Analysis of the High Resolution NMR Spectra of

Dihalogenated Toluenes

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The 56 and 60 MHz NMR spectra of six dihalogenated toluenes have been analysed. The long range proton-proton and proton-fluorine coupling constants are discussed in terms of $\sigma - \pi$ electron contribution to the coupling mechanism. It is found that $J^{o}_{F,CH_3} > J^{p}_{F,CH_3} > J^{m}_{F,CH_3}$ with positive sign for J^{o} and J^{p}. The sign of J^{m}_{F,CH_3} is presumably positive.

$\mathbf{M}$uch attention has been paid to the spin-spin coupling mechanism in aromatic systems.[1] Hoffmann introduced the methyl group replacement technique to measure the π-contribution J^{π} to ring proton-proton coupling constants.[2-4] Theoretical molecular orbital and valence bond descriptions of contact nuclear spin-spin couplings have been reported.[5] Much effort has been paid to correlation of the observed and theoretical values in aromatic [6,7] and olefinic systems.[8] NMR parameters are found to correlate with Hammett-sigma constants.[9]

A linear relationship between chemical shifts (^1H, ^{19}F, ^{13}C) and σ_p for parasubstituents has been theoretically related to modifications of the π-electron system upon substitution. $J^{o}_{H,H}$ and $J^{m}_{H,H}$ have been discussed by several workers in terms of σ and π coupling mechanism, and it is concluded that a σ-mechanism is dominant for these couplings.[7] The present work reports the NMR analysis of several dihalogenated toluenes and the couplings involved are discussed in terms of the $\sigma - \pi$ coupling mechanism.

EXPERIMENTAL

The compounds were all commercially available from Fluka. They were used without further purification and the NMR spectra were taken as evidence of purity. The compounds (neat liquids) were introduced into 5 mm OD sample tubes and small quantities of TMS were added to serve as NMR reference and locking substance. The samples were carefully degassed by the freeze-pump-thaw technique, and sealed under vacuum. The spectra were recorded on a JEOL 60 MHz (JNMC — 60H) spectrometer operating on 56 and 60 MHz at ambient temperature, approx. 27°C. The spectrometer was operated in one sample fixed lock mode with field-frequency sweep for the proton spectra. All proton

spectra which were used in the calculation procedure were calibrated every 5 Hz to minimize the error due to non-linearity in the sweep unit, using a frequency counter. The counter is accurate to 0.1 Hz. The fluorine spectra were calibrated by side band technique. The line positions were taken as an average from several spectra. The computations were carried out using an IBM 360/50 computer.

SPECTRAL ANALYSIS

The proton spectrum of each compound consists of two main regions, assigned to methyl protons ($\delta \simeq 2.1$) and aromatic protons ($\delta \simeq 6.6$ to 7.3). The total spectra were extremely complex in all cases, due to the number of nuclei involved. The separation between the two regions was much greater than any of the observed coupling constants. The spectra were all analyzed in terms of $ABCM_3X$ spin systems, using the iterative computer program LAOCN3 with some modifications. The aromatic protons constituted the ABC nuclei, the methyl group the M_3 nuclei and fluorine the X nucleus.

