LONG-RANGE COUPLING CONSTANTS
OF *ortho*-ALKYLPHENOLS

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Effects of the long-range coupling constants were investigated in the NMR spectra of *ortho*-alkyl-phenols. It has been shown, by means of the analysis of the NMR spectra, that the values of the long-range coupling constants between protons on the α-carbon atoms of an alkyl group and aromatic protons do not depend on the kind of the alkyl group.
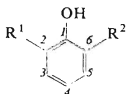
It is known that in the case of alkyl-substituted aromatic compounds the protons bound to the α-carbon atom of alkyl substituents can couple with the aromatic protons, owing to the hyper-conjugation effect[1]. As a consequence, some lines in the NMR spectra of the above compounds become broader, or even split[2−10]. It follows from the results of the papers published as yet that the long-range coupling constants, which account for these splittings, are comparatively independent of the electronegativity of the other substituents on the nucleus[3−6], in contrast with the coupling constants on the aromatic nucleus.

The present work has been devoted to an investigation of the long-range coupling constants of *ortho*-alkylphenols, the alkyl groups being methyl, ethyl, isopropyl, tert-butyl, and 1,1,3,3-tetramethylbutyl group. In the aromatic part of the NMR spectra of degassed solutions of these compounds, broadening of some lines can be observed with increasing number of protons on the α-carbon atom of alkyl substituents. It has been our objective to find out whether the broadening of the lines is due to a change in the long-range coupling constants values, or whether it is only a consequence of the higher line multiplicity in multispin systems.

EXPERIMENTAL

The NMR spectra of *ortho*-alkylphenols (Table I) were measured with a JNM-3-60 spectrometer operating at 60 Mc with a resolution 10^{-8}. The spectra were calibrated by the side-band method. For measurements of the NMR spectra, 0·5M degassed solutions of phenols in carbon tetra-chloride were prepared, and hexamethyldisiloxane ($\tau = 9.95$) was used as an internal standard.

TABLE I

Spin Systems of *ortho*-Alkylphenols

$$R^1 \underset{2}{\overset{OH}{\underset{3}{\bigcirc}}}_{6} R^2$$

Substituent		Spin[a]	Substituent		Spin[a]
R^1	R^2	system	R^1	R^2	system
CH_3	H	$ABCDX_3$	C_2H_5	C_2H_5	$AA'BX_2X_2'$
C_2H_5	H	$ABCDX_2$	$iso\text{-}C_3H_7$	$iso\text{-}C_3H_7$	$AA'BXX'$
$iso\text{-}C_3H_7$	H	$ABCDX$	$tert\text{-}C_4H_9$	$tert\text{-}C_4H_9$	A_2B
$tert\text{-}C_4H_9$	H	$ABCD$	$tert\text{-}C_8H_{17}{}^b$	$tert\text{-}C_8H_{17}{}^b$	A_2B
$tert\text{-}C_8H_{17}{}^b$	H	$ABCD$	CH_3	$tert\text{-}C_4H_9$	$ABCX_3$
CH_3	CH_3	$AA'BX_3X_3'$	CH_3	$tert\text{-}C_8H_{17}{}^b$	$ABCX_3$

[a] Hydrogen atoms at positions 3, 4, 5, 6 in the aromatic nucleus are successively designated by letters A, B, C, D; in the case of symmetrically substituted 2,6-dialkylphenols the hydrogen atom at position 5 is designated by A or A'. Protons at positions α of alkyl groups are designated by letters X and X'. [b] tert-C_8H_{17} = 1,1,3,3-tetramethylbutyl.

The half-width values and line frequencies were averaged from a large number of independent runs and determined with an accuracy of ± 0.1 c/s. A Minsk-22 computer was used in the calculations of the NMR spectra.

Phenols — either commercial or prepared by known procedures – were purified by crystallization or fractional distillation. The phenols used were chromatographically uniform, and their melting or boiling points were in agreement with the literature. So far, no description has been made in the literature of 2,6-bis(1,1,3,3-tetramethylbutyl)phenol, m.p. 50–51°C (pentane), which had been isolated from the reaction mixture after alkylation of phenol with diisobutylene catalyzed by aluminium phenolate, where it is formed in trace amounts; its structure has been proved by the NMR spectrum.

