Electronic Effect of the Tricyanomethyl Group by ^{13}C and ^{19}F NMR: Nature of Aryl ^{19}F NMR Polar Field Effects in the Benzene and Naphthalene Ring Systems

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A number of tricyanomethyl-substituted aryl derivatives (phenyl, 1- and 2-naphthyl, 1- and 2-fluoronaphthyl), 1-phenyl-4-(tricyanomethyl)bicyclo[2.2.2]octane, and several ammonio-substituted fluorophenyl and fluoronaphthyl derivatives have been synthesized and their ^{19}F and ^{13}C NMR chemical shifts have been measured. An analysis of the data provided the following information. (1) Definitive substituent parameters (σ_I and σ_R^0) for the $C(CN)_3$ group. (2) An unambiguous delineation of polar aryl ^{19}F NMR substituent chemical shifts (SCS) in the benzene and naphthalene ring system into direct field (F_D) and field-induced π polarization (F_π) contributions. (3) Experimental support for the overall validity of the dual substituent parameter (DSP) equation to dissect ^{13}C and ^{19}F SCS into polar and resonance effect contributions. (4) The effective dielectric constant term is a significant parameter determining solvent trends for polar ^{19}F SCS of the $C(CN)_3$ group.

In this paper we report the results of an extensive study of the electronic effects of the tricyanomethyl ($C(CN)_3$) and ammonio ($^+NH_3$) substituents in the benzene and naphthalene ring systems utilizing two sensitive electronic probes, namely, ^{13}C and ^{19}F NMR chemical shifts. The purpose of this investigation was threefold. First, we wanted to dissect the electronic effect of the $C(CN)_3$ substituent into its composite parts, and thus provide definitive values for the appropriate substituent parameters (σ_I and σ_R^0). This objective evolved from our recent analysis[1] of the $C(CN)_3$ group utilizing the β-fluoronaphthyl probe[2] (6β and 7β dispositions),[3] which clearly indicated that it functions in the neutral ground state as a modest hyperconjugative *electron donor*, i.e., σ_R^0 is *negative* (-0.10). At the time we had good reason to believe that this result was probably more reliable than that previously determined by Sheppard and co-workers[4] employing the ubiquitous fluorophenyl tag[5] ($\sigma_R^0 = \pm 0.02$; i.e., a negligible resonance effect). Hence, we presented[1] a very plausible rationale for the observed *negative* σ_R^0 value based on an alternating induced charge (AIC)[6] and hyperconjugative model.[7] An important corollary of this explanation is that hyperconjugation and not an inductomesomeric effect (I_π; π-inductive effect) is the mechanism responsible for the weak apparent electron-withdrawing resonance or mesomeric effect of the trifluoromethyl substituent[8] ($\sigma_R^0 = +0.10$).[9]

Subsequently, it was brought to our attention that more refined multiparameter regression analyses (DSP equation)[10] of ^{19}F NMR substituent chemical shift (SCS)[11] data indicate that previously reported polar susceptibility parameters (ρ_I) for strongly conjugated positions in various systems (*p*-fluorophenyl[5] and 6β-fluoronaphthyl[2]) may be seriously in error. Hence, the validity of the current correlative equations[2,5] on which ^{19}F NMR techniques for analyzing substituent electronic effects are based must clearly be in jeopardy. For this reason, coupled with the fact that the possible resonance contribution for the $C(CN)_3$ substituent is obviously very small relative to its overall large electron-withdrawing influence, the aforementioned ^{19}F NMR derived σ_R^0 values for $C(CN)_3$ must now be viewed as being very insecure.

Therefore, considering the ramifications of the possible *negative* σ_R^0 value for $C(CN)_3$ (vide supra), we deemed it imperative to reanalyze the electronic effect of this group using methodology which allows the measurement of each substituent parameter (σ_I and σ_R^0) in the complete absence of other complicating electronic interactions. In this regard, and bearing in mind the acid–base sensitivity of the $C(CN)_3$ substituent, the infrared intensity technique of Katritzky and Topsom[12] and the recent NMR method of Adcock and Khor[13] seemed highly appropriate for measuring respectively σ_R^0 and σ_I independently of one another.

Secondly, we wanted to quantitatively elucidate further[14] the nature of polar field effects upon ^{19}F chemical shifts[15,16]

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(11) Substituent chemical shifts (SCS) are defined as the difference (ppm) between the chemical shift (^{13}C or ^{19}F) of the substituted compound and that of the appropriate probe (^{13}C or ^{19}F) in the parent hydrocarbon.

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(15) The field effect of polar substituents perturb aryl ^{19}F chemical shifts in two distinct ways:[14,16] (i) the electric field acting through space can polarize the electrons in the CF bond (F_D); and (ii) the electric field can polarize the entire conjugated system, which may lead to a change in the π charge density at the carbon to which fluorine is attached with a concomitant response from fluorine (F_π).

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in the benzene and naphthalene ring systems in the light of our most recent study of this phenomenon in the phenylbicyclo[2.2.2]octane ring system.[17] The study of this model system[17] enabled the coefficient (A) of the Buckingham equation[18] (SCS = AE_z) for linear electric field effects on C_{sp^2}–F bonds [direct-field contribution (F_D)][15] to be reliably calculated as well as the proportionality constant relating ^{19}F and ^{13}C SCS determined only by field-induced π polarization (F_π).[15] We were hopeful that with these parameters,[17b] together with ^{19}F and ^{13}C SCS data for groups ($C(CN)_3$ and $^+NH_3$) with electronic effects dominated by field-inductive contributions, a clearer picture of the positional blend of F_D and F_π effects in aromatic systems determining ^{19}F NMR polar field effects would emerge.

Finally, we wanted to provide a stringent test of the validity of the much used dual substituent parameter (DSP) equation[10] for relating substituent properties (physicochemical or chemical) to reactivity based substituent parameters (σ_I and σ_R). Unfortunately, most experimental support for this equation has been restricted to studies in the benzene ring system which is severely limited by the small number of positions (meta and para) from which substituent electronic influences can be gleaned. Furthermore, this deficiency is compounded by the similar angle/distance dependency relationships (important parameters determining direct field effects) for these two dispositions. However, these handicaps can be readily overcome by utilizing naphthalene as the model system since here there is a large number of nonproximate positional dependencies (10), some with considerably different angle/distance dependency relationships, which provide a formidable testing ground for any general treatment of substituent electronic effects.

Accordingly, we have synthesized 1-phenyl-4-(tricyanomethyl)bicyclo[2.2.2]octane, (tricyanomethyl)benzene, 1- and 2-(tricyanomethyl)naphthalene (and the 4- and 6-deuterio analogues respectively), m-fluoro(tricyanomethyl)benzene, m- and p-ammoniofluorobenzene, as well as all the appropriate $C(CN)_3$- and $^+NH_3$-substituted 1- and 2-fluoronaphthalenes and recorded their ^{13}C and ^{19}F NMR spectra, whatever the case may be, in dilute solutions. In addition, the infrared spectra of (tricyanomethyl)benzene and its m-fluoro derivative were recorded and the intensity of the ν_8 vibrations was accurately measured.

Experimental Section

Synthesis. All the fluoro(tricyanomethyl)naphthalenes as well as (tricyanomethyl)benzene,[4a] m-fluoro(tricyanomethyl)benzene,[4a] and 1-[4a] and 2-(tricyanomethyl)naphthalene (and their 4- and 6-deuterio analogues, respectively) were prepared from the appropriate cyanomethyl precursor according to a method outlined by Sheppard and co-workers[4a] for m-fluoro(tricyanomethyl)benzene with some minor modifications. In particular, potassium hydride[19] was used instead of sodium hydride as a base while THF was employed as solvent instead of 1,2-dimethoxyethane. The new naphthalene derivatives were all purified by sublimation followed by recrystallization. Melting points for these compounds, together with similar information for the immediate precursors (bromomethyl and cyanomethyl derivatives), are reported in Table I.

Except for the 4α[20] and 4β derivatives, all the (bromomethyl)fluoronaphthalenes were obtained from the appropriate fluoromethylnaphthalene (see below) on treatment with N-bromosuccinimide according to a standard procedure.[20,21] The former two compounds were derived from the appropriate carboxylic acids, 4-[20,22] and 3-fluoro-1-naphthoic acid,[22] respectively, by reduction with borane/dimethyl sulfide[23] followed by treatment of the hydroxymethyl derivative with phosphorous tribromide.[24] The cyanomethyl precursors were all prepared in good yield from the bromomethyl compounds on treatment with hot aqueous ethanolic potassium cyanide for 1–2 h. 2-Fluoro-6-methylnaphthalene and 2-fluoro-7-methylnaphthalene were obtained in high yield by the cyclization route recently reported.[25] All the other required fluoromethylnaphthalenes were prepared by new procedures as described below. 1-(Bromomethyl)-4-deuterionaphthalene and 2-(bromomethyl)-6-deuterionaphthalene were prepared as previously described.[25,26] The fluoronaphthylamines were synthesized by standard methods from the corresponding fluorocarboxylic acids, fluoronaphthols, or fluoronitronaphthalenes which were available from previous investigations[2,27] except for 5-fluoro-2-naphthoic acid (see below). Similarly, m- and p-fluoroaniline were obtained from m-fluorobenzoic acid and p-fluoronitrobenzene, respectively, using standard methods.