The aromatic region is very complex due to the small chemical shift differences between these nuclei as compared with the coupling constants involved. In each case at least one of the couplings within the ABC system is comparable to one of the chemical shift differences.
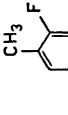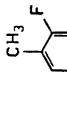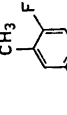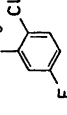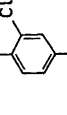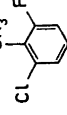
X-Approximation and sub-spectral breakdown of the spin systems give useful information about the ABC part in all compounds. The coupling to the methyl group splits all signals (ABC part) into quartets and these couplings were easily recognized. The magnitude of $J_{H,Me}$ reported for toluene,[10] appeared to be valuable in determining the relative chemical shifts of H_A, H_B, and H_C. The fluorine nucleus splits all the proton signals into doublets and the magnitude of the fluorine proton coupling constants made it easy to distinguish between signals due to protons *ortho* and protons *meta* and *para* to the fluorine substituent. Although the chemical shifts and coupling constants obtained by inspection of the spectra agreed fairly closely with refined values (Tables 1 and 3), the iterative computation did not converge properly. The difficulties arose when the magnitude of close lying energy levels for the same F_z value changed relative to each other. This swopping of lines is experienced in the analysis of systems with strongly coupled nuclei or highly symmetric spin systems. The iterative calculations were in all cases performed when about 200 lines were fitted and gave RMS errors less than 0.1 Hz. The deviation in line positions was 0.1 Hz or less.

DISCUSSION

The π-electron contribution to the proton-proton couplings in aromatic molecules can be predicted from single determinant molecular orbital (MO) theory.[11] McConnell [12] introduced electron spin resonance hyperfine splittings in free radicals as a criterion of and a measure for the interaction between σ and π electrons and obtained an expression relating the π electron contribution to the coupling constants

$$J^{\pi}_{NN'} = \beta^2 h^{-1} Q_N Q_{N'} P^2_{NN'} \Delta E^{-1}$$

Table 1. Proton-proton and proton-fluorine coupling constants in Hz.[a]

	J_{HH}			J_{HF}			$J_{CH_3,H}$			$J_{CH_3,F}$		
	o	m	p	o	m	p	o	m	p	o	m	p
I	8.04 / 8.13[b]	1.22 / 1.64[b]	0.22	9.07	7.93	0.46	−0.77	(1,3) 0.37 / (1,5) 0.40		2.12		
II	8.58 / 8.92[b]	2.79 / 2.30[b]	0.57	9.08	(2,4) 4.48 / (2,6) 6.66		−0.73	0.33	−0.65	2.10		
III	8.20 / 9.04[b]	2.79 / 2.58[b]	0.56	9.34	(2,4) 4.51 / (2,6) 6.59		−0.73	0.33	−0.66	2.25		
IV	8.16 / 9.04[b]	2.77 / 2.95[b]	0.99	(5,6) 9.17 / (4,5) 8.55	5.50		−0.70	0.32	−0.55		0.30	
V	8.80 / 8.61[b]	2.73 / 2.62[b]	0.25	(3,4) 8.39 / (4,5) 8.00	5.77		−0.75	(1,5) 0.39 / (1,3) 0.41				
VI	(3,4) 7.83 / (4,5) 7.54 / (3,4) 8.5[b] / (4,5) 8.14[b]	2.68 / 1.76[b]		8.78	5.90	−0.87		(1,3) 0.06 / (1,5) 0.02	−0.03	2.42		1.28

[a] Numbering commences at the methyl group. Numbers in parenthesis are the numbers of the ring carbon atoms carrying the coupled nuclei.
[b] Calculated coupling constants from ΔJ values (Table 2).

where ΔE is the average excitation energy to triplet states, Q_N the hyperfine coupling constant corresponding to the interaction between a π electron in a carbon atomic orbital and the adjacent proton N and $P_{NN'}$ is the mobile bond order between the carbon atoms carrying the protons N and N'.

The values of Q_{CH} for a proton attached to a carbon atom, is found to be dependent on charge [13] and hybridization of the carbon atom.[14] Q_{CH} has values near -23 G when the proton is attached to an aromatic system (sp^2-hybridization) and values about $+25$ G are found for protons at sp^3-hybridized carbon atoms in a freely rotating methyl group attached to an aromatic ring.[15]

