c] | Cl | $\frac{137.1}{136.7}$ | $\frac{129.7}{129.7}$ | $\frac{128.8}{129.0}$ | $\frac{132.5}{132.7}$ | 32.1 | 56.4 | — | — | — |
| **29** | $CH_2CCl_2CH_2CCl_3$[d] | $CH_3$ | $\frac{130.3}{130.0}$ | $\frac{131.3}{131.4}$ | $\frac{128.6}{128.3}$ | $\frac{137.2}{136.9}$ | 53.4 | 87.3 | 158 | 158 | 133 |
| **30** | $CH_2CCl_2CH_2CCl_3$[e] | $NO_2$ | $\frac{140.7}{138.9}$ | $\frac{128.4}{132.0}$ | $\frac{125.9}{122.3}$ | $\frac{147.5}{147.5}$ | 51.2 | 86.2 | — | — | — |

[a] $\delta_{CH_3} = 21.1$ ppm.
[b] $\delta_{OCH_3} = 55.0$ ppm.
[c] $\delta_{CCl_3} = 99.0$ ppm.
[d] $\delta_{CH_3} = 21.0$ ppm, $\delta_{CH_2} = 65.5$ ppm, $\delta_{CCl_3} = 94.0$ ppm.
[e] $\delta_{CH_2} = 66.6$ ppm, $\delta_{CCl_3} = 93.4$ ppm.
[f] DT = doublet of triplets, DD = doublet of doublets.

(see Table 3). A further argument for the assignment of these signals to the substituted C-4 carbon is their somewhat lower intensity as compared with the signals from the second substituted carbon, in agreement with the well-known increased relaxation time, $T_1$, of chlorinated carbons, which leads to a decreased intensity of the corresponding signal. The aromatic ring carbon chemical shifts in $p\text{-}ClC_6H_4CH_2CCl_3$ and $p\text{-}ClC_6H_4CH_2CHCl_2$, calculated according to Savitsky, are as follows:

| R | X | C-1 | C-2<br>C-6 | C-3<br>C-5 | C-4 |
|---|---|---|---|---|---|
| $CH_2CCl_3$ | Cl | 131.0 | 132.7 | 128.5 | 134.2 |
| $CH_2CHCl_2$ | Cl | 133.2 | 131.0 | 128.0 | 134.7 |

The calculation results predict the C-2 and C-6 signals to be shifted downfield from those of C-3 and C-5 and the corresponding signals of **24**–**27** have been assigned accordingly. Their multiplicities in the single resonance spectra confirm the assignment suggested: the $^{1}J$(CH) values for C-2 and C-6 differ from those for C-3 and C-5 by 7–14 Hz; the two former atoms give a doublet of triplets (DT) with $^{1}J$(CH) of 159–162 Hz, whereas the signal from C-3 and C-5 is a doublet of doublets (DD) with $^{1}J$(CH) of 166 to 176 Hz and $^{2}J$(CH) of 4 Hz. The single resonance spectrum of a similar compound, **28**, which was assigned unambiguously, contains a doublet of triplets from C-2, C-6 and a doublet of doublets from C-3, C-5. The signal multiplicities in **28** thus coincide with those in compounds **24**–**27** (Table 3).

The experimental data on **24**–**27**, Savitsky's scheme, and the $\Delta_X^{i}$ (X = Cl) values have been used to calculate the $\Delta_X^{i}$ values for $CH(Ar)CCl_3$ and $CH(Ar)CHCl_2$, where Ar is $o\text{-}ClC_6H_4$, $p\text{-}ClC_6H_4$ by the formula $\Delta_X^{i} = \delta^{i}_{found} - 128.5 - \Delta_{Cl}^{i}$. The resulting $\Delta_X^{i}$ values for these groups are listed in Table 4 together with known $\Delta_X^{i}$ increments for X = Cl, $NO_2$, $OCH_3$.

**Table 4. Data on $\Delta_X^{i}$ values for monosubstituted benzenes $C_6H_5X$**

| Substituent X | $\Delta_X^{i}$ C-1 | *o*- | *m*- | *p*- | Refs. |
|---|---|---|---|---|---|
| $NO_2$ | 18.6 | −5.3 | 0.8 | 6.0 | 2 |
| Cl | 6.2 | 0.4 | 1.3 | −1.9 | 1 |
| $OCH_3$ | 32.4 | −14.4 | 1.0 | −7.9 | 1 |
| $CH(p\text{-}ClC_6H_4)CCl_3$ | 9.6 | 1.5 | −0.4 | −0.5 | |
| $CH(p\text{-}ClC_6H_4)CHCl_2$ | 10.9 | 0.0 | −0.1 | −1.2 | |