1-Fluoro-3-methylnaphthalene. Phenylacetone was converted to 3-methyl-4-phenylbutanoic acid according to the method outlined by Newman and co-workers.[28] The acid was cyclized by treatment with trifluoroacetic anhydride[29] to 3-methyl-1-

Table I. Melting Points of the Bromomethyl-, Cyanomethyl-, and Tricyanomethyl-Substituted Fluoronaphthalene Derivatives[a]

orientation[b]	mp, °C		
	CH_2Br[c]	CH_2CN[c]	$C(CN)_3$[c,d,e]
3α	54-56	47-48	104-105
4α	66-67[f] (66-67)[g]	92-93	112-115
5α	75-76	52-54	145-146
6α	43-44	75-77	129-130
7α	61-62	55-57	85-86.5
4β	69-70	129-130	103-104
5β	68-70	76-78	133-134
6β	52-52.5[h] (52-52.5)[g]	77-78	156-157[i]
7β	64-65[j] (66-66.5)[k]	85-86	135-137[l]
8β	60-61	64-65	112-115

[a] A full description of the synthetic procedures including yields, purification techniques, and spectral details of all these compounds may be found elsewhere (Cox, P. C. Ph.D. Dissertation, The Flinders University of South Australia, 1979). [b] See ref 3. [c] The proton NMR and mass spectra were clearly in accord with the assigned structures. [d] The elemental analyses agreed well with those calculated (C, ±0.3; H, ±0.2). [e] 1- and 2-(tricyanomethyl)naphthalene and the corresponding 2-$CH(CN)_2$ derivative have mp's of 108–109 °C (lit.[4a] 109–110 °C), 78–79.5 °C; and 122–123 °C (lit.[m] 123–124 °C), respectively. [f] $CHBr_2$, mp 97–99 °C. [g] Reference 20. [h] $CHBr_2$, mp 88–89 °C. [i] $CH(CN)_2$, mp 90–92 °C. [j] $CHBr_2$, mp 60–61.5 °C. [k] Adcock, W.; Rizvi. S. Q. A.; Kitching, W.; Smith, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 369. [l] $CH(CN)_2$, mp 116–117 °C. [m] Eicher, T.; Eiglmeier, K. *Chem. Ber.* **1971**, *104*, 605.

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tetralone in good yield, which distilled as a colorless oil: bp 80 °C (0.1 mm); ^{1}H NMR[30] (CCl_4, from $SiMe_4$ at δ 0.00) δ 1.1 (3 H, doublet of doublets, CH_3, J = 3, 2 Hz), 2.0–2.9 (5 H, m, aliphatic), 7.42 (3 H, m, aromatics), 7.92 (1 H, d of d, aromatic, J = 7, 2 Hz). The tetralone was converted[22] to the oxime (mp 120.5–121.5 °C; lit.[31] 122.5–123.5 °C), which was treated according to the procedure described by Adcock and Dewar[22] to yield 3-methyl-1-naphthylamine as the hydrochloride. The amine hydrochloride was then converted via the diazonium hexafluorophosphate salt[22] to 1-fluoro-3-methylnaphthalene as previously described for 1-fluoro-7-methylnaphthalene,[2] obtained as a colorless oil: n^{23}_D 1.5828 (lit.[2] n^{18} 1.589).

1-Fluoro-5-methylnaphthalene. The Grignard reagent derived from 1-bromo-5-fluoronaphthalene[2] in ether containing HMPA was treated with freshly distilled dimethyl sulfate under reflux for 6 h. Workup in the usual manner afforded 1-fluoro-5-methylnaphthalene as a colorless oil (82% yield): bp 122–124 °C (18 mm); n^{21}_D 1.5931 (lit.[2] n^{25}_D 1.5923).

1-Fluoro-6-methylnaphthalene. 3-Methylbenzyl chloride (85 g, 0.6 mol) was converted to 4-(*m*-tolyl)butanoic acid (85 g) according to the method recently outlined by Newman et al.[32] for the synthesis of 4-(3-chloro-5-methylphenyl)butanoic acid from 3-chloro-5-methylbenzyl bromide. The acid (24 g, 0.13 mol) was cyclized by treatment with polyphosphoric acid[33] at 90 °C for 2 h in good yield to 6-methyl-1-tetralone,[34] distilled as a colorless oil (18 g, 84%): ^{1}H NMR (CCl_4, from $SiMe_4$ at δ 0.00) δ 2.10 (2 H, m, H3 and H3′), 2.33 (3 H, s, CH_3), 2.50–2.64 (2 H, m, H2 and H2′), 2.85 (2 H, t, H4 and H4′, J = 5.5 Hz), 6.90–7.12 (2 H, m, H5 and H7), 7.80 (1 H, d, H8, J = 8.0 Hz). The oxime (mp 122–122.5 °C, 82 g, 0.47 mol) was converted by the methods indicated above for the conversion of the 1,3 isomer to 1-fluoro-6-methylnaphthalene, obtained as a colorless oil (13.5 g): n^{23}_D 1.5840.

1-Fluoro-6-methylnaphthalene was treated with *N*-bromosuccinimide in the usual way[20,21] to obtain 2-(bromomethyl)-5-fluoronaphthalene (see Table I). A sample of the bromomethyl compound was converted to 5-fluoro-2-naphthaldehyde (mp 53–55 °C) according to the method outlined by Hass and Bender[35] for the preparation of *o*-tolualdehyde. Chromic acid oxidation of the aldehyde afforded 5-fluoro-2-naphthoic acid (mp 229–230 °C), which was converted to 2-amino-5-fluoronaphthalene in the usual way.[22] This amine was identical with a sample of 2-amino-5-fluoronaphthalene previously prepared by an entirely different route[22] (see Table VIII for ^{19}F SCS).

1-Fluoro-7-methylnaphthalene was prepared in good yield by treatment of the hydroxyacetal derivative derived from *o*-fluorobenzylmagnesium chloride and 4,4-dimethoxybutan-2-one with 10% sulfuric acid for 2 days under reflux. 1-Fluoro-7-methylnaphthalene, distilled as a colorless oil, was identical with a sample previously obtained by a less convenient route.[2]

It should be noted that we have previously shown[25] that this cyclization procedure[36] is an excellent method for the preparation of the 2,6 and 2,7 isomers.

2-Fluoro-5-methylnaphthalene. β-(*m*-Fluorophenyl)-propionic acid[37] was converted to 4-(*m*-fluorophenyl)butanoic acid according to the classical Arndt–Eistert procedure[38] for one-carbon homologation of aliphatic carboxylic acids. It should be noted that the recent homologation procedure of Newman et al.,[32] which was employed in this work for synthesizing 4-(*m*-tolyl)butanoic acid (vide supra), is clearly a superior method for fairly large scale operations. The acid was cyclized to 6-fluoro-1-tetralone as described above for the methyl analogue. The tetralone was identical with a sample previously prepared[27] by a less efficient procedure.[39] Treatment of 6-fluoro-1-tetralone with methylmagnesium bromide in the usual manner afforded 6-fluoro-1-methyl-1-tetralol, which was dehydrated by heating with potassium bisulfate[40] to 6-fluoro-1-methyl-3,4-dihydronaphthalene. A benzene solution of this compound was treated with 2,3-dichloro-5,6-dicyanoquinone under reflux[41] to afford 2-fluoro-5-methylnaphthalene, distilled as a colorless oil: n^{23}_D 1.5821 (lit.[2] n^{21}_D 1.587).

2-Fluoro-8-methylnaphthalene was prepared from 7-fluoro-1-tetralone[22] in the same way as described above for the conversion of 6-fluoro-1-tetralone to the 2,5 isomer. 2-Fluoro-8-methylnaphthalene distilled as a colorless oil: n^{22}_D 1.5825 (lit.[21] n^{17}_D 1.5872).

1-Phenyl-4-(tricyanomethyl)bicyclo[2.2.2]octane. 4-Phenyl-1-bicyclo[2.2.2]octylcarboxylic acid[17b,42] (8.8 g, 0.038 mol) was treated with borane–THF[43] (25 mL of 2 M solution, 0.05 mol) to afford 1-(hydroxymethyl)-4-phenylbicyclo[2.2.2]octane, which was obtained as a white solid after sublimation (6 g, 73%), mp 80–81.5 °C. Treatment of the alcohol with Ph_3P/CCl_4[44] afforded 1-(chloromethyl)-4-phenylbicyclo[2.2.2]octane (mp 61–63 °C) almost quantitatively. The chloromethyl derivative (4.0 g, 0.017 mol) was converted to 1-(cyanomethyl)-4-phenylbicyclo[2.2.2]-octane in poor yield (250 mg, 7%, mp 98–100.5 °C) according to a method outlined by Smiley and Arnold.[45] An attempt to convert the nitrile derivative directly to 1-phenyl-4-(tricyanomethyl)-bicyclo[2.2.2]octane in the usual manner[4a] (vide supra) was unsuccessful. 1-(Chloromethyl)-4-phenylbicyclo[2.2.2]octane (9 g, 0.039 mol) was converted via the Grignard in the usual way to 4-phenyl-1-bicyclo[2.2.2]octylacetic acid. Sublimation followed by recrystallization from hexane afforded white needles (6.4 g, 68%), mp 146–147 °C. The acid was converted to 4-phenyl-1-bicyclo[2.2.2]octylmalonic acid according to the procedure of Pfeiffer et al.[46] for carboxylating alkanoic acids. Recrystallization from aqueous ethanol afforded the malonic acid derivative as fine white needles (5.5 g, 76%), mp 245–247 °C. A small sample of the dimethyl ester (mp 66–67 °C) was prepared for characterization (^{1}H NMR, mass spectrum): ^{1}H NMR ($DCCl_3$, from $SiMe_4$ at δ 0.00) δ 3.13 (1 H, s, aliphatic), 3.40 (12 H, s, aliphatic) 3.60 (6 H, s, aliphatic), and 7.17 (5 H, s, aromatic); m/e 252.

