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The Internal Chemical Shift - A Key To Bonding In Aromatic Molecules. 2. Substituent Effects On The Carbon-13 Magnetic Resonance Spectra Of The 1,4-disubstituted Benzenes

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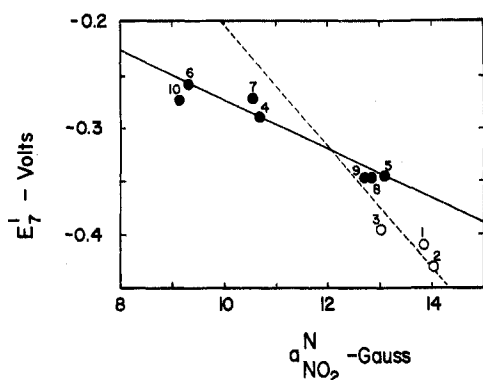


Figure 3. Correlation of one-electron redox potentials E_7^1 with nitrogen hyperfine constants $a_{\text{NO}_2}^{\text{N}}$. Numbers relate to number of compounds in Table II. For the values of $a_{\text{NO}_2}^{\text{N}}$ used see Table III and text. The dashed line is the line drawn in ref 7 and fits the mononitrobenzoates (open circles). The dinitro derivatives (solid circle) are correlated by the solid line.

the result of the difference in spin density distribution. The carbon para to the nitro group bears a considerable spin density ($\sim 15\%$) while the meta carbon has a negligible amount. Therefore, in the *p*-nitrobenzoato complex, a channel is provided for the electron to be transferred to the metal center; in the *m*-nitrobenzoato complex, such channeling is limited. The 100-fold faster electron transfer rate in the ortho isomer probably arises from overlap of the nitro and carboxylate orbitals providing an efficient pathway to the metal center. The spin densities on the coordinated radical appear to establish the trends and correlation with the intramolecular rates for other nitroaromatic carboxylate complexes will be discussed in a separate publication.²⁴

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The Internal Chemical Shift—A Key to Bonding in Aromatic Molecules. 2. Substituent Effects on the Carbon-13 Magnetic Resonance Spectra of the 1,4-Disubstituted Benzenes¹

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Carbon-13 magnetic resonance shifts were determined for six families of 1,4-disubstituted benzenes. Linear least-squares correlations between the internal shifts of the families suggest an additivity relationship for ^{13}C substituent effects at all four nonidentical ring carbons and at the α position when one of the substituents has a central carbon. The correlation of ^1H and ^{13}C shifts for these compounds is also linear, implying that the additivity relationships derived in a previous ^1H study can be generalized to ^{13}C .

Introduction

The ^{13}C spectra of many aromatic substances have been reported in recent years. Except for early investigations by Lauterbur,²⁻⁶ Spiess and Schneider,⁷ and Savitsky⁸ little attention was paid the substituted benzenes before 1965. Perhaps the need to characterize more complex systems

prompted that neglect. In any case Dhimi and Stothers⁹⁻¹¹ and Grant et al.¹² were among the few later investigators who showed any marked interest in the substituted benzenes.

The studies of Grant and co-workers¹² suggested a possible theoretical model for ^{13}C shifts. The shift was attributed to contributions from the π -charge density, ΔQ_{π} , the σ -charge

TABLE I: ^{13}C Shifts of the 4-Z-Substituted Nitrobenzenes (in ppm) Relative to TMS

Z	$\text{C}_1(\text{Z})$	$\text{C}_2(\text{Z})$	$\text{C}_3(\text{NO}_2)$	$\text{C}_4(\text{NO}_2)$	ΔC_{23}
NMe ₂	154.09	110.08	125.83	135.75	-15.75
OMe	164.52	113.93	125.67	141.39	-12.0
F	160.99	115.79	125.99	144.29	-9.92
	171.23	116.75	126.39		
Me	145.79	129.64	123.29	146.07	6.35
Et	151.83	128.45	123.49	146.19	5.16
<i>t</i> -Bu	158.65	126.03	123.17	145.79	2.86
Cl	141.15	129.44	124.80	146.43	4.64
Br	129.71	132.46	124.80	146.87	7.66
I	102.38	138.45	124.68	147.62	13.77
COOMe	135.40	130.60	123.45	150.48	7.15
CH=O	140.0	130.36	124.21	151.07	6.15
CN	116.67	133.33	124.17	150.0	9.16
COCl	137.94	132.10	123.89	151.47	8.21

