

Some Correlations involving ^{13}C Chemical Shifts of Monosubstituted Derivatives of Hexafluorobenzene

By John M. Briggs *† and Edward W. Randall, Department of Chemistry, Queen Mary College, Mile End Road London E1 4NS

^{13}C Chemical shifts in a series of 17 mono-substituted derivatives of hexafluorobenzene have been measured and correlations sought with (i) ^{13}C shifts of monosubstituted benzenes and para-substituted fluorobenzenes; (ii) ^{19}F chemical shifts of monosubstituted hexafluorobenzenes; and (iii) Taft's σ_I and σ_R reactivity parameters. The nuclear Overhauser enhancement in our ^{13}C - $\{^{19}\text{F}\}$ experiments is shown to be small.

ALTHOUGH the first use of ^{19}F wideband decoupling was reported as early as 1966,¹ and despite the now routine use of ^1H decoupling for the observation of ^{13}C spectra at natural abundance levels, there is only one report of the simplification of ^{13}C spectra of fluorinated compounds by noise decoupling techniques.² Since the range of ^{19}F chemical shifts can be as great as 200 p.p.m.³ attempts at complete ^{19}F noise decoupling present a stringent test of the available equipment. The present work has been restricted to a study of mono-substituted derivatives of hexafluorobenzene⁴ where the ^{19}F chemical shift range is only of the order of 30 p.p.m. or 2500 Hz at a field strength of 21.14 kG.

EXPERIMENTAL

Pure specimens of $\text{C}_6\text{F}_5\text{X}$, where $\text{X} = \text{F}, \text{Cl}, \text{NH}_2, \text{NO}_2, \text{CO}_2\text{H}, \text{Me},$ and OMe , were purchased from Fluorochem Ltd., and samples where $\text{X} = \text{Br}, \text{I}, \text{H}, \text{OH}, \text{CH}_2\text{Br}, \text{CH}=\text{CH}_2, \text{CHO}, \text{C}\equiv\text{N}, \text{Ph},$ and SH , were kindly loaned by Dr. A. G. Massey, University of Technology, Loughborough.

^{13}C Spectra at 22.63 MHz were obtained using a Bruker HFX-13 spectrometer operating in the Fourier transform mode at a field strength of 21.14 kG. Samples were contained in 10 mm o.d. tubes, concentrically fitted with 5 mm tubes which held tetramethylsilane (TMS). The ^1H signal of TMS was used to provide a heteronuclear field-frequency lock, and the ^{13}C signal to provide an external homonuclear reference. The lock was maintained on the first lowfield 4.167 kHz sideband of TMS occurring at 90.00 MHz, and ^{19}F wideband decoupling of the fluorine signals of the pentafluorophenyl compounds was performed at 84.67 MHz. Most of the spectra were obtained from neat liquids with the exceptions of $\text{C}_6\text{F}_5\text{-NH}_2, \text{-OH},$ and -CHO , which were dissolved to saturation in CCl_4 . Methanol and benzene were used as solvents for $\text{C}_6\text{F}_5\text{CO}_2\text{H}$ and $\text{C}_6\text{F}_5\text{Ph}$ respectively.

The BSV-2 decoupler proved incapable of performing satisfactory decoupling over a range > 1.5 kHz (18 p.p.m.), and it was therefore necessary to perform more than one experiment for some derivatives in order to observe sharp signals from non-equivalent ^{13}C nuclei. In many cases, this greatly assisted the assignment of the ^{13}C spectrum. The use of noise modulation gave sufficient power over the ^{19}F shift range to reduce the one-bond splitting of ^{13}C signals by ^{19}F , and to remove totally longer range ^{13}C - ^{19}F couplings.

Typical natural abundance ^{13}C spectra were obtained

† Present address: Department of Chemistry, King's College, Strand, London, WC2R 2LS.

‡ A referee comments 'The results in ref. 2 are consistent with either a N.O.E., or longer T_1 for quaternary carbon, and both explanations are possible.' Dr. G. Hawkes (personal communication) suggests that our negative result may be due to low power in the decoupling field.

from hexafluorobenzene derivatives using 512 pulses, each of 12 μs duration, and accumulated in 4 K points using a Fabritek 1074 c.a.t. at a dwell time of 200 μs per point. Fourier transformation of the free induction decays was by means of a Digital PDP 8-I computer interfaced with the 1074 to give spectra 2.5 kHz wide in 2 K points. Total measurement times were of the order of 2.1×10^3 s, and line positions were obtained with an accuracy of 0.05 p.p.m. Bulk diamagnetic susceptibility corrections, theoretically necessary to allow for the use of an external reference, were calculated from Pascal's constants, and found to be less than 0.2 p.p.m. between C_6F_6 and $\text{C}_6\text{F}_5\text{I}$. Since these corrections are small by comparison with the chemical shifts themselves and only slightly larger than other errors, they have been ignored.