4-Phenyl-1-bicyclo[2.2.2]octylmalonic acid (576 mg, 0.002 mol) was heated under reflux with purified thionyl chloride (0.6 g, 0.005 mol) in ether (50 mL) for 24 h. Ammonia gas was then rapidly passed into the solution for 20 min. Workup followed by recrystallization from ethanol gave 4-phenyl-1-bicyclo[2.2.2]-octylmalonamide (500 mg, 87%), mp 288–290 °C. On a larger scale, decarboxylation became a significant side reaction. The malonamide (572 mg, 0.002 mol) was converted to 4-phenyl-1-bicyclo[2.2.2]octylmalononitrile according to the procedure of Campagna et al.[47] for the synthesis of nitriles from primary amides. Sublimation followed by recrystallization from hexane afforded white needles (330 mg, 66%), mp 139–141 °C.

The malonitrile (500 mg, 0.002 mol) was converted to 1-phenyl-4-(tricyanomethyl)bicyclo[2.2.2]octane in the usual manner[4a] (vide supra). Sublimation and then recrystallization from hexane gave white needles (400 mg, 73%), mp 164–165.5 °C.

Anal. Calcd for $C_{18}H_{17}N_3$: C, 78.52; H, 6.22. Found: C, 77.99; H, 6.41.

Spectra. The broad-band proton-decoupled ^{13}C NMR spectra were recorded in the pulse Fourier transform mode on Bruker instruments operating at 67.89 MHz (spectral width 15 000 Hz, 16K/8K data points, resolution of 0.03 ppm) and 22.625 MHz (spectral width 6024 Hz, 16K/8K data points, resolution of 0.03 ppm) using $DCCl_3$, $(CH_3)_2CO/(CD_3)_2CO$, and c-C_6H_{12}/c-C_6D_{12}

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solutions (0.2–0.5 M) with Me_4Si as an internal reference. The probe temperature was 310 ± 3 K. The 270-MHz ^1H NMR spectra for 1- and 2-(tricyanomethyl)naphthalene were recorded on a Bruker spectrometer in the pulse Fourier transform mode. Routine ^1H NMR spectra were measured with a Varian A-60 spectrometer.

Most of the fluorine NMR spectra were measured with a Varian DP-60 spectrometer operating at 56.4 MHz under proton-coupled conditions (ambient probe temperature), using solutions containing 5% (w/w) of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFB) as internal reference. The Varian DP-60 instrument had been modified to obtain spectra in the HA mode which were calibrated using a Racal SA35 universal counter timer. A dilution study on several compounds indicated that the chemical shifts can be considered accurate to ±0.03 ppm.

The ^{19}F NMR spectra for the tricyanomethyl-substituted fluoronaphthalenes in cyclohexane were obtained under proton-decoupled conditions in the pulse Fourier transform mode at 84.66 MHz with a Bruker 90 spectrometer. A spectral width of 1202 Hz was used and the data were collected into 16K/8K data points giving a resolution of better than 0.01 ppm. Each sample consisted of a mixture of the unsubstituted and substituted compound at a total concentration of less than 10% w/w. The probe temperature, because of solubility problems, was 343 ± 3 K.

Results

The ^{13}C NMR data for various compounds are listed in Tables II–IV. Assignments have been made by standard procedures (chemical shift, intensity, substituent effects, and proton-coupled spectral considerations) which were greatly assisted by the "fluoro-substitution" technique[14,25] (see calculated spectra in Table V). Deuterio substitution (^2H effects characteristic perturbations on ^{13}C NMR spectra)[14,26,48] at C-4 and C-6 in 1- and 2-(tricyanomethyl)naphthalene, respectively, together with details of the fully ^1H coupled spectra[49] confirmed completely the spectral assignments for these two compounds. In addition, it should be noted that ^1H spectra of these two compounds in $DCCl_3$ were recorded at 270 MHz. The spectrum of the α isomer was virtually first order in appearance and, thus, was readily assigned by consideration of the characteristic splitting patterns as well as long-range H–H couplings in naphthalene,[50,51] which are not markedly altered by the presence of substituents,[51,52] and the corresponding ^1H spectrum for the 4-deuterio analogue. H-6 and H-7 were distinguished on known proton SCS in naphthalene[50,51] (H-2, 8.02; H-3, 7.59; H-4, 8.11; H-5, 8.03; H-6, 7.70; H-7, 7.89; and H-8, 8.20). Thus, this assignment allowed selective $^{13}C(^1H)$ decoupling experiments to be made on the α isomer, which further confirmed the listed assignments (Table II). This single-frequency proton spin-decoupling technique for assigning ^{13}C NMR spectra was not applied to the β isomer, since the complexity of the ^1H spectrum precluded simple spectral analysis.

The ^{13}C NMR spectra of the phenylbicyclo[2.2.2]octyl compounds were assigned in the manner previously outlined.[17b]

Tables VI–VIII give the ^{19}F SCS determined in this study. All these SCS can be considered accurate to at least ±0.05 ppm except those for $C(CN)_3$ in cyclohexane (accurate to ±0.01 ppm). It should be noted that the ^{19}F SCS of the CH_3 compounds in at least DMF as solvent, except for the 6α isomer (new compound, see text), have been previously reported and discussed in other studies.[2,21,25] However, we have taken the opportunity here to remeasure them (except 4α[21]) in three different solvents and to collate them all together (Table VII) for the first time.

Discussion

Substituent Parameters for $C(CN)_3$. The infrared intensity technique of Katritzky and Topsom[12] is now regarded as an established method for quantitatively assessing substituent resonance interactions in an inert solvent (CCl_4) in the absence of other complicating electronic interactions. Normally, the ν_8 (1600 and 1585 cm^{-1}) intensities of the appropriate monosubstituted benzene is determined and the σ_R^0 value is derived by employing the best fit equation (eq 1) relating intensities

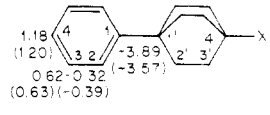
$$|\sigma_R^0| = 0.0075(A - 100)^{1/2} \quad (1)$$

(A) and resonance parameters (σ_R^0).[12] For $C(CN)_3$, two peaks (1603.1 and 1592.2 cm^{-1}) were usually integrated with intensities (A) of the order of 63.3 and 155.7, respectively. The average total A value of a number of spectra was 234 ± 12. Substitution of this value in eq 1 affords a σ_R^0 value of ±0.09. Interestingly, this value is the same order of magnitude as that previously determined by the β-fluoronaphthyl probe.[1] However, because of uncertainties in the overtone correction term and because low intensities are difficult to measure, σ_R^0 values of less than 0.10 are generally not well determined by eq 1[12] and, thus, the derived value for $C(CN)_3$ can be considered accurate only to ±0.03–0.04. In addition, the sign of σ_R^0, which is of particular importance in the current context, does not emerge from eq 1. These problems, however, may be circumvented by employing the appropriate m-fluoro-substituted benzene derivative and utilizing eq 2.[12]

$$A = 18\,230[0.1156 + (\sigma_R^0)^2 - 0.34\sigma_R^0] + 500 \quad (2)$$

It was found that m-fluoro(tricyanomethyl)benzene has an intensity of 4570 (concentration independent) which on substitution in eq 2 leads to two possible σ_R^0 values for $C(CN)_3$, −0.20 or +0.54. As we shall see later on, these values must be regarded as being spurious.[53]

Recently, we have shown that aryl ^{13}C SCS (C-4) determined from bridgehead-substituted phenylbicyclo[2.2.2]octyl derivatives (I),[13] a stereochemically well-defined



I

model system, provide a convenient and reasonably

(48) Kitching, W.; Bullpitt, M.; Doddrell, D.; Adcock, W. *Org. Magn. Reson.* **1974**, *6*, 289.
(49) Günther, H.; Schmickler, H.; Jikeli, G. *J. Magn. Reson.* **1973**, *11*, 344; Jikeli, G.; Herrig, W.; Günther, H. *J. Am. Chem. Soc.* **1974**, *96*, 323.
(50) Crecely, R. W.; Goldstein, J. H. *Org. Magn. Reson.* **1970**, *2*, 613, and references cited therein.
(51) Lucchini, V.; Wells, P. R. *Org. Magn. Reson.* **1976**, *8*, 137.
(52) Attimonelli, M.; Sciacovelli, D. *Org. Magn. Reson.* **1977**, *9*, 601, and references cited therein.