TABLE II: ^{13}C Shifts of the 4-Z-Substituted Benzonitriles (in ppm) Relative to TMS

Z	$\text{C}\equiv\text{N}$	$\text{C}_1(\text{Z})$	$\text{C}_2(\text{Z})$	$\text{C}_3(\text{CN})$	$\text{C}_4(\text{CN})$	ΔC_{23}
NMe ₂	97.22	150.34	111.31	133.14	120.48	-21.83
NH ₂	99.76	150.44	114.29	133.57	120.04	-19.28
OMe	103.85	162.7	114.68	133.77	119.01	-19.09
OH	102.98	160.12	116.39	134.17	119.0	-17.78
Me	109.29	143.49	129.64	131.83	118.93	-2.19
H	112.46	132.58	128.97	131.98	118.65	-3.01
Cl	110.75	139.40	129.52	133.17	117.70	-3.65
Br	111.27	127.78	133.17	132.46	117.78	0.71
I	111.71	100.00	138.29	132.94	117.86	5.35
COMe	116.23	139.84	128.53	132.30	117.70	3.77
NO ₂	118.29	150.0	124.17	133.33	116.67	9.16

density, ΔQ_σ , and the mobile bond order, ΔP , by the empirical relation

$$\delta_{^{13}\text{C}} = 100\Delta Q_\pi + 67\Delta Q_\sigma - 76\Delta P \quad (1)$$

Equation 1 predicted the ^{13}C shift relative to benzene to a sufficient accuracy that later refinements¹³ have not been published. The Schneider model for the shifts of aromatic protons^{14,15}

$$\delta = k\Delta\rho \quad (2)$$

related changes in π -charge density at carbon, $\Delta\rho$, to the shift, δ , of the attached proton. Unlike the Grant model, no theoretical basis was used to derive the latter and all other contributions were combined in k .

Several difficulties plague these shift models. The data bases used in their construction were slight and disorganized, and some anomalous substituent effects were required. A recent report¹⁶ summarizes the differences one notes between the conclusions drawn from preliminary ^1H shift studies and the fruits of an exhaustive approach and a current paper¹⁷ summarizes some theoretical considerations. Similar thoroughness should be required for a proper analysis of the ^{13}C shifts of these compounds if the results are to be useful to theoreticians and to students of higher aromatic compounds.

Experimental Section

The ^{13}C shift measurements were made at 25.2 Mhz with a Varian XL-100 high-resolution spectrometer and peripherals. The typical spectrum was obtained on a sample of the purified benzene in DCCl_3 (~100 mg/3 ml) in a 12-mm tube

using TMS as the internal standard. Proton and noise decoupling were employed and all accumulations were obtained by standard pulse delay techniques.¹⁸ Assignments were based on spin coupling measurements, relaxation times, and relative peak intensities. Sample sources and purification techniques have been reported elsewhere.^{16,19}

Computer graphics were run on a Texas Instruments Model 980A computer equipped with JEOL 10 bit DAC's and a Tektronics Model 604 oscilloscope at a resolution of 1024 channels. Linear least-squares analyses of the data were performed on an IBM 370/168 computer as well as the TI 980A. A detailed description of these systems is contained in a recent ACS Symposium Monograph.²⁰

Results and Discussion

The ^{13}C shifts for the 4-substituted nitrobenzenes and benzonitriles are summarized in Tables I and II. Those data, together with the shifts of other 4-substituted benzenes (see Tables III and VI), give a consistent picture for substituent interactions.

Figure 1 is an example of the linear relationships found between the internal shifts, ΔC_{23} , of the families of 1,4-disubstituted benzenes. A listing of the calculated slopes and intercepts for the correlations is given in Table VII. Obviously the additivity relationships that were suggested for the ^1H internal shifts¹⁶ must apply to their ^{13}C counterparts because the substituents again seem well behaved.