RESULTS AND DISCUSSION

The Nuclear Overhauser Enhancement (N.O.E.).—The maximum theoretical N.O.E. of ^{13}C spectra noise decoupled from ^{19}F for an exclusively one bond dipolar relaxation mechanism may be shown to be 2.871.⁵ We have observed no significant effect for ^{13}C nuclei in trifluoroacetic acid presumably owing to the effects of spin rotation contributions to the ^{13}C relaxation mechanism which may result from both the tumbling of the molecule and from internal rotation contributions. The relaxation mechanism may also be partly affected by a chemical shift anisotropy contribution. Approximate comparisons of the *ortho*- ^{13}C resonance of pentafluorotoluene with the ^{13}C resonance of the methyl group, and of the *para*- ^{13}C signals in $\text{C}_6\text{F}_5\text{OMe}, \text{C}_6\text{F}_5\text{-CH}_2\text{Br},$ and $\text{C}_6\text{F}_5\text{CHO}$ with the $^{13}\text{CH}_3, ^{13}\text{CH}_2,$ and ^{13}CHO signals respectively, avoiding the complication of comparisons with ^{13}C nuclei without one-bond ^{19}F coupling where T_1 may be long, show that the N.O.E. in these cases is much smaller than the theoretical maximum enhancement. These findings are in contrast to those of Abraham *et al.*,² but it must be emphasised these apply to smaller molecules where spin rotation contributions may be significant.‡

Chemical Shifts.—The chemical shifts of aromatic ^{13}C nuclei in hexafluorobenzene derivatives are presented in the Table. For the sake of completeness ^{13}C chemical shifts of nuclei not in the aromatic ring are included

¹ R. R. Ernst, *J. Chem. Phys.*, 1966, **45**, 3845.

² R. J. Abraham, D. F. Wileman, G. R. Bedford, and D. Greatbanks, *J.C.S. Perkin II*, 1972, **12**, 1733.

³ J. W. Emsley and L. Phillips, *Progr. N.M.R. Spectroscopy*, 1971, **7**, 36.

⁴ J. M. Briggs, Ph.D. Thesis, London University, 1972.

⁵ I. Solomon, *Phys. Rev.*, 1955, **99**, 559.

along with ^{13}C - ^1H coupling constants, where measurable. The ^{13}C spectra of $\text{C}_6\text{F}_5\text{H}$, noise decoupled from ^{19}F , are shown in the Figure.

Emsley and Phillips³ have discussed theoretical calculations of ^{19}F chemical shifts in perfluoroaromatic

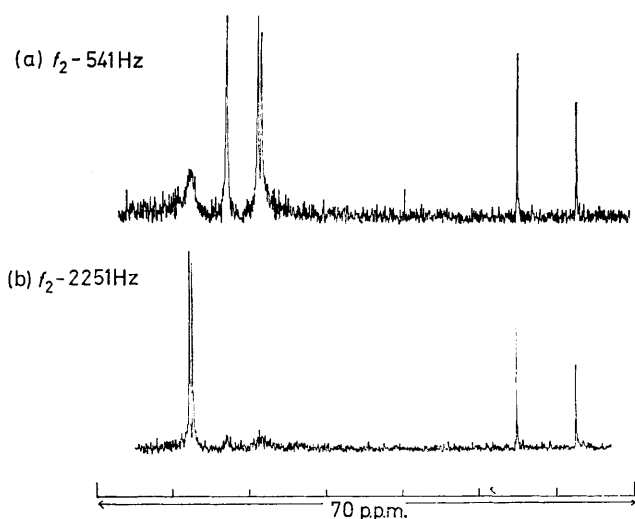
monofluorobenzenes; (ii) ^{19}F chemical shifts in perfluoroaromatics; and (iii) Hammett reactivity parameters.

^{13}C versus ^{13}C Shifts in Substituted Benzenes.— ^{13}C Chemical shifts appearing in the literature have been