(53) (a) It has been brought to our attention by Professor R. D. Topsom that this result is the first clearly documented failure of eq 2 to provide a reliable measure of the magnitude and sign of σ_R^0 for a weak resonance interacting substituent. A possible explanation (suggested by Professor R. D. Topsom) can be advanced based on the idea that the strong field effect of $C(CN)_3$ increases the resonance effect (field-induced resonance effect)[53b] of fluorine as a substituent. Hence, if a σ_R^0 value of 0.10 is taken for $C(CN)_3$, then the effective σ_R^0 value of fluorine comes out at −0.51 from eq 2 compared to the normal value of −0.34. It must be pointed out, however, that the ^{13}C SCS for fluorine at positions 2, 4, and 6 (−12.07, −3.98, and −12.49 ppm, respectively) in m-fluoro(tricyanomethyl)benzene [Table III; SCS determined relative to the appropriate chemical shifts of (tricyanomethyl)benzene (Table II)] offer no support for an enhanced electron-donating resonance effect for fluorine. Note that ortho and para ^{13}C SCS for fluorine from fluorobenzene are −12.9 and −4.5 ppm, respectively.[53c] (b) Broxton, T. J.; Butt, G.; Liu, R.; Teo, L. H.; Topsom, R. D.; Katritzky, A. R. *J. Chem. Soc., Perkin Trans. 2* **1974**, 463. (c) Nelson, G. L.; Levy, G. C.; Cargioli, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 3089.

Table II. Carbon-13 NMR Chemical Shifts of Some Substituted Benzenes and Naphthalenes[a,b,c]

compd	carbon no. 1	2	3	4	5	6	7	8	9	10	other
					$DCCl_3$						
(tricyanomethyl)benzene[d,f]	125.42	126.36	130.92	132.38	130.92	126.36					33.32 (C), 107.87
1-(tricyanomethyl)naphthalene[e,g]	119.13	126.86	125.14	133.93	130.17	127.87	128.97	122.02	127.66	134.75	107.61 (CN)
2-(cyanomethyl)naphthalene[d,h]	126.79	127.37	125.49	129.00	127.73	126.49	126.79	127.73	133.35	132.70	23.60 (CH_2), 117.94
2-(dicyanomethyl)naphthalene[d,h]	127.21	123.54	123.54	130.49	128.02	128.02	127.76	128.25	132.25	133.68	28.35 (CH), 111.90
2-(tricyanomethyl)naphthalene[e,g]	126.87	122.27	121.53	131.56	128.13	129.19	128.48	128.70	133.00	134.34	107.91 (CN)
					$(CD_3)_2CO$						
(tricyanomethyl)benzene[d,f]	126.85	127.18	131.57	132.87	131.57	127.18					34.46 (C), 109.17
1-(tricyanomethyl)naphthalene[d,i]	120.42	128.19	126.31	134.56	131.05	128.46	129.54	122.69	127.82	135.48	32.37 (C), 108.88
2-(tricyanomethyl)naphthalene[d,i]	127.82	123.88	122.69	132.13	128.79	129.71	129.00	129.71	133.75	134.94	34.72 (C), 109.36

[a] Chemical shifts (ppm) relative to Me_4Si. [b] Dilute solutions (0.2 M). [c] Positive values indicate decreased shielding. [d] Recorded at 22.625 MHz. [e] Recorded at 67.89 MHz. [f] Benzene, internal (relative to Me_4Si): 128.48 ($DCCl_3$); 129.03 ($(CD_3)_2CO$). [g] Naphthalene ($DCCl_3$, relative to Me_4Si): 127.90 (C1); 125.82 (C2); 133.56 (C9, 10). [h] Naphthalene ($DCCl_3$, relative to Me_4Si): 127.89 (C1); 125.78 (C2); 133.55 (C9, 10). [i] Naphthalene ($(CD_3)_2CO$, relative to Me_4Si): 128.66 (C1); 126.67 (C2); 134.38 (C9, 10).

Table III. Carbon-13 NMR Parameters of Some Fluoro-Substituted Benzenes and Naphthalenes[a,b,c]

substitutent/ position	carbon no. 1	2	3	4	5	6	7	8	9	10	other
						$DCCl_3$					
m-F, $C(CN)_3$[d]	127.32 (8.08)	114.29 (25.74)	163.46 (252.97)	119.89 (20.60)	132.89 (8.83)	122.38 (3.67)					32.93 (C), 107.51 (CN)
6-F-2-CH_2CN[e]	126.90		126.57	128.41 (5.55)	110.92 (20.35)	161.04 (247.84)	117.20 (25.89)	130.18 (9.25)	130.44	133.58 (9.0)	23.65 (CH_2), 117.66 (CN)
6-F-2-$CH(CN)_2$[e]	127.17	123.00	124.61	129.72 (5.55)	111.28 (20.35)	161.81 (249.69)	118.21 (25.9)	130.78 (9.15)	130.22	134.62 (~10)	28.25 (CH), 111.83 (CN)
6-F-2-$C(CN)_3$[d]	126.75	121.43	122.50	130.7 (br)	111.56 (20.6)	162.24 (256.02)	119.08 (24.0)	131.46 (~10)	129.79	135.35 (~10)	107.60 (CN)
7-F-2-$C(CN)_3$[d]	126.0 (6.8)	123.17	121.0	131.46	130.6 (10.3)	119.69 (24.1)	161.07 (248.83)	112.01 (20.60)	132.98 (~10)	131.00	107.60 (CN)
3-F-1-$C(CN)_3$[e]		117.95 (20.52)	158.66 (249.69)	116.78 (19.42)	129.64 (5.55)	128.87	128.22 (1.85)	122.16	124.95	135.60 (8.33)	107.15 (CN)
4-F-1-$C(CN)_3$[d]	114.8 (~5)	127.36 (~10)	109.10 (20.63)	161.36 (258.0)	122.80 (6.9)	128.12	129.94	122.04 (br)	129.30 (~6)	124.1 (~18)	32.35 (C), 107.25 (CN)
6-F-1-$C(CN)_3$[e]	119.71	126.30	126.30	133.24 (3.70)	113.56 (20.34)	161.20 (251.54)	119.27 (25.9)	124.54 (9.25)	124.31	136.12 (9.25)	107.39 (CN)
						$(CD_3)_2CO$					
4-F-1-$C(CN)_3$[d]	116.5 (3.9)	129.3 (10)	110.22 (21.97)	162.40 (259)	123.09 (6.1)	129.06	130.67	123.0 (br)	129.77 (7.3)	125.31 (16.6)	33.63 (C), 108.72 (CN)
6-F-2-$C(CN)_3$[d]	127.92	123.88	123.88	131.65 (~5)	112.06 (21.98)	162.99 (249.03)	119.27 (25.63)	132.67 (9.76)	130.95	136.24 (~10)	109.31 (CN)
7-F-2-$C(CN)_3$[d]	127.28 (~5)	125.18	122.21	132.03	131.81 (9.76)	119.72 (25.63)	162.43 (247.8)	112.71 (21.93)	134.78 (9.77)	132.03	109.21 (CN)

[a] Chemical shifts (ppm) relative to Me_4Si. ^{13}C–^{19}F coupling constants (Hz) are given in parentheses. [b] Dilute solutions (0.5 M). [c] Positive values indicate decreased shielding. [d] Recorded at 22.625 MHz. [e] Recorded at 67.89 MHz.

Table IV. Carbon-13 NMR Chemical Shifts of 1-X-4-Phenylbicyclo[2.2.2]octanes[a]

substituent, X	carbon no.[b] 1	2	3	4	1′	2′	3′	4′	other
					$DCCl_3$				
H[c]	150.68	125.62	128.05	125.42	34.13	32.12	26.56	24.51	
CH_2OH[c]	149.90	125.62	128.12	125.62	35.18	32.05	28.48	33.42	71.55 (CH_2)
CH_2Cl[c]	149.41	125.55	128.15	125.68	34.92	32.02	29.45	28.44	55.14 (CH_2)
CH_2CN[c]	148.89	125.49	128.25	125.84	34.36	32.05	31.27	30.98	29.65 (CH_2); 118.07 (CN)
CH_2COOH[c]	149.64	125.52	128.12	125.52	34.43	32.31	31.47	31.11	45.84 (CH_2); 178.93 (CO)
CH_2COOCH_3[c]	149.74	125.55	128.15	125.55	34.46	32.38	31.53	31.14	45.81 (CH_2); 51.14 (CH_3); 172.50 (CO)
$CH(CN)_2$[c]	147.79	125.39	128.41	126.20	34.13	31.60	29.26	28.90	34.04 (CH); 111.57 (CN)
H[d]	150.68	125.58	128.02	125.39	34.23	32.19	26.60	24.60	
$C(CN)_3$[d]	146.79	125.26	128.64	126.57	34.03	31.71	27.79	26.87	44.08 (C); 107.34 (CN)
					$c\text{-}C_6H_{12}/c\text{-}C_6D_{12}$[e]				
H[d]	150.87	125.89	128.48	125.85	34.86	33.06	27.52	*f*	
$C(CN)_3$[d]	147.30	125.50	129.11	127.05	34.80	32.54	28.32	*f*	44.13 (C); 107.79 (CN)

[a] Chemical shifts (ppm) relative to Me_4Si. Dilute solutions (0.2 M). Positive values indicate decreased shielding. [b] The carbon-numbering system is as shown in structure I. [c] Recorded at 22.625 MHz. [d] Recorded at 67.89 MHz. [e] Probe temperature, 343 K. [f] Not observed.