The $\alpha$- and $\beta$-side chain substituent effects on the shielding of C-1 are additive in disubstituted benzenes **22** and **23** as well as in monosubstituted species **13** and **14**. Substitution of the $\Delta_X^{i}$ values for X = $OCH_3$ or $NO_2$ into

$$\delta_{C\text{-}1}^{calc} = 143.4 + \Delta^{Z} + \Delta^{Y} + \Delta_X^{para}$$

where $\Delta^{Z}$ and $\Delta^{Y}$ are the parameters from Table 2, yields the values of 127.3 and 141.2 ppm for **22** and

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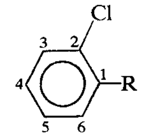
**Table 5. $^{13}$C chemical shifts of *ortho*-disubstituted benzenes**



| | | $\delta$ (ppm) $\frac{\text{found}}{\text{calcd}}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | Substituent R | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 |
| **31** | $CH_2OH$ | $\frac{138.2}{140.6}$ | $\frac{129.2}{133.5}$ | $\frac{128.4}{127.7}$ | $\frac{128.4}{128.6}$ | $\frac{126.8}{125.4}$ | $\frac{128.4}{128.6}$ | 62.2 | — |
| **32** | $\overset{7}{C}H(OH)\overset{8}{C}HCl_2$ | $\frac{135.1}{137.8}$ | $\frac{132.0}{133.1}$ | $\frac{128.6}{128.6}$ | $\frac{129.7}{129.9}$ | $\frac{126.8}{126.3}$ | $\frac{129.2}{128.2}$ | 74.5 | 74.8 |
| **33** | $CH(OH)CCl_3$ | $\frac{134.9}{135.6}$ | $\frac{133.5}{135.4}$ | $\frac{129.8}{128.1}$ | $\frac{129.5}{127.8}$ | $\frac{126.6}{125.8}$ | $\frac{130.5}{130.5}$ | 79.3 | 102.4 |
| **27** | $CH(p\text{-}ClC_6H_4)CHCl_2$ | $\frac{136.8}{139.8}$ | $\frac{134.2}{134.7}$ | $\frac{128.5}{128.8}$ | $\frac{128.7}{128.6}$ | $\frac{127.1}{126.5}$ | $\frac{130.2}{129.8}$ | 57.2 | 73.7 |
| **25** | $CH(p\text{-}ClC_6H_4)CCl_3$ | $\frac{134.6}{138.5}$ | $\frac{134.6}{136.2}$ | $\frac{128.9}{128.5}$ | $\frac{128.9}{129.3}$ | $\frac{126.7}{126.2}$ | $\frac{129.9}{131.3}$ | 64.6 | 100.8 |

**23**, against the experimental chemical shifts of 127.2 and 142.0 ppm, respectively.

***ortho*-Disubstituted benzenes.** Table 5 contains the data on five *ortho*-disubstituted benzenes. The assignment of the aromatic ring carbon signals has also been made in this case by comparing the observed $\delta_C^{arom}$ values with those calculated according to Savitsky's scheme. As seen from the results cited, the C-3–C-6 chemical shifts follow the additivity rule to within ±1 ppm. In the case of the substituted C-1 and C-2 atoms the observed chemical shifts are, however, lower by 2–4 ppm than the calculated values. This may be due to a direct steric interaction between the two *ortho*-substituents, which gives non-additive contributions to the shielding of C-1 and C-2. For the same reason Eq (1) above fails to describe the chemical shifts of the substituted carbons.

## Side chains

The chemical shifts of the side chain carbon atoms are influenced by the substituents in both the aromatic ring and the side chain. In the main, the compounds studied contain chlorinated substituents. The manifold nature of the electronic effects of chlorine considerably complicates the rigorous interpretation of the side chain $^{13}$C patterns. Certain qualitative observations can, however, be made.

The chemical shift of the C-7 carbon atom, adjacent to the phenyl group, varies over a rather wide range (22–97 ppm), depending on the side chain substituent in the series of monosubstituted benzenes (Table 1). The effects caused by chlorinated groups are similar to those present in polychloroalkanes[2,17,18] and to the effects caused by other substituents in normal alkanes.[15,19] Thus, the $\delta_{C\text{-}7}$ values in compounds **1–4** (Table 1), differing in the number of benzyl chlorine atoms, show an almost strictly additive dependence on the accumulation of chlorine substituents, each of which shifts the C-7 signal by 24.4–26.0 ppm to lower field. This is, in fact, the $\alpha$-effect of the benzyl chlorine; it is noticeably weaker than the chlorine $\alpha$-effect in aliphatic systems[2] (30 ppm) and is practically the same as the $\alpha$-chlorine effect in perchloroalkanes.[20] The C-7 signals observed in **6–9** (accumulation of $\beta$-chlorine substituents in ethylbenzene) also undergo regular downfield shifts of 9.5–11.0 ppm per chlorine substituent (the usual $\beta$-chlorine effect in alkyl systems). Lastly, comparison of the data on **15** and **16** shows that three geminal $\gamma$-chlorine substituents in propylbenzene display the opposite effect and produce an upfield shift equal to −5.6 ppm for the C-7 signal.