The negative signs of J^o_{H,CH_3} and J^p_{H,CH_3} found for the compounds studied in this work are in agreement with electron spin resonance data and with the qualitative predictions made by Hoffman and Gronowitz.[2] MO calculation [12] predicts $J^m_{H,CH_3} = 0$, but valence bond studies of contact nuclear spin coupling [5] predict a positive coupling constant. The calculated coupling between α-methyl and *meta* protons in toluene [5] (0.59 Hz) is about twice the experimental value (0.33 − 0.44 Hz). The theoretical value, 0.59 Hz, is obtained when the one center exchange integral for an aromatic carbon is fitted to the experimental value of J^p_{H,CH_3} in toluene. The authors assume that this disagreement arises because of too much correlation between electrons in the same subset of an alternant system in their valence bond calculations. The theoretical (VB) value $J^o_{H,CH_3} = -0.73$ Hz for toluene correlates well with experimental values in this work (-0.73 to -0.77 Hz). There is, however, appreciable variation in the series of *meta* and *para* J_{H,CH_3} (Table 1). It is not clear which effects cause these variations. The influence of substitution on the coupling mechanism, bond order or the variation in the magnitude of Q_{CH} is not clearly understood. There seems to be evidence for a smaller variation in Q for protons attached to a benzene ring as compared to Q values for protons in an α-methyl group attached to an aromatic ring, when values for different molecules are compared.[16,17] The couplings, J_{H,CH_3}, found in this work lie reasonably near values predicted for the $\sigma - \pi$ coupling, and it is assumed that there are substantial π-electron contributions to the long range proton-proton coupling constants in these molecules. Hoffman [3,4] suggested that replacement of a hydrogen in a $C(sp^2) - H$ bond by a methyl group should change the sign of J^π and slightly increase its magnitude. This replacement criterion also indicates an appreciable π-electron contribution to J_{H,CH_3} in the molecules studied.

The sign and magnitude for J^o_{F,CH_3} are similar to those observed in o-fluorotoluene [18] and 2-fluoro-4-chloro-5-nitrotoluene.[6] The *para* α-methyl-fluorine coupling found in compound (V) ($J^p_{F,CH_3} = 1.28$) is the same as reported for 2-iodo-4-fluorotoluene. The magnitude of J^m_{F,CH_3} in compound (IV) (Table 1) is nearly equal to the value found in 3-fluoro-4-amino-5-bromo-toluene,[6] but the sign is not here determined as the spectrum appears to be insensitive to change in sign of this coupling constant. The assumption that dominant π-contribution to J^o_{F,CH_3} does imply a positive Q_{CF} is not certain, as this term consists of positive and negative contributions from diagonal and off-diagonal elements in the π-electron spin density matrix.[19] There is, however, evidence for a positive sign of Q_{CF} [6] based on the negative sign of J^m_{F,CH_3}

in 3-fluoro-4-amino-5-bromotoluene. Support for this assumption is provided by the Q_{CF} values found for *ortho*, *meta*, and *para* fluorophenyl substituted complexes of Ni(II) aminotropone-iminates,[8] $+47$, $+4$, and $+41$ G, respectively. Q_{CH} varies within a smaller range than Q_{CF} and the magnitude of Q_{CF}[8] shows the same trend as the J_{F,CH_3} values, $J^o > J^p > J^m$. In spite of the lack of reliable Q_{CF} values from spin resonance studies it is assumed that the π-electron contribution to J^o_{F,CH_3} and J^p_{F,CH_3} is substantial. Estimation of the $\sigma - \pi$ contribution to J^m_{F,CH_3} is not possible until the sign has been determined for a variety of substituted fluorotoluenes.

Table 2. Effects of substituents on the proton-proton coupling constant in monosubstituted benzenes.[a]

Subst.[b]	J^o_{23}[c]	J^m_{24}	J^p_{25}	J^m_{26}	J^o_{34}	J^m_{35}	Calculated from Ref.
CH_3[d]	0.10	-0.12	-0.08	0.49	-0.01	0.13	10
I	0.39	-0.23	-0.22	0.51	-0.07	0.48	26
Cl	0.51	-0.24	-0.21	0.90	-0.03	0.35	26
F[d]	1.0	-0.25	-0.28	1.35	0.1	0.43	25

[a] The benzene values used; $J^o = 7.54$ Hz, $J^m = 1.37$ Hz and $J^p = 0.69$ Hz.
[b] The C-atom carrying the substituent is designated C-1.
[c] $\Delta J = J_{C_6H_5X} - J_{C_6H_6}$.
[d] Values for neat liquid.