^{13}C Chemical shifts of monosubstituted hexafluorobenzene derivatives					
Compound $\text{C}_6\text{F}_5\text{X}$	$\delta^{13}\text{C}(1)$	$\delta^{13}\text{C}(2)$	$\delta^{13}\text{C}(3)$	$\delta^{13}\text{C}(4)$ ^{a,b}	Miscellaneous
F	138.34	138.34	138.34	138.34	
Cl	108.02	144.81	138.34	140.66	
Br	94.74	145.61	138.38	141.29	
I	65.66	147.88	137.74	142.38	
H	100.00	146.53	137.68	141.89	$ J_{\text{C}(1)-\text{H}} $ 169.7 \pm 1.2 Hz $ J_{\text{C}(3)-\text{H}} $ 9.8 \pm 1.2 Hz $ J_{\text{C}(2)-\text{H}} $ 7.3 \pm 1.2 Hz
OH	131.01	138.52 ^c	138.30 ^c	136.14	
OMe	135.02	141.88	138.31	137.34	$\delta^{13}\text{CH}_3$ 61.30 ^a $ ^{\text{CH}_2}J_{\text{CH}} $ 146.5 \pm 2.4 Hz $ J_{\text{C}(1)-\text{H}} $ 4.3 \pm 0.6 Hz
NH ₂	122.55	137.47	138.52	133.93	
Me	110.88	145.41	137.53	139.58	$\delta^{13}\text{CH}_3$ 4.61 ^a $ ^{\text{CH}_2}J_{\text{CH}} $ 131.0 \pm 2.4 Hz $ J_{\text{C}(1)-\text{H}} $ 7.3 \pm 1.2 Hz $ J_{\text{C}(2)-\text{H}} $ 5.3 \pm 1.2 Hz
CH ₂ Br	112.86	145.51	138.21	142.15	$\delta^{13}\text{CH}_2$ 15.50 ^a $ ^{\text{CH}_2}J_{\text{CH}} $ 158.7 \pm 2.4 Hz $ J_{\text{C}(1)-\text{H}} $ 4.3 \pm 0.6 Hz $ J_{\text{C}(2)-\text{H}} $ 4.9 \pm 1.2 Hz
CHCH ₂		145.00	137.75	140.23	$ J_{\text{C}(1)-\text{H}} $ 4.9 \pm 1.2 Hz C(1) Not observed
CHO	111.50	147.81	138.04	145.38	$\delta^{13}\text{CHO}$ 181.14 ^a $ ^{\text{CHO}}J_{\text{CH}} $ 192.9 \pm 1.2 Hz $ J_{\text{C}(1)-\text{H}} $ 26.9 \pm 1.2 Hz
CO ₂ H	108.88	145.51	137.96	143.19	$\delta^{13}\text{CO}_2\text{H}$ 160.67 ^a
SH	106.80	143.98	138.26	139.38	
NO ₂		141.46	138.28	144.32	C(1) Not observed
Ph		143.99	137.68	140.66	C(1) Not observed
CN	90.16	148.37	138.65	145.89	$\delta^{13}\text{CN}$ 106.24 ^a

^a Chemical shifts in p.p.m. to low field of external [^{13}C]TMS; accuracy \pm 0.05 p.p.m. ^b Assignments follow those of ^{19}F resonances, see Table A26 of ref. 3. ^c Assignment ambiguous.

systems; it is clear that they have limited reliability. A variety of empirical correlations is possible, however,



^{13}C Spectra of $\text{C}_6\text{F}_5\text{H}$ at 22.63 MHz noise decoupled from ^{19}F

and conventional comparisons of ^{13}C shifts in the perfluoroaromatics can be made with (i) ^{13}C chemical shifts in monosubstituted benzenes and *para*-substituted

used as a source of comparison with the observed shifts appearing in the Table.^{6,7}

Using the sign convention that chemical shifts are positive to low field of the ^{13}C reference (TMS), for C(1) the relationships are (1) and (2). It is apparent from

$$\delta\text{C}(1)_{\text{C}_6\text{F}_5\text{X}} = 1.045 \delta\text{C}(1)_{\text{C}_6\text{H}_5\text{X}} - 33.26 (\pm 1.22) \text{ p.p.m.} \quad (1)$$

$$\delta\text{C}(1)_{\text{C}_6\text{F}_5\text{X}} = 1.043 \delta\text{C}(1)_{\text{C}_6\text{H}_4\text{FX}} - 28.09 (\pm 1.41) \text{ p.p.m.} \quad (2)$$

equations (1) and (2) that the ^{13}C shift of the substituted carbon atom can be predicted with good accuracy on the basis of a purely additive relationship of the shifts since the slopes of the least mean squares fitted plots are very close to unity and the r.m.s deviations are small by comparison with the range of chemical shifts examined. An initial ambiguity in the assignment of signals from C(1) and CN in $\text{C}_6\text{F}_5\text{CN}$ was removed by using equation (1). For ^{13}C nuclei further from the substituent than C(1), correlations between chemical shifts in $\text{C}_6\text{F}_5\text{X}$, $\text{C}_6\text{H}_5\text{X}$, and *p*- $\text{C}_6\text{H}_4\text{FX}$ are more tenuous; in general, the differences in chemical shift at C(2)—C(4) are much

⁶ H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 1961, **55**, 731.