RESULTS AND DISCUSSION

Symmetrically Substituted 2,6-Dialkylphenols

The aromatic parts of the NMR spectra of degassed solutions of symmetrically substituted 2,6-dialkylphenols in carbon tetrachloride, recorded at a rate lower than 0·5 c/s, differ in dependence on the alkyl substituent. If the substituent in both positions is represented by a tertiary alkyl group (tert-butyl or 1,1,3,3-tetramethylbutyl), we obtain NMR spectra typical of the A_2B system, whereas in the presence of methyl, ethyl, or isopropyl groups at the positions *ortho*, a more or less clear structure appears on the basic bands of the A_2B system; this structure can be elucidated only if all the protons on the α-carbon atoms of alkyl substituents are included into calculations (Table I).
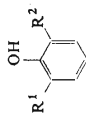
TABLE II
NMR Data of 2,6-Dialkylphenols

R^1 — (OH) — R^2

Substituents		Chemical shifts τ						Coupling constants, c/s			
R^1	R^2	A^a	$A'(C)^a$	B^a	alkyl groups		OH	J_{AB}	$J_{A'B}$ J_{CB}	$J_{AX}+J_{A'X}^b$ $J_{AX}+J_{CX}$	J_{BX}^b
CH_3	CH_3	3·19	3·19	3·41	7·82	7·82	5·63	7·5	7·5	−1·35	0·35
C_2H_5	C_2H_5	3·15	3·15	3·32	8·80	8·80	5·65	7·4	7·4	−1·30	0·4
iso-C_3H_7	iso-C_3H_7	3·02	3·02	3·18	8·71 6·85	8·71 6·85	5·50	7·75	7·75	−1·35	0·4
tert-C_4H_9	tert-C_4H_9	2·99	2·99	3·35	8·59	8·59	5·03	7·9	7·9	—	—
tert-C_8H_{17} ^{c}	tert-C_8H_{17} ^{c}	2·95	2·95	3·31	9·25 8·56 8·08	9·25 8·56 8·08	4·92	7·9	7·9	—	—
CH_3	tert-C_4H_9	3·20	3·04	3·39	7·83	8·62	5·48	7·4	7·9	−1·35	0·35^d
CH_3	tert-C_8H_{17} ^{c}	3·19	3·01	3·38	7·81	9·30 8·59 8·09	5·45	7·4	7·9	−1·35	0·35^d

^{a} Aromatic hydrogen atoms (cf. Table I). ^{b} Absolute signs assigned in agreement with literature[6,10–12]. ^{c} tert-C_8H_{17} = 1,1,3,3-tetramethyl-butyl. ^{d} J_{AC} = 1·7.

   With respect to the fact that the interaction between the alkyl and aromatic protons is weak, it is possible to use methods of subspectral analysis[11] for the analysis of these systems. In the case of the AA'BXX' system, an analysis of two a_2b subspectra corresponding to the values of the spin quantum number $F_z(XX') = \pm 1$ of the XX' nuclei will yield coupling constants J_{AB}, J_{BX}, $J_{AX} + J_{AX'}$ and the difference δ_{AB} between the chemical shifts of the nuclei A and B. All transitions in the a_2b sub-systems are independent of the value of the coupling constant $J_{AA'}$. Similarly, in the spectra of the AA'BX$_2$X$_2'$ and AA'BX$_3$X$_3'$ systems two a_2b subspectra can be found for each value of the spin quantum numbers $F_z(X_2X_2') = \pm 2$ and $F_z(X_3X_3') = \pm 3$. However, the parameters of these large spin systems cannot be calculated from the a_2b subspectra, since the transitions in the a_2b subsystems are of low intensity if compared with the total spectrum.

   The character of the NMR spectra of the symmetrically substituted *ortho*-alkyl-phenols is greatly dependent on the values and relative signs of the long-range coupling constants; according to the relative signs, all possible spectra of the AA'. .BX$_n$X$_n'$ system for $n = 1, 2, 3$ can be arranged in four groups:

   1. sign J_{AX} = sign $J_{A'X}$ = sign J_{BX}

   2. sign J_{AX} $\neq$ sign $J_{A'X}$ = sign J_{BX}

   3. sign J_{AX} = sign $J_{A'X}$ $\neq$ sign J_{BX}

   4. sign J_{AX} $\neq$ sign $J_{A'X}$ $\neq$ sign J_{BX}

Each group yields different characteristic spectra of the AA'B type, which include $(3/n)(2n + 3) 2^{2n+2}$ main transitions. Only in case that $J_{AX} = J_{AX'}$, which is possible in groups 1 and 3, the transition frequencies are arranged so as to form symmetrical multiplets for $F_z(X_nX_n') = \pm n$. The transitions between the energy levels as well as their relative intensities can be described in terms of explicit expressions, derived by means of the effective frequency method[12].

