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LONG RANGE ^4J- AND ^6J-INTERACTIONS IN 2,6-DIMETHYL-3,4-DIBROMOPHENOL AND 3,5-DIMETHYL-4-HYDROXYBENZALDEHYDE

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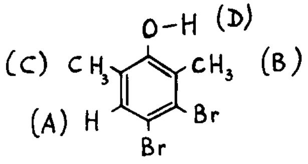
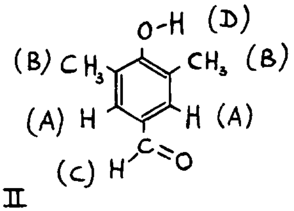
In recent literature $^{1-8)}$ considerable attention has been paid to the spin-spin interactions of ring protons with protons, attached to sp_2 and sp_3 hybridized α-carbon atoms in substituted benzenes. In this connection we will report here long range interactions in 2,6-dimethylphenolderivatives I and II:



I



II

The chemical shift values and the coupling constants for these compounds are presented in TABLE I. In 2,6-dimethyl-3,4-dibromophenol (I) long range interactions were observed between all the protons with the exception of the OH proton. The H(A) signal, originally a septet with line spacings of 0.68 Hz, changed on irradiation of the CH_3(B) protons in a double resonance experiment, into a quartet with line spacings of 0.73 Hz, due to the remaining coupling with CH_3(C). A quartet with spacings of 0.60 Hz was observed for H(A) on irradiation of the CH_3(C) protons. Thus the interactions of H(A) over four bonds with CH_3(C) and over six bonds with CH_3(B) are of the same magnitude.

These results are in agreement with the data reported by Rottendorf and Sternhell $^{3)}$, viz. 0.63 Hz for the CH_3-H coupling constants in 2,3,4,5- and 2,3,5,6-tetrachlorotoluenes. Recently Kotowycz and Schaefer $^{8)}$ reported almost equal coupling constants for the interaction of the CH_3-protons with the ortho and para ring protons in 2-bromo-5-chlorotoluene (0.63 and 0.58 Hz respectively). By applying multiple resonance they showed that both interactions were of the same sign, while the coupling with the meta proton was of opposite sign. In accordance with their results we found that in I J_{AB} and J_{AC} are of equal sign. This could be established owing to the existance of a long range interaction between CH_3(B) and CH_3(C), whose signals show a doublet of quartets each (FIG. 1a). By irradiation either at the high field or the low field quartet of CH_3(C), the high field or the low field quartet of CH_3(B) was decoupled (FIG. 2b and a), indicating that J_{AB} and J_{AC} are of like sign.

Irradiation of H(A) caused a collapse of the doublets and clearly showed the presence of a coupling over six bonds ($|J_{AB}| = 0.21$ Hz). As far as we know long range interactions of methyl groups in meta positions were not yet reported in literature.

The coupling of methyl protons with aromatic protons presumably involve σ-π configuration interaction $^{1,3,5,6,8-11)}$. The couplings are thought to be strongly dependent on the π-bond order between the carbon atoms, holding the methyl group and the aromatic proton. Our observation of equal signs is in agreement with predictions by Dewar and Fahey $^{10)}$ on the basis of a modified McConnell equation $^{11)}$, for the coupling constants of the aromatic and aliphatic protons in acenaphtene.

In 3,5-dimethyl-4-hydroxybenzaldehyde (II) a long range interaction between the aldehyde proton H(C) and the equivalent ortho protons H(A) was detected and confirmed by double resonance experiments. The H(C) signal shows a poorly resolved triplet (FIG. 3a) with line spacings of 0.16 Hz. Irradiation on the methyl protons did not affect this triplet but a change into a narrow line was observed by irradiating at the H(A) signal position (FIG. 3b). Conversely the septet of H(A), due to interaction with the methyl protons, appeared better resolved with H(A) decoupled from H(C). Long range interactions between the aldehyde proton and the meta protons in benzaldehyde have been studied by a number of investigators (5, 12-14), but interactions with ortho protons were not yet reported. A somewhat similar type of long range coupling has been found between ortho ring protons and α-olefinic protons in styrene derivatives $^{1)}$.