Table V. Calculated Carbon-13 Chemical Shifts of Some Substituted Benzenes and Naphthalenes[a]

substituent/position	carbon no. 1	2	3	4	5	6	7	8	9	10
						$DCCl_3$				
$C(CN)_3$[b]	125.92	127.19	128.66	132.79	131.49	126.88				
2-CH_2CN[c]	126.95		125.56	128.98	127.96	126.20	126.78	127.79	133.44	132.88
2-$CH(CN)_2$[c]	127.22	123.75	123.60	130.29	128.32	126.97	127.79	128.39	133.22	133.92
2-$C(CN)_3$[c]	126.80	122.18	121.49	131.27	128.60	127.40	128.66	129.07	132.79	134.65
2-$C(CN)_3$[d]	126.57	122.16	121.75	131.51	128.21	129.27	126.23	129.05	132.28	134.00
1-$C(CN)_3$[e]		127.53	123.82	133.82	130.21	127.86	128.97	122.21	127.95	134.90
1-$C(CN)_3$[f]	119.06	127.60	125.52	130.41	130.17	127.80	128.96	122.42	127.86	132.11
1-$C(CN)_3$[c]	119.76	127.05	125.29	133.81	130.60	126.36	128.85	122.15	127.31	135.42
						$(CD_3)_2CO$				
1-$C(CN)_3$[f]	120.76	129.54	126.64	131.45	130.46	128.74	129.69	123.38	128.33	133.32
2-$C(CN)_3$[c]	127.76	124.37	122.62	132.12	129.15	128.12	129.05	129.80	133.82	135.47
2-$C(CN)_3$[d]	127.85	124.17	122.96	132.08	129.42	129.50	127.59	129.80	134.08	135.96

[a] ^{13}C SCS for fluorine in benzene and naphthalene were taken from ref 53c and 14 respectively. [b] From *m*-fluoro derivative (Table III). [c] From 6-fluoro derivative (Table III). [d] From 7-fluoro derivative (Table III). [e] From 3-fluoro derivative (Table III). [f] From 4-fluoro derivative (Table III).

Table VI. ^{19}F Substituent Chemical Shifts (SCS) of Tricyanomethyl- and Ammonio-Substituted Fluoronaphthalenes[a,b]

solvent	substituent	orientation[c] 3α	4α	5α	6α	7α	4β	5β	6β	7β	8β
cyclohexane	$C(CN)_3$	+7.64	+9.25	+5.14	+2.33	+2.55	+2.43	+4.04	+6.17	+5.23	*d*
methylene chloride	$C(CN)_3$	+7.86	+9.95	+5.61	+2.40	+2.44	+2.24	+3.74	+5.83	−4.73	+8.40
benzene	$C(CN)_3$	+7.71	+8.76	+4.76	+1.70	+2.44	+2.44	+3.42	+5.21	+3.90	+8.50
methanol	$C(CN)_3$	+7.06	+9.31	+5.49	+2.03	+2.09	+2.16	+3.42	+5.14	+4.13	+7.62
DMF	$C(CN)_3$	+6.18	+8.76	+5.26	+1.75	+1.70	+1.63	+2.89	+4.67	+3.56	+7.08
CF_3CO_2H	$^+NH_3$	+7.87	+7.11	+4.79[e]	+2.16	+1.59	+2.55	+4.21	+4.56[e]	+4.47[e]	+6.98

[a] Positive sign implies deshielding. [b] Accurate to ±0.05 ppm. [c] See ref 3. [d] Insufficient sample. [e] Take from ref 2.

Table VII. ^{19}F Substituent Chemical Shifts (SCS) of Methyl-Substituted Fluoronaphthalenes[a,b]

solvent	orientation[c] 3α	4α	5α	6α	7α	4β	5β	6β	7β	8β
DMF	−0.95	−2.94[d]	+1.01	−0.24	−0.62	−0.70	−1.09	−1.47	−0.23	+0.98
benzene	−1.16	−2.96[d]	+1.02	−0.22	−0.61	−0.80	−1.16	−1.44	−0.22	+0.81
cyclohexane	−1.09		+1.06	−0.27	−0.75	−0.78	−1.20	−1.45	−0.20	+0.88

[a] Positive sign implies deshielding. [b] Accurate to ±0.05 ppm. [c] See ref 3. [d] Taken from ref 21.

sensitive means for quantitatively measuring polar field phenomena (σ_I effect) in total isolation of other electronic mechanisms. ^{13}C SCS of the various aryl carbon centers for I where X = $C(CN)_3$ may be calculated from the data set out in Table IV. These values are displayed on structure I ($c\text{-}C_6H_{12}$ results are in parentheses). Now since the polar susceptibility parameter (ρ_I) for the ^{13}C SCS ($DCCl_3$) of C-4 in I is +1.17 ± 0.07,[54] σ_I for $C(CN)_3$ must be +1.01 ± 0.06. It should be noted that by employing the least-squares correlative equation for the ^{13}C SCS ($DCCl_3$) of C-4 in I presented by Toyne et al.,[55] then σ_I for $C(CN)_3$

(54) This value is the result of a further refinement of the correlations recently reported.[17b]

Table VIII. ^{19}F Substituent Chemical Shifts (SCS) of Some Miscellaneous Substituted Fluoronaphthalenes[a,b]

substituent	orientation[c]	solvent: benzene	solvent: DMF
CH_2Br	3α	+0.99	+0.90
CH_2Br	4α	+2.65	+2.7 (+2.66)[e]
CH_2Br	5α	+1.67 (+1.83)[d]	+1.77
CH_2Br	6α	+0.41 (+0.52)[d]	+0.41
CH_2Br	7α	+0.69 (+0.57)[d]	+0.48
CH_2Br	4β	−0.52 (−0.38)[d]	−0.42
CH_2Br	5β	+0.05	+0.05
CH_2Br	6β	+1.07 (+1.28)[d]	+1.04 (+1.00)[e]
CH_2Br	7β	+0.73 (+1.06)[d]	+0.72
CH_2Br	8β	+2.86 (+3.15)[d]	+2.45
CH_2CN	3α	+1.27	+1.20
CH_2CN	4α	+0.84	+0.75
CH_2CN	5α	+2.09	+1.95
CH_2CN	6α	+0.36	+0.44
CH_2CN	7α	+0.32	−0.02
CH_2CN	4β	+0.32	+0.04
CH_2CN	5β	+0.28	+0.28
CH_2CN	6β	+0.79	+0.53
CH_2CN	7β	+1.16	+0.98
CH_2CN	8β	+2.69	+2.51
$CHBr_2$	4α	+4.85	+5.00
$CHBr_2$	7α	+1.30 (+1.12)[f]	+0.97
$CHBr_2$	6β	+2.31	+2.32 (+2.35)[f]
$CHBr_2$	7β	+1.40	+1.57
$CH(CN)_2$	6β	+3.05	+2.49
$CH(CN)_2$	7β	+2.55	+2.22
CBr_3	4α	+6.14	+6.52
CBr_3	6β	+3.25	+3.38 (+3.59)[f]
CBr_3	7β	+1.78	+2.12
CHO	6α	+1.56 (+1.72)[d]	+1.35
NH_2	6α	−0.62 (−0.71)[d]	−1.00 (−1.05)[g]
COOH	6α		+0.86

[a] Positive sign implies deshielding. [b] Accurate to ±0.05 ppm. [c] See ref 3. [d] Solvent, cyclohexane. [e] Taken from ref 20. [f] Taken from ref 21. [g] Taken from ref 67.

is calculated to be +1.05. The corresponding ^{13}C SCS (C-4) in cyclohexane as solvent (+1.20 ppm; measured at 343 K for solubility reasons) leads to a σ_I value of +0.94 ± 0.03 based on a ρ_I value of +1.28 ± 0.04.[54] Although this σ_I value is smaller than that determined from the SCS measured in $DCCl_3$ and, therefore, may imply that the polar parameter for $C(CN)_3$ is slightly solvent dependent, it should be noted that the two determinations of σ_I agree within the limits of experimental error for defining the respective polar susceptibility parameters in the two different solvents. However, because the ρ_I value for system I in c-C_6H_{12} was determined from ^{13}C SCS data measured at ambient probe temperatures (310 K)[17b] and, since it appears that ^{13}C SCS for C-4 in I may be slightly temperature dependent [^{13}C SCS (ppm) of C-4 for NO_2 in I (c-C_6H_{12}): +0.92 (310 K); +0.87 (343 K)], we have adopted the σ_I value (+1.01) determined from the $DCCl_3$ data.