   Since all lines in the AA'B part of the NMR spectra of symmetrically substituted 2,6-dialkylphenols either have a symmetrical shape or are symmetrically split, the value of the coupling constant J_{AX} must be close to that of the constant $J_{AX'}$. At the same time, however, it follows from the analysis of the multiplets of the lines A and B transitions that sign J_{BX} $\neq$ sign J_{AX} = sign $J_{AX'}$. Subspectral analysis makes it possible to obtain the value of the coupling constant J_{BX} directly from the magnitude of the splitting of line 3 of the A_2B system (lines designated according to Emsley[13], *cf*. Fig. 2), and the sum of the coupling constants $J_{AX} + J_{AX'}$ from an analysis of multiplets of lines 5 and 7. If multiplets in the NMR spectra are not well resolved, the values of splittings can be estimated from the ratio of intensities of the line under

investigation and the one whose half-width is independent of the long-range coupling constant values.

On the assumption that the multiplet consists of lines of Lorentzian shape, having half-width Δ and height V_0 and separated by an interval $\delta \leqq \Delta$, the change of the height of the multiplet, V, in dependence on the change δ/Δ, can be determined from the relationship

$$V = \sum_{k=0}^{N} \binom{N}{N-k} V_0 / \{\langle [(N-2k)\,\delta]/\Delta \rangle^2 + 1\} \tag{1}$$

for $N = 2n$ and $k = 0, 1, \ldots N$.

The same procedure was used to determine the coupling constant J_{BX} of all the symmetrically substituted 2,6-dialkylphenols, based on the ratio of the intensities of lines 3 and 2 (Fig. 1). The sum of the coupling constants $J_{AX} + J_{AX'}$ can easily be determined in the case of 2,6-dimethyl- and 2,6-diethylphenol from the resolved multiplets of the A A' part of the NMR spectra, whereas in the case of 2,6-diisopropylphenol the sum of these constants must be obtained on the basis of an analysis of the shape of unresolved bands in the A A' region of the NMR spectra.

The spectral parameters obtained from the analysis of the NMR spectra of symmetrically substituted 2,6-dialkylphenols (Table II) were employed in the calculations of the NMR spectra (Fig. 2, 3). In the calculated and experimental spectra of symmetrically substituted *ortho*-alkylphenols, frequencies, line intensities and half-widths were compared (Table III). It can be seen from the Table that while lines 4B and 2B are almost insensitive towards the long-range coupling constant values,
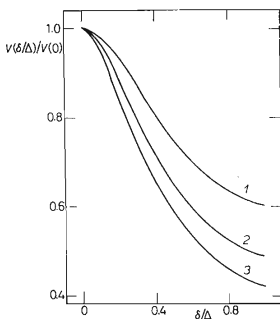

FIG. 1

Dependence $V(\delta/\Delta)/V(0)$ on δ/Δ in the AA'BX$_n$X$_n'$ System

Curves *1, 2, 3* correspond to $n = 1, 2, 3$.

the half-width of line 7 is the most affected one in the region A, and the half-width of line 3 is the most affected one in the region B.

Unsymmetrically Substituted 2,6-Dialkylphenols

The basis for obtaining parameters of unsymmetrically substituted 2,6-dialkylphenols consists in an analysis of unsymmetrical spin systems ABC and ABCD. For this analysis, coupling constants and chemical shifts of phenols[14-16] were used in the first approximation, corrected by including the substituent constants of the corresponding alkyl groups[17-19]. In the case of 2-isopropylphenol, the spectral parameters were read in the first approximation from a NMR spectrum measured at a frequency 220 Mc. The resulting NMR values of the spectral parameters of the ABC and ABCD systems were obtained by a series of iterations (Table II and IV). For the analysis of systems involving the long-range coupling (Table I), the long-range coupling constant values were used in the first approximation, which had been de-
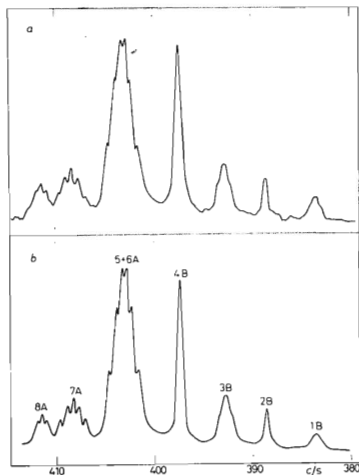

Fig. 2

Experimental and Theoretical Spectrum of the Aromatic Protons of 2,6-Dimethylphenol
  a) Experimental; *b*) theoretical, half-width 0·7 c/s.