⁷ G. E. Maciel and J. J. Natterstrad, *J. Chem. Phys.*, 1965, **42**, 2427.

smaller than at C(1). Indeed, for *meta*-¹³C nuclei, C(3), plots of ¹³C chemical shift for C₆F₅X against C₆H₅X or *p*-C₆H₄FX show no direct correlation, and the chemical shift of C(3), with respect to external TMS is constant to within ±0.5 p.p.m. Correlation of the C(2) shifts is better, and shows a closer approach to linearity for the plot of δC(2)_{C₆F₅X} versus δC(2)_{C₆H₅X} than is the case for the plot of δC(2)_{C₆F₅X} versus δC(2)_{C₆H₄FX}. The quality of the fit, nevertheless, is poor. The most successful correlation of unsubstituted carbon chemical shifts is for C(4) where steric interaction and nearest neighbour anisotropy effects are anticipated to be small.

The relationships are expressed in the form (3) and (4)

$$\delta C(4)_{C_6F_5X} = 0.696 \delta C(4)_{C_6H_5X} + 51.68 (\pm 0.90) \text{ p.p.m.} \quad (3)$$

$$\delta C(4)_{C_6F_5X} = 1.279 \delta C(4)_{C_6H_4FX} - 66.45 (\pm 1.80) \text{ p.p.m.} \quad (4)$$

¹⁹F and ¹³C Chemical Shifts.—The ¹³C chemical shift of C(4) may be predicted with satisfactory accuracy from the chemical shift F(4)⁸ of a fluorine nucleus in the *para*-position of C₆F₅X. Comparisons were made of the chemical shifts by referring the ¹³C shift to the ¹³C resonance of external C₆F₆ and the ¹⁹F resonance to the same compound used as ¹⁹F standard.

The relationship is given by equation (5). Correlation

$$\delta C(4)_{C_6F_5X} = 0.393 \delta F(4)_{C_6F_5X} - 0.124 (\pm 0.38) \text{ p.p.m.} \quad (5)$$

between the ¹³C and ¹⁹F chemical shifts in the *ortho*-position displays linearity within rather large limits of error but is poor for the *meta*-resonances.

Taft⁹ has suggested that the ¹⁹F chemical shift in a series of fluorobenzenes is proportional to changes in the π electron density at the carbon atom to which fluorine is attached. If changes in the ¹³C chemical shift with substituent result predominantly from changes in π electron density, then δF(*i*) ∝ δC(*i*). The change of π electron density is larger at the *ortho*- and *para*-positions of the aromatic ring than at the *meta*-position, and good

⁸ M. I. Bruce, *J. Chem. Soc. (A)*, 1968, 1459.

⁹ R. W. Taft, F. Prosser, L. Goodman, and G. T. Davis, *J. Chem. Phys.*, 1963, **38**, 380.

¹⁰ I. J. Lawrenson, *J. Chem. Soc.*, 1965, 1117.

correlations of the ¹⁹F and ¹³C resonances in the *para*-position are obtained, but the poorer relationship for the chemical shifts in the *ortho*-position suggests that other effects, possibly steric or resulting from neighbour anisotropy may be important.

Lawrenson¹⁰ has correlated the ¹⁹F(3) and ¹⁹F(4) chemical shifts in monosubstituted pentafluorophenyl derivatives with the Taft¹¹ parameters σ_I and σ_R. The ¹³C chemical shift may similarly be expressed as in equation (6) and the method of least squares may be

$$\delta C(i) = a\sigma_I + b\sigma_R + c \quad (6)$$

adapted to determine mean values of the constants a—c. For a series of twelve substituents, the ¹³C shift of the *para*-carbon nucleus was found to obey the relationship (7) where chemical shifts are expressed in p.p.m. to low

$$\delta C(4)_{C_6F_5X} = 10.41\sigma_R + 4.01\sigma_I + 3.07 (\pm 0.64) \text{ p.p.m.} \quad (7)$$

field of ¹³C₆F₆.

Ehrenson¹² has examined the relationship between free energy changes in a reaction and changes in electronic energy resulting from changes in substitution and finds the linear relationship of the two to be broadly justified. It may however be misleading to interpret the chemical shifts in close detail in terms of σ_I and σ_R. Equation (7) does however suggest that δC(4) is more strongly influenced by the mesomeric contribution than by the inductive one, as is the case for δF(4). This suggests that the correlation in equation (5) is a reasonable first approximation. However, even in the most favourable case, C(4), the dependence on σ_I suggests that calculations based on π density alone should not be expected to rationalise the ¹³C chemical shifts of C₆F₅X compounds; Levy¹³ has pointed out that both total electron density and π electron density calculations correlate well with δC(4) in monosubstituted benzenes.

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¹¹ R. W. Taft, 'Steric Effects in Organic Chemistry,' ed. Newman, Wiley, New York, 1956.

¹² S. Ehrenson, *Progr. Phys. Org. Chem.*, 1964, **2**, 195.

¹³ G. C. Levy and G. L. Nelson '13C N.M.R. for Organic Chemists,' Wiley, New York, 1972.