An interesting feature to note concerning the aryl ^{13}C SCS for I where X = $C(CN)_3$ is that they reflect a field-induced polarization pattern of the phenyl ring very similar to that recently defined in this model by employing conventional weaker polar groups.[17,55] Most importantly, the relative magnitude of this phenomenon at C-4 and C-3, the two positions previously considered to most likely characterize similar polarizing influences at the para and meta carbon positions of monosubstituted benzene derivatives[17b] (vide infra), is identical (2:1) with the result previously observed.[17,55]

(55) Ewing, D. F.; Sotheeswaran, S.; Toyne, K. J. *Tetrahedron Lett.* **1977**, 2041.

Although it is unfortunate that the infrared method failed to provide an unambiguous quantitative estimate of σ_R^0 for $C(CN)_3$, the fact that σ_I (+1.01; $DCCl_3$) is now clearly well-defined by model system I (X = $C(CN)_3$) provides an alternative means. ^{13}C SCS data for the para carbon of monosubstituted benzenes, a disposition very sensitive to resonance perturbations, are well correlated (eq 3)[56] by the DSP equation[10a,b] without the complications

$$^{13}C\ SCS\ (DCCl_3;\ para) = 4.7\sigma_I + 21.6\sigma_R^0 \qquad (3)$$

associated with the fluorophenyl tag.[10c] Hence, substitution in eq 3 with the appropriate ^{13}C SCS in $DCCl_3$ (+3.90 ppm; Table II) and the aforementioned σ_I result yields a σ_R^0 value of −0.04 ± 0.01 for the $C(CN)_3$ group. This value is in excellent agreement with that (σ_I = 0.94; σ_R^0 = −0.05) derived from the ^{13}C SCS ($DCCl_3$) of C-6 and C-7 in 2-(tricyanomethyl)naphthalene (Table II; +3.37 and +2.66 ppm, respectively) and the appropriate DSP correlative equations.[14,25,57] Thus, although the previously derived σ_R^0 value (-0.10)[1] for $C(CN)_3$ is apparently too large,[58] the new result does not impinge seriously on our previous conclusions[1] concerning apparent electron donation by this group in the neutral ground state and the associated ramifications regarding the electronic mechanism of the CF_3 substituent.

Finally, it is of interest to note that the ^{13}C chemical shifts of the intermediates (Table IV) prepared during the course of synthesizing 1-phenyl-4-(tricyanomethyl)bicyclo[2.2.2]octane (I; X = $C(CN)_3$) provide accurate measures of σ_I values [ρ_I(C-4; $DCCl_3$) = 1.17][54] for various substituted methyl groups: CH_2OH, 0.17; CH_2Cl, 0.22; CH_2CN, 0.36; CH_2COOH, 0.09; CH_2COOCH_3, 0.11; and $CH(CN)_2$, 0.67. It should be noted that the σ_I values for CH_2OH and CH_2COOH pertain only to $CDCl_3$ as solvent, since their electronic effects are medium dependent. However, the most significant aspect of these results is that they are in excellent accord with those (CH_2Cl,[57b] CH_2CN,[57b] and $CH(CN)_2$) determined from the ^{13}C SCS of C-6 and C-7 in 2-substituted naphthalenes (Table II) and the appropriate DSP correlative equations[14,25,57] (CH_2CN: σ_I = 0.36, σ_R^0 = −0.10; $CH(CN)_2$: σ_I = 0.71, σ_R^0 = −0.08). Note that, except for the $C(CN)_3$ group (vide supra),[4] the σ_I values derived from the fluorophenyl tag are, by comparison, considerably underestimated (CH_2CN, 0.26; $CH(CN)_2$, 0.55).[59]

^{19}F NMR Polar Field Effects. Although recent studies[14,16,17] have clearly established the dual nature of aryl ^{19}F NMR polar field effects,[15] a satisfactory delineation of the relative magnitude of the contributing polar mechanisms (F_D + F_π)[15] determining ^{19}F SCS in the various nonproximate orientations of monosubstituted fluorobenzenes and fluoronaphthalenes remains an unresolved problem. Reynolds et al.[16] have presented an estimate of the direct field contribution (F_D)[15] to ^{19}F SCS

(56) (a) The correlative equation (SD = 0.26; SD/RMS = 0.05; n = 12) represents a further refinement of that previously published.[56b] We are grateful to Professor R. W. Taft for this information prior to publication. (b) Bromilow, J.; Brownlee, R. T. C.; Topsom, R. D.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 2020.

(57) (a) Adcock, W.; Aldous, G.; Kitching, W. *Tetrahedron Lett.* **1978**, 3387. (b) Kitching, W.; Alberts, V.; Adcock, W.; Cox, D. P. *J. Org. Chem.* **1978**, *43*, 4652.

(58) This is also exemplified by the *positive* ^{13}C SCS observed (Table II) for the resonance dominated C10 position[14] in 2-(tricyanomethyl)-naphthalene. Unfortunately, although ^{13}C SCS data for this position have been effectively employed for delineating σ_R^0 values of *weak* polar groups,[25,57] it has limited application for groups with very weak resonance effects coupled with a powerful inductive influence. This is not surprising since the DSP correlative analysis cannot be expected to exactly dissect out the relatively small polar susceptibility parameter for this position.

(59) Sheppard, W. A. *Tetrahedron* **1971**, *27*, 945.

Table IX. Estimates of Direct Field (F_D) and Field-Induced π Polarization (F_π) Contributions (ppm) to ^{19}F SCS of Fluorobenzenes and Fluoronaphthalenes for $C(CN)_3$ as Substituent

	^{13}C SCS × constant		^{19}F SCS − F_π		SCS = AE_z[d]	
disposition[a]	$F_\pi(1)$[b]	$F_\pi(2)$[c]	$F_D(1)$	$F_D(2)$	$F_D(1)$[e]	$F_D(2)$[f]
meta	3.34	3.54	3.12	2.92	3.28	2.89
para	6.44	6.82	1.47	1.09	2.79	2.29
3α	5.01	5.31	2.85	2.55	3.28	2.89
4α	8.26	8.74	1.69	1.21	2.79	2.29
5α	3.11	3.29	2.50	2.32	1.94	1.31
6α	0.32	0.33	2.08	2.07	0.92	0.80
7α	1.10	1.16	1.34	1.28	0.19	0.79
4β	−0.93	−0.99	3.17	3.23	3.28	2.89
5β	2.81	2.97	0.93	0.77	1.91	1.30
6β	4.62	4.89	1.21	0.94	1.00	0.80
7β	3.64	3.86	1.09	0.87	1.00	0.86
8β	4.32	4.57	4.08	3.83	2.05	2.06

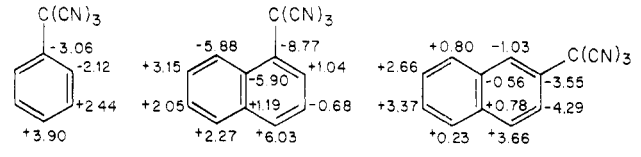
[a] See ref 3. [b] Proportionality constant (1.37) associated with eq 4. [c] Proportionality constant (1.45) associated with eq 5. [d] Buckingham equation. [e] Equation 4; $A = 31.0 \times 10^{-12}$ (esu). See ref 17b. [f] Equation 5; $A = 25.4 \times 10^{-12}$ (esu). See ref 17b

of para-substituted fluorobenzenes, using the NO_2 group as an example, based on the Buckingham equation for linear electric field effects[18] in which the coefficient (A) was evaluated from the ^{19}F chemical shifts of 4-substituted β,β-difluorostyrenes. The calculation was expressed as a percentage (45%) of the total polar field effect, the latter quantity being estimated from the result of a DSP correlative analysis ($\rho_I\sigma_I$ term). On the other hand, based on the premise that field-induced π polarization (F_π)[15] in the 5α and 6α dispositions[3] of naphthalene is negligible (indicated by ^{13}C SCS data for a classical range of substituent electronic effects), we[14] have estimated F_D contributions (using the *fluoro* substituent as an example) in para-substituted fluorobenzenes as well as in various orientations of fluoronaphthalenes by utilizing relative angle/distance relationships and results of DSP correlative analyses. The estimated percent F_D contribution to the ^{19}F NMR polar field effect in the para position of fluorobenzene by this method (70–77%) differed significantly from the estimate provided by Reynolds and co-workers.[16]

