THE EFFECT OF STERIC HINDRANCE
UPON C^{13} - H^1 COUPLING CONSTANTS AND METHYL PROTON CHEMICAL SHIFTS

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The steric inhibition of resonance model has served as a rationalization for a wide variety of "anomalous" chemical and physical characteristics[1]. We have found that the magnitude of methyl C^{13} - H^1 coupling constants can be correlated with Hammett σ constants in substituted aromatic systems[2]. In order to study the effect of steric hindrance upon this parameter in crowded aromatic systems, a series of ortho- and di-ortho- substituted dimethylanilines, diethylanilines, and methylanilines were obtained, and the C^{13} - H^1 coupling constants for the N-methyl groups were determined (Table I).

If the validity of the Fermi contact mechanism and the isovalent hybridization concept is accepted, a decrease in the N-methyl C^{13} - H^1 coupling is indicative of a decrease in the effective electronegativity of the alkylamino nitrogen[3].

2,6-Dimethyl substitution in toluene, anisole, and N-methylaniline produces a decrease of ca. 0.5 Hz in coupling constant relative to the unsubstituted parents; this effect is presumed to be primarily an inductive one. Analogous substitution in the N,N-dialkylanilines results in a decrease of at least 1.5 Hz, of which approximately 0.5 Hz can be attributed to the "normal" electrical effect of 2,6-dialkyl substitution. Steric inhibition of resonance interactions of the type:
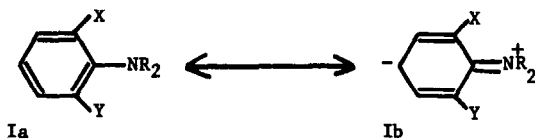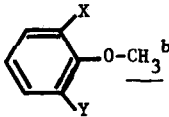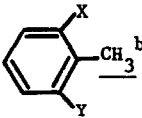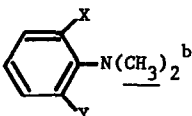

Ia   Ib
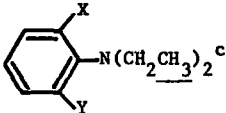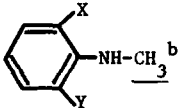
Table I. Methyl $C^{13} - H^1$ Coupling Constants $(\pm 0.2$ Hz$)^a$

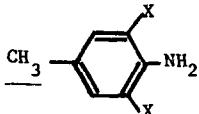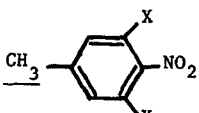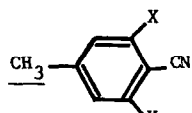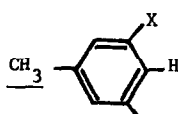| Compound	X	Y	$J(CH_3)$
ortho-disubstituted $-O-CH_3$ [b]	H	H	143.2
	CH_3	CH_3	142.7
ortho-disubstituted $-CH_3$ [b]	H	H	125.8
	CH_3	CH_3	125.4
	Cl	Cl	129.5
ortho-disubstituted $-N(CH_3)_2$ [b]	H	H	134.5
	CH_3	H	133.9
	CH_3	CH_3	133.0
	C_2H_5	H	133.9
	C_2H_5	C_2H_5	132.9
	Cl	H	135.0
	Cl	Cl	135.1
	CH_3	Cl	134.3
ortho-disubstituted $-N(CH_2CH_3)_2$ [c]	H	H	133.8^d
	CH_3	H	132.1^d
	CH_3	CH_3	131.7^d
ortho-disubstituted $-NH-CH_3$ [b]	H	H	135.1
	CH_3	CH_3	134.65
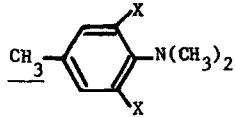
(a) The constants were obtained on a Varian A-60D spectrometer by standard sidebanding techniques using a Hewlett-Packard 200 CD oscillator and a 522B electronic counter. Each value is the average of at least five traces.

(b) 0.30 ml or 0.30 g of solute/1 ml of carbon tetrachloride

(c) 0.50 ml or 0.50 g of solute/1 ml of carbon tetrachloride

(d) ±0.4 Hz

Table II. para-Methyl Chemical Shifts[a] ($\pm$0.3 Hz)

Compound	X	$\underline{\delta}$(CH$_3$)	$\underline{\Delta}$
II	H	132.3	
	CH$_3$	131.3	1.0
III	H	131.7	
	CH$_3$	127.6	4.1
IV	H	147.8	
	CH$_3$	137.5	10.3
V	H	144.4	
	CH$_3$	138.6	5.8
VI	H	139.7	
	CH$_3$	133.8	5.9

(a) 1% solutions in carbon tetrachloride

provides a rationalization for the remainder of this decrease. As the importance of resonance contributor Ib decreases, the effective electronegativity of nitrogen decreases with an accompanying attenuation of the $C^{13} - H^1$ coupling constant. The coupling constants observed for the ortho-chloro derivatives of N,N-dimethylaniline can be explained in a similar fashion. The constant for the 2,6-dichloro derivative is only 0.6 Hz greater than that of the parent, whereas 2,6-dichlorotoluene and toluene differ by 3.7 Hz.

Chemical shift data for aromatic methyl groups (Table II) provide further evidence for steric inhibition of resonance. The chemical shifts for those 2,6-dialkyl compounds having little or no ortho steric interaction (compounds III, V, and VI) are 4-6 Hz less than those of the unsubstituted parents. The 1.0 Hz difference observed in the N,N-dimethyltoluidines (II) is indicative of decreased resonance interactions, as is the 10.3 Hz difference for the nitrotoluenes (IV).

References

1. For examples, see: (a) G. S. Hammond and M. F. Hawthorne, "Steric Effects in Organic Chemistry", M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 164; (b) R. W. Taft, Jr. Reference 1a, p. 556; for a more recent application of the model to some mass spectroscopic data, see: (c) M. M. Bursey, J. Am. Chem. Soc., 91, 1861 (1969).

2. Claude H. Yoder, Richard H. Tuck, and Ronald E. Hess, J. Am. Chem. Soc., 91, 539 (1969).

3. H. A. Bent, Chem. Rev., 61, 275 (1961).