FIG. 1a and b

a. Spectrum of the CH_3(B) (low field) and the CH_3(C) (high field) protons of compound I. b. Spectrum of the same **compound decoupled from H(A).**

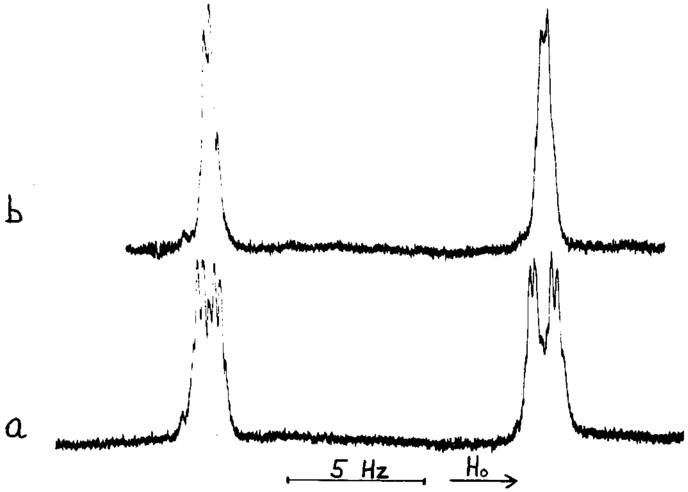


FIG. 2a and b

Double resonance spectra of the CH_3(B) protons of compound I, resulting from irradiation of the low field and the high field quartets of the CH_3(C) protons respectively.

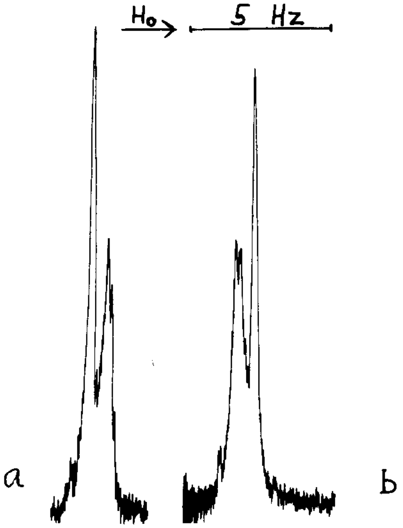


FIG. 3a and b

a. Spectrum of the aldehyde proton H(C) of phenol II. **b. Spectrum of the same protons decoupled from H(A).**

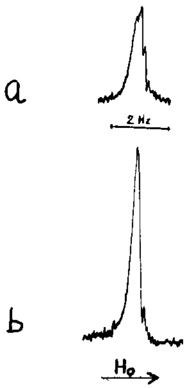


TABLE I

Chemical shift values and coupling constants for the compounds I and II

Compound	protons	Chemical shift values a) (δ in ppm) and multiplicities	Coupling constants a) (in Hz)
I	A	7.13 (septet)	$\lvert J_{AB}\rvert = 0.60$ } of equal signs
	B	2.33 (doublet of quartets)	$\lvert J_{AC}\rvert = 0.73$ }
	C	2.14 (doublet of quartets)	
	D	4.50 (singlet)	$\lvert J_{BC}\rvert = 0.21$
II	A	7.61 (septet)	$\frac{1}{2}(\lvert J_{AB}\rvert + \lvert J_{A'B}\rvert) = 0.67$ c)
	B	2.31 (triplet) b)	
	C	9.78 (triplet)	$\lvert J_{AC}\rvert = 0.16$
	D	5.93 (singlet)	

a) The coupling constants are accurate to within 0,03 Hz and the chemical shift values to within 0.03 ppm. The spectra were recorded from 5-10 (w/v) % deoxygenated solutions in carbon disulfide (compound I) or deuterochloroform (compound II), using TMS as internal standard ($\delta = 0$ ppm). The spectrometers were a Varian A 60 and DA 60-IL.

b) At optimal conditions the centre line of this triplet appeared as a **doublet** with a line spacing of 0.14 Hz.

c) J_{AB} and $J_{A'B}$ refer to the coupling between the methyl protons and the ortho and para ring protons respectively.

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