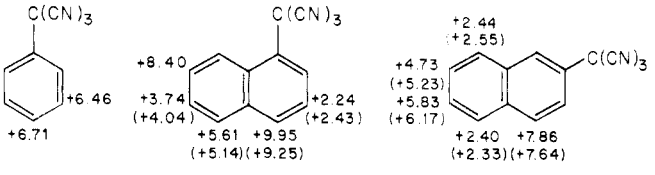
A possible flaw common to both these dissections is the reliance on the results of DSP correlative analyses[10] to factor out the total ^{19}F NMR polar field effect in the various orientations of fluorobenzene and the fluoronaphthalenes. Clearly, the definitive substituent parameters determined above for the $C(CN)_3$ group (σ_I = 1.01; σ_R^0 = − 0.04) indicate that this powerful inductive neutral dipolar group, which is coupled with a feeble resonance capacity, can be effectively employed to circumvent this problem. Hence, except for very strongly conjugated orientations (para and 4α), aryl ^{13}C and ^{19}F SCS at nonproximate sites for this substituent can be considered manifestations of only polar field effects and, thus, are direct measures of this latter quantity. The ^{13}C and ^{19}F SCS for $C(CN)_3$ in benzene and naphthalene (Tables II and VI, respectively)[60] are set out in Chart I in order to facilitate comparison. The appropriate corrections for a weak electron-donating resonance perturbation on the para ^{13}C and ^{19}F SCS are 0.80 ($\rho_R \sim 20$)[56] and 1.20 ppm ($\rho_R \sim 30$)[5], respectively. Most significantly, the relative magnitude of the para (corrected for resonance) and meta ^{13}C SCS in the phenyl ring for the $C(CN)_3$ group (4.70:2.44 ~ 2:1), which is a manifestation of dominant F_π effects[15,17] at these two positions, is identical with that inferred above from the results of the phenylbicyclooctyl system.[17] The

Chart I

^{13}C SCS ($DCCl_3$)



^{19}F SCS (CH_2Cl_2; c-C_6H_{12} results in parentheses)



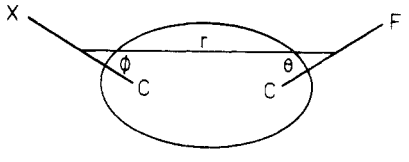


Figure 1. Diagram illustrating angle and distance factors for electric field calculations.

^{13}C and ^{19}F SCS for the strongly conjugated position in naphthalene (4α) need not be corrected since structural influences here (downfield shift)[2,14,21] should approximately cancel out the weak resonance influence (upfield shift) of the $C(CN)_3$ group.

Now since aryl ^{13}C NMR shielding effects at nonproximate sites are dominated by F_π,[14,16] the ^{13}C SCS (Chart I) can be used to calculate the contribution by this polar mechanism[15] to the corresponding ^{19}F SCS (Chart I; CH_2Cl_2) by employing proportionality constants recently derived from the phenylbicyclooctyl system.[17b] Two proportionality constants emerged from this latter study (1.37 and 1.45) depending on whether an approximate (eq 4) or a more definitive expression (eq 5) for the electric

$$E_z = 2\mu \cos\theta / r^3 \quad (4)$$

$$E_z = (\mu/r^3)(2\cos\theta\cos\phi - \sin\theta\sin\phi) \quad (5)$$

field (E_z) was used in the calculations [μ is the dipole moment of the polar CX bond from which the electric field originates, θ and ϕ are the angles between the CF and CX bond vectors, respectively, and a line of length r drawn between the midpoints of the CF and CX bonds (see Figure 1)]. These results for F_π are set out in Table IX together with corresponding F_D contributions determined

(60) (a) The ^{19}F SCS of $C(CN)_3$ for fluorobenzene ($FCCl_3$, solvent) were taken from ref 4. (b) ^{13}C SCS (ppm) for $C(CN)_3$ in (tricyanomethyl)benzene for CCl_4 and c-C_6H_{12} are as follows respectively: −2.18 (C1), −2.02 (C2), +2.42 (C3), +3.68 (C4); and −1.74 (C1), −1.93 (C2), +2.29 (C3), +3.51 (C4).

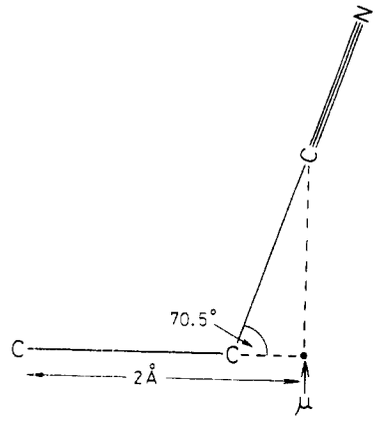


Figure 2. Assumed location of point dipole in $C(CN)_3$ group.

by dissecting out the former component from the observed ^{19}F SCS (Chart I; CH_2Cl_2). It should be noted that the F_D values computed in this way should not be seriously impaired by residual resonance effects, since these will be effectively cancelled out by the nature of the calculation even for the uncorrected strongly conjugated positions. In addition, F_D contributions determined by utilizing the Buckingham equation[18] (SCS = AE_z, where E_z is given either by eq 4 or 5) are also listed in Table IX. For these calculations (eq 4 or 5), since the bond dipole moment (μ) for $C(CN)_3$ is unknown, it was necessary to determine this parameter in an indirect way by utilizing ^{13}C SCS (C-4) data (ppm) from the phenylbicyclooctyl system (I) which are a manifestation of polar field phenomena. Thus, by employing the ^{13}C SCS (C-4) for $C(CN)_3$ (see structure I) and those for various substituents (X) measured in $DCCl_3$ (F, 0.52; Cl, 0.55; Br, 0.52; CN, 0.68; NO_2, 0.85),[61] then $SCS(C(CN)_3]/SCS(X) = E_z(C(CN)_3)/E_z(X)$, where $E_z = 2\mu/r^3$ (r is the distance between the carbon center (C-4; I) and the origin of the electric field of the substituent at the bridgehead). By assuming the origin of the electric field associated with $C(CN)_3$ is located at a point 2.0 Å from the bridgehead carbon (see Figure 2),[62] and that for the CX bonds is as previously indicated,[17b] then by using aliphatic bond dipole moment data[63] and standard structural parameters,[64] μ for $C(CN)_3$ is calculated (average) to be 7.30 D.

Several important conclusions follow from the results set out in Table IX. First, it can be seen that for the 6β and 7β dispositions,[3] the two orientations in naphthalene we have previously proposed as being extremely suitable for assessing substituent electronic effects by ^{19}F and ^{13}C NMR in the absence of other complicating phenomena,[2,14,21,25,57] there is an excellent accord between the two sets of calculated direct field effects (F_D). This is a most impressive result given that we were forced to use data in halogenated solvents ($DCCl_3$ and CH_2Cl_2) rather than CCl_4 or c-C_6H_{12}[65] due to the poor solubility of the naphthalene derivatives in the latter solvents for ^{13}C NMR measurements. Although the almost exact agreement is probably somewhat fortuitous, we believe two important corollaries follow from this result: (i) the inherent assumption that ^{19}F NMR polar field effects may be considered an additive blend of F_D and F_π effects[15] appears to be a good first-order approximation.[17b] Hence, field-induced π polarization (F_π)[15] of the aromatic system as reflected by ^{13}C SCS clearly leads to a proportionate change in ^{19}F chemical shifts when fluorine is substituted for the ^{13}C nucleus as an electronic probe. We believe this represents compelling evidence for the belief that the most important factor determining the chemical shift of carbon and fluorine in aryl systems is the π-electron density on carbon (Δq_π^C) and fluorine (Δq_π^F) respectively.[16,66] These two theoretical parameters have been shown to be linearly related to one another.[16,66] Thus, in situations where small changes in π-electron density at the carbon adjacent to fluorine occurs, nonlinearity between ^{13}C and ^{19}F SCS[14,66,67] may clearly arise due to significant F_D effects determining the latter quantity (meta, 5α, 6α, 7α, 4β; vide infra). Of course, it is possible that in some situations nonlinearity may also be the result of dominant σ charge density perturbations[68] or bond order effects [14,69] determining ^{13}C chemical shifts of various π systems; (ii) the Buckingham equation (SCS = AE_z),[18] in conjunction with the newly derived coefficients (A),[16,17b] appears to provide a reliable estimate of direct field contributions to aryl ^{19}F SCS. This is despite the fact that, in this study, the assumed length of the $C(CN)_3$ dipole relative to the distance between this group and the ^{19}F probe is not particularly small and, thus, might have been expected to impinge seriously on the approximations inherent in the derivation of eq 4 and 5.[70] However, it should be borne in mind that the use of eq 4 and 5 for determining F_D might be more severely compromised in other orientations where θ or ϕ, or both (Figure 1), deviate significantly from 180 and 0°, respectively.

Second, it can be seen (Table 9) that although the F_π contribution in the 6α orientation is very small, which is in line with our previous conclusion,[14] the corresponding values in the 5α orientation appear unrealistically large given that we previously concluded that the F_π effect here is negligible.[14] We believe that structural factors, of the kind we previously alluded to in connection with other apparent anomalous ^{13}C and ^{19}F SCS in the 5α orientation,[2,14,71] are responsible for this latter result. Hence, since mesomeric effects in this formally conjugated disposition have been shown to be *zero* in neutral ground-state measurements,[2,14] potential structural factors for $C(CN)_3$ may be effectively cancelled out by employing the weakly inductive alkyl groups as the reference substituent[72] to calculate ^{13}C and ^{19}F SCS rather than hydrogen. Thus, in this way, the following new dissection emerges for the

(61) Adcock, W.; Aldous, G. unpublished results. These SCS values (±0.06 ppm) in $DCCl_3$ are more accurate than those recently reported (±0.14 ppm)[17b] mainly because the digital resolution of the spectrometer has been upgraded from 8K/4K (±0.07 ppm) to 16K/8K data points (±0.03 ppm).