One can use these internal shift correlations together with the data in Tables I-VI to predict the shifts of other members of a family. For example, if one required the internal shift for 4-fluorobenzonitrile he could insert the shift of -16.53 ppm for 4-fluorobenzoic acid (see Table III) into the equation,

TABLE III: ^{13}C Shifts for the 4-Z-Substituted Benzoic Acids (in ppm) Relative to TMS

Z	COOH	C ₁ (Z)	C ₂ (Z)	C ₃ (COOH)	C ₄ (COOH)	$\Delta_{\text{C}_{23}}$
NMe ₂	167.26	152.82	110.56	130.67	116.79	-20.11
NH ₂	167.14	152.82	112.34	130.95	116.71	-18.61
OMe	166.71	162.54	113.53	131.07	122.82	-17.54
F	169.64	166.15	115.83	132.10	127.38	-16.53
		159.72	114.96	131.75	127.26	
H	172.42	133.65	128.33	130.12	129.29	-1.79
Br	166.31	126.63	131.39	129.82	131.03	1.57
I	166.55	100.79	137.30	130.79	130.12	6.51

TABLE IV: ^{13}C Shifts for the 4-Z-Substituted Acetophenones (in ppm) Relative to TMS

Z	COMe	C ₁ (Z)	C ₂ (Z)	C ₃ (COMe)	C ₄ (COMe)	$\Delta_{\text{C}_{23}}$
NH ₂	196.27	151.31	113.45	130.60	127.34	-17.15
OMe	196.35	163.33	113.61	130.44	130.28	-16.83
F	196.07	170.67	115.95	130.99	133.61	-15.28
		160.56	115.08	130.60	133.53	
H	197.18	132.82	128.10	128.33	136.98	-0.23
Cl	196.39	139.33	129.52	128.73	135.32	0.79
Br	196.47	135.71	131.67	129.60	128.02	2.07
CN	196.15	117.70	132.30	128.53	139.84	3.77
I	196.71	100.83	137.62	129.44	136.19	8.88

TABLE V: ^{13}C Shifts of the 4-Z-Substituted Benzoyl Chlorides (in ppm) Relative to TMS

Z	COCl	C ₁ (Z)	C ₂ (Z)	C ₃ (COCl)	C ₄ (COCl)	$\Delta_{\text{C}_{23}}$
NH ₂	167.02	150.91	113.61	131.43	119.25	-17.82
OH	166.39	165.52	114.37	133.85	125.04	-19.48
<i>i</i> -Pr	167.58	157.14	126.94	131.55	130.71	-4.61
Cl	166.47	141.98	129.53	132.34	131.35	-2.81
I	166.55	100.83	137.30	130.79	130.04	6.51
NO ₂	166.75	151.47	123.89	132.10	137.94	8.21

TABLE VI: ^{13}C Shifts of the 4-Z-Substituted Benzaldehydes (in ppm) Relative to TMS

Z	CH=O	C ₁ (Z)	C ₂ (Z)	C ₃ (CHO)	C ₄ (CHO)	$\Delta_{\text{C}_{23}}$
NMe ₂	189.72	154.17	110.91	131.71	125.12	-20.8
OH	190.79	161.27	115.83	132.30	129.88	-16.5
Me	192.18	138.73	127.80	129.80	133.37	-2.0
<i>i</i> -Pr	191.63	155.99	126.94	129.80	134.48	-2.86
Cl	190.40	140.67	129.29	130.67	134.64	-1.38
I	190.91	102.58	138.25	130.60	135.52	7.65
NO ₂	189.96	151.07	124.21	130.36	140.0	6.15

$\Delta_{\text{F,CN}} = 0.990\Delta_{\text{F,COOH}} + 0.893$ (see Table VII) and obtain a predicted value for $\Delta_{\text{F,CN}} = -15.47$ ppm. Similar calculations for shifts known in both families suggest an uncertainty of less than 2 ppm in the estimates of large negative shifts such as this and 0.5 ppm for the smaller, positive shifts. The approximate error is about 10% for most estimates. Considering the relative magnitudes of ^{13}C shifts an uncertainty of that magnitude is small enough to make line assignments when it is used in conjunction with intensity data from the FT output of the spectrometer.

Similar correlations were found between the $\Delta_{\text{C}_1-\text{C}_3}$ (and their $\Delta_{\text{C}_2-\text{C}_4}$ reciprocals) for these series (see Table VIII). These correlations of internal shifts at alternate carbons are quite good in all cases, suggesting an additivity of substituent effects even at C₁ and C₄.