It is important that substitution of methyl, methoxy or chlorine for the *para*-hydrogen atom in *para*-disubstituted benzenes (Table 3) does not affect the side chain carbon chemical shifts. Compare, for example, the C-7 and C-8 chemical shifts in the pairs of compounds: **9** and **20**, **14** and **22**, **16** and **28**, **19** and **29**.

The sensitivity of the benzyl carbon atom (C-7) shielding to the position of the chlorine substituent in the ring is also important. In compounds **25** and **27**, containing *ortho*-chlorophenyl groups, the C-7 signal is shifted by 3.6–5.2 ppm to higher field from the isomeric analogues containing *para*-chlorophenyl groups (**24**, **26**). Rather unexpectedly, this influence is similar to the known $\gamma$-effect of chlorine in purely aliphatic systems.[2,14] A similar dependence of the side chain methylene carbon atom signals on the position of the substituent in the aromatic ring is observed in the pair $o$-$ClC_6H_4CH_2CCl_3$ and $p$-$ClC_6H_4CH_2CCl_3$.[17]

The aliphatic chain substituent effects on the $^{13}CCl_3$ chemical shift have been studied earlier.[17] As can be seen from Tables 3 and 5, the shielding of this group is only slightly affected by substituents in the ring and the corresponding signals fall within rather a narrow range of 99.0–103.4 ppm. On the contrary, the introduction of substituents into the side chain influences $\delta_{CCl_3}$ noticeably. Thus, chlorine substitution at the position $\beta$ to $CCl_3$ (**29**, **30**) shifts the signal by 5.3–5.9 ppm to higher field whereas the $\alpha$-hydroxyl group (**22**, **23**) induces a downfield shift (cf. **21**).

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## REFERENCES

1. G. C. Levy and G. L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, p. 81. Wiley Interscience, New York (1972).
2. J. B. Stothers, *Carbon-13 NMR Spectroscopy*, p. 197. Academic Press, New York (1972).
3. G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.* **42**, 2427 (1965).
4. H. O. Krabbenhoft, *J. Org. Chem.* **43**, 1830 (1978).
5. P. Lazzaretti and F. Taddei, *Org. Magn. Reson.* **3**, 283 (1971).
6. N. Inamoto and Sh. Masuda, *Tetrahedron Lett.* 3287 (1977).
7. G. B. Savitsky, *J. Phys. Chem.* **67**, 2723 (1963).
8. M. Yamazaki, T. Usami and T. Takeuchi, *Nippon Kagaku Kaishi* 2135 (1973).
9. V. Formáček, L. Desnoyer, H. P. Kellerhals, T. Keller and J. T. Clerc, *$^{13}$C Data Bank*, Vol. 1, Bruker-Physik, Karlsruhe (1976).
10. L. F. Johnson and W. C. Jankowsky, *Carbon-13 NMR Spectra*, Wiley Interscience, New York (1972).
11. Ya. G. Bal'on, V. E. Parnik and M. D. Shul'man, *Zh. Organ. Khim.* **44**, 2634 (1974).
12. E. C. Chukovskaya, M. A. Rozhkova and R. Kh. Freidlina, Dokl. Akad. Nauk SSSR **212**, 382 (1973).
13. R. Kh. Freidlina, N. A. Kuz'mina, L. V. Yashkina, B. V. Kopylova, V. I. Dostovalova and E. C. Chukovskaya, *Dokl. Akad. Nauk SSSR* **236**, 637 (1977).
14. M. Bullpitt and W. Kitching, *J. Org. Chem.* **41**, 760 (1976).
15. J. T. Clerc, E. Pretsch and S. Sternhell, *$^{13}$C-Kernresonanz-Spektroskopie*, Akademische Verlagsgesellschaft, Frankfurt am Main (1973).
16. V. A. Palm, *Osnovy Kolichestvennoi Teorii Organicheskikh Reaktsii* (Introduction to Quantitative Theory of Organic Reactions), p. 331. Leningrad, Khimiya (1977).
17. F. K. Velichko, V. I. Dostovalova, N. A. Kuz'mina, E. I. Fedin and R. Kh. Freidlina, *Org. Magn. Reson.* **7**, 46 (1975).
18. F. K. Velichko, E. C. Chukovskaya, V. I. Dostovalova, N. A. Kuz'mina and R. Kh. Freidlina, *Org. Magn. Reson.* **7**, 361 (1975).
19. E. Lippmaa, T. Paasivirta, N. Belikova and A. Platé, *Org. Magn. Reson.* **2**, 581 (1970).
20. G. E. Hawkes, R. A. Smith and J. D. Roberts, *J. Org. Chem.* **39**, 1276 (1974).

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