The aromatic proton-proton coupling constants found in this work fall within the characteristic range for these constants. The effects on the proton-proton couplings appear to be essentially determined by inductive effects.[20] These couplings are attributed to σ-electron interaction except for the *para* coupling which is assumed to operate through a $\sigma - \pi$ mechanism.[21] J^o_{HH} and $J^m_{H,H}$ have been calculated for several dihalogenated toluenes (Table 1), based on the additivity of the substituent effects, ΔJ (Table 2) on the couplings involved. The substituent constant, ΔJ, has been calculated from appropriate values for the coupling constants in benzene together with parameters for the relevant monosubstituted benzenes. The agreement between experimental and calculated coupling constants is reasonable and the disagreement in these values can be attributed to errors in the ΔJ values which may be cumulative. The differences between calculated and experimental values are larger when the two halogen atoms are in positions 2 and 5 relative to the methyl group than when 2,4-substitution is present. This variation might be due to medium effect, errors in the ΔJ values or interaction between the halogen substituents.

From the observation that both J^o_{H,CH_3} and J^p_{H,CH_3} are negative whereas J^o_{F,CH_3} and J^p_{F,CH_3} are positive, it follows[2] that the π-electron contribution to J^o_{HF} is negative. The π-contribution to J^o_{HH} and J^o_{HF} in

Table 3. Proton chemical shifts in Hz from TMS.

Compound	CH_3	H_3	H_4	H_5	H_6
I	124.9	427.5		428.4	400.8
II	125.2	395.0	435.6		438.1
III	125.4	403.1	414.8		414.3
IV	130.55	423.3	398.4		402.3
V	129.1	411.8		400.2	414.5
IV	129.3	403.0	410.5	415.8	

benzene derivatives is usually smaller than the σ contribution.[12] Blears *et al.*[6] rationalized the negative sign of $J^p{}_{HF}$ for 3-fluoro-4-amino-5-bromotoluene on the basis of a substantial contribution from the π-electrons together with a positive Q_{CF}. It is reasonable to expect a similar mechanism for $J^p{}_{HF} = -0.87$ Hz in compound (VI) (Table 1). Apparently, the value of $J^p{}_{HF}$ (0.46 Hz) for compound I does not fit into the proposed mechanism, but both negative and positive values have been reported.[21] The range of $J^p{}_{HF}$ (-2.1 to 2.2 Hz)[21] can be attributed qualitatively to the larger range of Q_{CF}[22] and partly to changes in the bond order for the CF bond. Dharmatti *et al.*[23] correlated the *para* H−F coupling in *ortho* and *meta* substituted fluorobenzenes to the σ and π electron density in the benzene ring and concluded that $J^p{}_{HF}$ decreases with increasing electronegativity of the substituents. A greater effect was observed for substitution *meta* to the fluorine atom. Relative sign determination by spin decoupling has shown that $J^p{}_{HF}$ can have either sign.[6,21,24] The observed $J^o{}_{HF}$ values are well within the reported range[21] (6.2 to 11.4 Hz); the variation in $J^o{}_{HF}$ is expected because substitution primarily perturbs the π-electron system and this variation indicates a substantial π-electron contribution to this coupling.

It is surprising to note that $J^m{}_{HF}$, where only small contribution is expected, also varies over an anomalous π-electron range, 4.5 to 7.9 Hz (Table 1), but $J^m{}_{HF}$ is reported to vary with the electronegativity of the substituents.[25]

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