Tables II-VI contain the ^{13}C shifts for sites external to the skeleton of the ring. The shifts for these α -carbons on 4 substitution parallel the trends at C₂ and are consistent with observations reported for other external nuclei such as ^{19}F in

substituted fluorobenzenes^{21,22} and ^{11}B in the benzenboronic acids.²³ One observes a threefold increase in the magnitude of the shift induced at the α -carbon of the benzonitriles over that induced at an α -boron (see Figure 2). The ^{13}C shift ranges for the other families are much smaller however, spanning only 2 ppm in the benzaldehyde family.

When one plots the internal shifts between the families of 1,4-disubstituted benzenes that are reported here against those of a previous ^1H NMR study,¹⁶ he notes some very interesting and distinctive relationships. Take Figure 3 for example. The substituents seem to fall into two sets when $\Delta_{\text{C}_2-\text{C}_3}$ is plotted against $\delta_{\text{(H}_2-\text{H}_3)}$. That is, two parallel lines correlate the substituents and the jump from one set to the other is equal in every case to the internal proton shift of the parent compound in the family. One set of substituents correlates directly while the other set correlates with its corresponding relative internal proton chemical shift.

In the previous paper¹⁶ the shift additivity relationship for ring protons suggested that the internal shifts due to the ref-

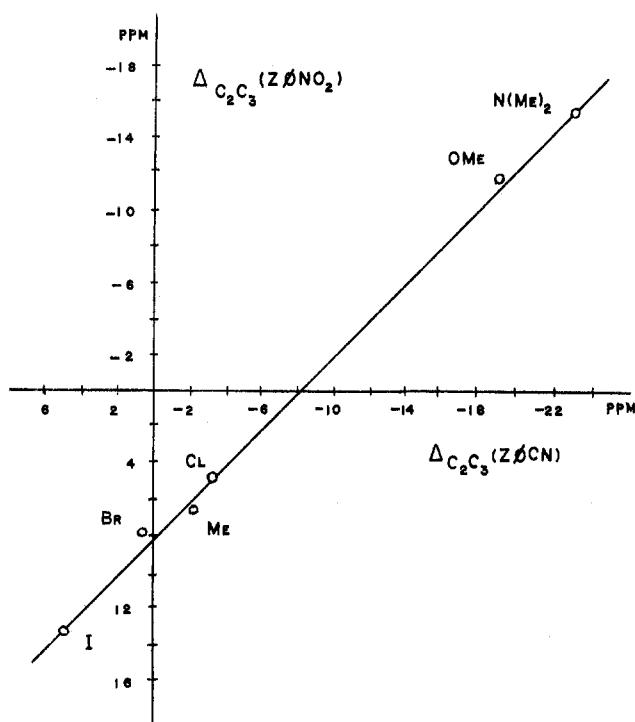


Figure 1. Internal ($\Delta_{C_2-C_3}$) shift correlation for the 4-substituted nitrobenzenes vs. the 4-substituted benzonitriles.

TABLE VII: Internal ^{13}C Shift Correlations (C_2-C_3) between Families of 1,4-Disubstituted Benzenes

Groups	Slope	Intercept	Corr coeff
$\text{NO}_2\text{-CN}$	0.931	-7.73	0.999
$\text{NO}_2\text{-COOH}$	0.914	-6.78	0.998
$\text{NO}_2\text{-CHO}$	0.955	-5.59	0.986
$\text{NO}_2\text{-COCH}_3$	0.985	-5.40	0.998
CN-COCl	1.008	+0.264	0.993
CN-COOH	0.990	+0.893	0.999
CN-CHO	0.952	+0.585	0.987
CN-COCH_3	1.038	+2.840	0.999
COCl-CHO	0.879	+0.746	0.992
COOH-H	1.084	+1.77	0.994
CN-H	1.130	+2.67	0.996
$\text{NO}_2\text{-H}$	1.158	-5.81	0.995

TABLE VIII: Internal Shift Correlations (C_1-C_3) between Families of 1,4-Disubstituted Benzenes