TABLE III

Band Half-Widths of the AA′B System of Aromatic Protons in Symmetrically Substituted 2,6-Dialkylphenol

$$\underset{\text{OH}}{\text{R}}\overset{\text{OH}}{\bigodot}\text{R}$$

R	Half-widths of experimental bands, c/s[a]						
	1 B	2 B	3 B	4 B	5 + 6 A	7 A	8 A
$CH_3{}^c$	1·15	0·76	1·48	0·96	2·24	2·60	1·95
$C_2H_5{}^c$	1·02	0·78	1·44	1·06	1·68	2·20	1·25
iso-$C_3H_7{}^c$	1·00	0·75	1·31	1·00	1·49	1·88	1·05
tert-$C_4H_9{}^d$	0·83	0·89	0·92	0·91	1·59	1·15	1·10
tert-$C_8H_{17}{}^{d,e}$	0·84	0·92	1·05	0·89	1·61	1·10	1·05

[a] Lines designated according to ref.[13]; only nuclei A, B have been interchanged. [b] Long-range coupling constant values (cf. Table II) have been used in the calculations. [c] Theoretical half-width of the individual lines, forming bands of the AA′B systems, is 0·7 c/s. [d] Theoretical half-width of the individual lines, forming bands of the AA′B systems, is 0·8 c/s. [e] tert-$C_8H_{17} = 1,1,3,3$-tetramethylbutyl.

termined for unsymmetrically substituted 2,6-dialkylphenols. The same values can also be used in the analysis of unsymmetrically substituted alkylphenols, which has been confirmed on the grounds of the agreement found between the frequencies, line intensities and line half-widths in the case of calculated and measured spectra. A more precise determination of the long-range coupling constant values is limited by the quality of recording of the NMR spectra.

It follows from the results of the analysis and from a comparison of the half-widths of experimental and theoretical lines of 2,6-dialkylphenols that the long-range coupling constants of 2,6-dialkylphenols are not very sensitive to differences in the substitution with a methyl, ethyl or isopropyl group (Table II, IV). The differences between the long-range coupling constants are very small and always lie within the limits of accuracy of our measurements. The values of the long-range coupling constants obtained by us agree with those described in the literature for the derivatives of toluene[2−6]. The relative signs of the long-range coupling constants of 2,6-dialkylphenols are in agreement with McConnell's theory of coupling constants, based on the assumption of a pure electron contribution[20−22]. It also follows from the results of the analysis of the NMR spectra of *ortho*-alkylphenols that the band half-widths in the aromatic parts of the NMR spectra can be fully explained in terms of the multiplicity of lines of a given spin system and are not due to the difference between the values of the long-range coupling constants.

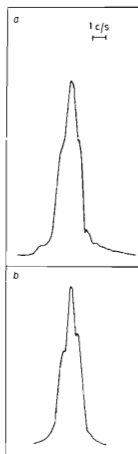| Half-widths of theoretical bands, c/s^{a,b}						
1 B	2 B	3 B	4 B	5 + 6 A	7 A	8 A
1·25	0·8	1·55	0·9	2·2	2·5	2·05
1·2	0·8	1·3	0·9	1·7	2·1	1·3
1·1	0·7	1·3	0·9	1·6	2·0	1·0
0·8	0·85	0·85	0·8	1·45	0·85	0·8
0·8	0·85	0·85	0·8	1·5	0·85	0·8

FIG. 3

Experimental and Theoretical Spectrum of the Methyl Protons of 2,6-Dimethylphenol

a) Experimental; *b*) theoretical, half-width 0·7 c/s.

TABLE IV

NMR Data of 2-Alkylphenols

Substituent R	Chemical shifts τ						Coupling constants^b, c/s				
	A^a	B^a	C^a	D^a	alkyl groups	OH	J_{AB}	J_{AC}	J_{BC}	J_{BD}	J_{CD}
CH$_3$^{c}	3·00	3·27	3·13	3·40	7·82	5·22	7·5	1·7	7·4	1·3	7·8
C$_2$H$_5$	2·98	3·25	3·06	3·43	8·81	5·25	7·4	1·7	7·4	1·25	7·8
					7·42						
iso-C$_3$H$_7$	2·92	3·23	3·09	3·46	8·80	5·33	7·6	1·75	7·4	1·15	8·1
					6·83						
tert-C$_4$H$_9$	2·86	3·27	3·09	3·61	8·65	5·58	7·9	1·75	7·4	1·1	8·2
tert-C$_8$H$_{17}$^{d}	2·83	3·25	3·07	3·59	9·29	5·40	7·9	1·8	7·4	1·1	8·2
					8·59						
					8·09						

^{a} Aromatic hydrogen atoms (*cf.* Table I). ^{b} $J_{AD} < 0.5$ c/s. ^{c} $J_{AX} + J_{CX} = -1.35$; $J_{BX} = J_{DX} = 0.35$; absolute signs assigned in accordance with the literature[6,10−12]. ^{d} tert-C$_8$H$_{17}$ = 1,1,3,3-tetramethylbutyl.

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