Groups	Slope	Intercept	Corr coeff
CHO-CN	1.029	-4.382	0.999
COOH-CN	0.9803	-3.143	0.995
$\text{NO}_2\text{-CN}$	1.016	-10.43	0.999
$\text{NO}_2\text{-COCH}_3$	1.013	-6.807	0.996
COOH-COCH_3	0.955	1.475	0.995
H-COCH_3	0.895	4.845	0.999
H-NO_2	0.906	11.03	0.995
H-CN	0.935	0.715	0.997

reference substituent were subtracted out of the relative internal shift. If so the correlation of substituents on the lower line in Figure 2 might infer that the ^{13}C internal shifts for that set of substituents were perturbed by the reference substituent while the ^1H shifts were not, relative to ^{13}C . Also, the slopes

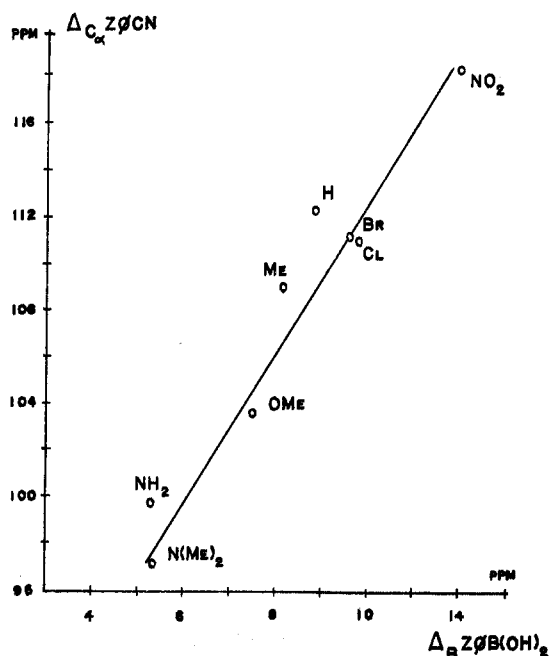


Figure 2. Correlation of the α -carbon shifts of a series of 4-substituted benzonitriles vs. the ^{11}B shifts of the 4-substituted benzenboronic acids.

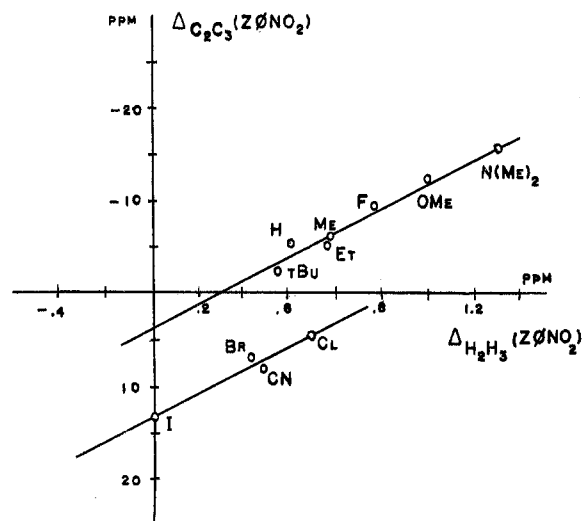


Figure 3. Internal ($\Delta_{C_2-C_3}$) shifts vs. internal ($\delta_{\text{H}_2-\text{H}_3}$) shifts of the 4-substituted nitrobenzenes.

for the other families of shifts should be equal and they are nearly identical for the benzonitriles and benzoic acids, differing only slightly for the nitrobenzenes. Apparently an interaction term does not subtract out in the latter series.

On close inspection an additional factor must be considered when analyzing these data. When one considers the shift relationships using computer graphics, it becomes obvious that both the ^{13}C and ^1H internal shifts always can be scaled to an interval of 0 to π . The transition from one parallel line to the other always comes at $\pi/2$ in the interval regardless of the substituent that falls there. That is, the proton shift range is 0 to 1.51 ppm for the nitrobenzenes, -0.46 to 0.77 ppm for the benzonitriles, and 0.17 to 1.08 ppm for the benzoic acids. The median values ($\pi/2$) are 0.75, 0.15, and 0.49, respectively, and the divergence occurs for each series at about those shifts. Further, when one makes a similar scaling of the ^{13}C shifts for

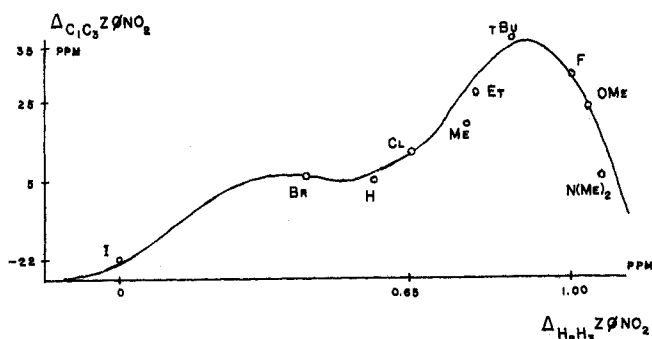


Figure 4. Internal ($\Delta_{C_1-C_3}$) shifts vs. the internal ($\Delta_{H_2-H_3}$) shifts of the 4-substituted nitrobenzenes. The shape function is $-\sum_{k=1}^4 (-1)^k (2/k) \sin kx$.

these three series the respective median positions of 6.99, -6.34, and -6.80 ppm also seem to represent the points of divergence. These positions correspond to a shift of less than *t*-Bu but greater (more negative) than Cl for the nitrobenzene series, less than OH but greater than H for the benzonitrile series, and less than H but greater than Br for the benzoic acid series. So the absolute electronic properties of the substituent itself do not seem to be a factor of import.

When one examines the relationships between $\Delta_{C_1-C_3}$ and $\Delta_{H_2-H_3}$ the scope of this proposed angular relationship becomes even clearer. Figure 4 was obtained by a computer graphics analysis of the fit of the Euler-Fourier²⁴ series

$$-\sum_{n=1}^k (-1)^n \left(\frac{2}{k}\right) \sin kx$$

to the data. This series gives $y = mx$ as k becomes infinite and the series is finite over the interval, $-\pi < x < \pi$.²⁵ For these data sets an excellent fit is obtained when $k = 4$ and other expansions in k are entirely unsuitable.

The Laplace solution²⁶ for differential equations of the form, $\nabla^2 \phi(x, y) = 0$, is a sine series similar to this. The differential equations can be used to describe field gradients within a two-dimensional frame which result in distortions in the z direction. There $y = b$ and $x = a$ at the boundaries where ϕ vanishes and $\phi_n = \sinh [n\pi(b-y)/a] \sin (n\pi x/a)$ reduces to $\phi_n = \sin (n\pi x/a)$ when $(b/a) = 0.28$. Noting that $\nu_0(^{13}\text{C})/\nu_0(^1\text{H}) = 0.25$, we may be observing the effects of a frequency boundary on the magnetic gradients.

Perhaps it is not surprising that one sees a possible angular dependence in data such as these. After all the empirical equation²⁷

$$H_i = \frac{2\pi\nu_0}{\gamma(1 - \sigma_i)}$$

contains a shielding term, $(1 - \sigma_i)$, suggestive of the range of a cosine function. Also, the well-known " τ " scale of Roberts implies that an entire family of hydrocarbons is bounded within a shift interval of 0 to 10. That interval might well be 0 to 3π . To find parallels among the shifts induced by moieties on the various nuclei to which they can be bonded, we may only need to scale the total absolute shift ranges for each type of nucleus, C, P, B, Sn, etc., to an interval in $n\pi$. A thorough examination of these possible theoretical implications is underway at the present time. If correctly interpreted they could

provide a model from which the now empirical shift equations can be derived.

It has been shown that the substituents induce well-behaved ^{13}C and ^1H chemical shifts in the 1,4-disubstituted benzenes. By well behaved one means that shift additivity prevails at C and H sites throughout the benzenoid system and any substituent interactions are of minor importance. Substituents capable of π conjugation do not seem to interact with their electronic environment in that mode because their influence on the ring current is negligible.¹⁶ In addition the correlation of α -C and α -B magnetic resonance shifts, a most sensitive test of either π conjugation or polarization effects, almost certainly negates that mechanism.

The 1,4 substitution was chosen to minimize any steric interactions so that inductive and conjugation effects could be isolated and examined. According to these ^1H and ^{13}C shift studies it would seem that conjugation effects are negligible and only inductive interactions play a significant role. Further the shift additivity and proportional decrease in shift at the 2, 3, and 4 positions suggests that the inductive influences are transmitted through the σ bonds. If so, the mathematical models proposed by Grant and others can be simplified considerably.

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