(62) (a) Based on known structural data for this group.[62b] (b) Britton, D.; Farooq, S.; Keese, R. *Helv. Chim. Acta* **1977**, *60*, 1393, and references cited therein.

(63) Cumper, C. W. N. *Tetrahedron* **1969**, *25*, 3131.

(64) (a) Sutton, L. E., Ed., *Chem. Soc., Spec. Publ.* **1958**, *No. 11*. (b) Yokozeki, A.; Kuchitsu, K.; Morimo, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2017.

(65) (a) Intramolecular electric-field phenomena are best observed in these solvents (CCl_4 or c-C_6H_{12}) since reaction field effects[65b] and bulk dielectric influences[17b] are minimized. (b) Hamer G. K.; Peat, I. R.; Reynolds, W. F. *Can. J. Chem.* **1973**, *51*, 897, and references cited therein.

(66) Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159, and references cited therein.

(67) Adcock, W.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1967**, *89*, 379.

(68) For recent discussions of charge density ^{13}C NMR chemical shift correlations see Seidman, K.; Maciel, G. E. *J. Am. Chem. Soc.* **1977**, *99*, 3254, and Henry, H.; Fliszár, S. *ibid.* **1978**, *100*, 3312, and references cited therein.

(69) Adcock, W.; Gupta, B. D.; Khor, T. C. *Aust. J. Chem.* **1976**, *29*, 2571.

(70) Smith, J. W. "Electric Dipole Moments"; Butterworths: London, 1955.

(71) Bullpitt, M.; Kitching, W.; Adcock, W.; Doddrell, D. *J. Organomet. Chem.* **1976**, *116*, 161.

(72) (a) ^{13}C SCS (ppm; $DCCl_3$) for 5α orientation: CH_3, +0.61;[14] $C(CH_3)_3$, +1.70.[14,71] (b) ^{19}F SCS (ppm; benzene) for 5α orientation: CH_3, +1.02 (see Table VII), $C(CH_3)_3$, +2.79.[72c] (c) Adcock, W.; Aldous, G. unpublished work. (d) Although recent studies[13] have indicated that the σ_I effect of alkyl groups attached to an sp^3 carbon atom is *zero*, there may be an effect when these groups are bonded to an sp^2 carbon center.

5α orientation: $F_\pi(1) = 2.27$, $F_\pi(2) = 2.41$, $F_D(1) = 2.32$, $F_D(2) = 2.18$ (relative to CH_3);[72] $F_\pi(1) = 0.78$, $F_\pi(2) = 0.83$, $F_D(1) = 2.04$, $F_D(2) = 1.99$ (relative to $C(CH_3)_3$).[72] The important point to note from these calculations is that although the F_D contribution remains fairly constant, there is clearly a marked reduction in the F_π component particularly when the $C(CH_3)_3$ group is employed as the reference substituent.[73] However, even in this instance, the F_π contribution in the 5α orientation is apparently *not* negligible. Although this result appears to contradict our previous conclusion[14] regarding the magnitude of F_π effects in this disposition, it is pertinent to note that the effective steric size of the $C(CN)_3$ group is predicted to be significantly larger than that for $C(CH_3)_3$.[73] Hence the residual F_π effect indicated in the 5α orientation from the $C(CN)_3$ group is probably a manifestation of largely structural phenomena.

A final feature worth noting from the dissection in the 5α and 6α orientations is that although there is good agreement between the two sets of calculated F_D contributions for the former disposition (compare calculated F_D values for 5α using $C(CH_3)_3$ as a reference), there is a more significant differential between the calculations for the latter. This could imply that either the equations (4 or 5) for calculating E_z are beginning to be compromised by this orientation or that there is a contribution to the observed ^{19}F SCS for $C(CN)_3$ from the formal positive charges residing at the ortho and other adjacent carbon centers. In connection with this latter point, it should be noted that mesomeric-field effects have been previously recognized to be a significant factor affecting ^{19}F SCS in this orientation.[14,67]

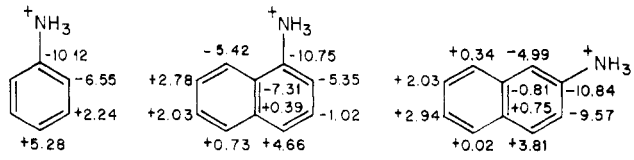
Third, it can be seen that in the 4β disposition, but not in the other formally meta orientations (meta and 3α), F_D and F_π effects are clearly *opposed*, which leads to a net ^{19}F NMR polar field response not in accord with expectations based on the polarity parameter (σ_I) and the results for the other meta orientations. Thus, this result, previously indicated[14] but not as definitively, unambiguously confirms our recent conclusions[14] regarding the origin of the "anomalously" small ^{19}F SCS observed for +F + M substituents (NO_2, CN, COOH, CF_3)[2,67] in the 4β disposition as well as the failure of the DSP equation to fit the ^{13}C and ^{19}F SCS data in this orientation.[2,10a,14]

Finally, it can be seen (Table IX) that the dissections for the 7α and 8β orientations (a disposition pair) clearly indicate the importance of F_π relative to F_D effects in these two dispositions. This result is of interest since its importance was clearly not recognized when the previously observed greater polar electron-withdrawing influence of +F + M substituents (NO_2, CN, COOH) in the 8β compared to the 7α orientation,[67] as monitored by ^{19}F NMR, was tendered as unequivocal evidence for through-space field effects.[67,74] Fortunately, the dissection also indicates that F_D is greater in the 8β than the 7α disposition, by at least a factor of 2, which clearly upholds the validity of the latter conclusion.

A similar analysis was also carried out for the ammonio ($^+NH_3$) substituent utilizing the SCS data (relative to *methyl* as reference)[75] set out in Chart II. The ^{13}C SCS for the anilinium ion in CF_3CO_2H was taken from a study by Reynolds and co-workers.[76] It should also be noted that the ^{13}C SCS for the ammonionaphthalenes have been remeasured but differ only in a minor way from those previously reported,[14] except for C7 and C8 since the assignments here have been reversed. The ^{19}F SCS for $^+NH_3$ in naphthalene (Chart II) were determined from the data set out in Table VI ($^+NH_3$, CF_3CO_2H) and Table VII (CH_3, benzene) while those for benzene (Chart II) were determined from the ^{19}F SCS relative to H [$^+NH_3$-(CF_3CO_2H): meta, + 6.30 ppm; para, + 4.57 ppm] and the corresponding SCS for CH_3 (CCl_4).[66] Calculations of F_D (direct field)[15] for the ammonio substituent using the Buckingham equation[18] pose somewhat of a problem since the adoption of a full electronic charge ($e = 4.8 \times 10^{-10}$ esu) on nitrogen has already been shown to drastically overestimate the polar effect of this group.[77a] This is to be

Chart II

^{13}C SCS (CF_3CO_2H)



^{19}F SCS (CF_3CO_2H)

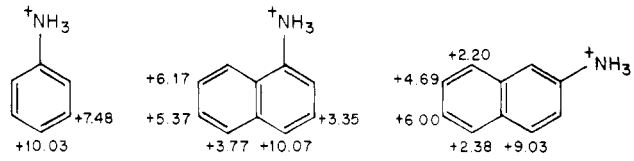


Table X. Estimates of Direct Field (F_D) and Field-Induced π Polarization (F_π) Contributions (ppm) to ^{19}F SCS of Fluorobenzenes and Fluoronaphthalenes for $^+NH_3$ as Substituent

disposition[a]	F_π(^{13}C SCS × constant)[b]	F_D(^{19}F SCS − F_π)	$F_D(AE_z)$[c]
meta	3.14	4.34	2.69
para	7.39	2.64	2.50
3α	5.33	3.70	2.69
4α	6.52	3.55	2.50
5α	1.02	2.75	1.67
6α	0.03	2.35	0.97
7α	0.48	1.72	0.31
4β	−1.43	4.78	2.69
5β	2.84	2.53	1.80
6β	4.12	1.88	1.17
7β	2.84	1.85	1.13
8β	3.89	2.28	1.70

[a] See ref 3. [b] Proportionality constant, 1.40, which is an approximate average of those associated with eq 4 and 5. [c] $A = 31 \times 10^{-12}$ (esu); $E_z = e \cos\theta / r^2$, where θ is the angle between the CF bond vector and a line of length r drawn between the midpoint of the CF bond and $^+NH_3$. $e = 1.96 \times 10^{-10}$ (esu).

(73) (a) Calculation of the steric parameters for the $C(CN)_3$ group as described by Charton[73b] gives the following results: $\nu_{v,max} = 4.07$, $\nu_{v,min} = 2.84$, $\nu_{v,par} = 2.47$, and $\nu = 1.64$. The corresponding results for $C(CH_3)_3$[73b] are 3.15, 2.44, 2.28, and 1.24, respectively. Hence the $C(CN)_3$ group is apparently significantly larger than $C(CH_3)_3$. (b) Charton, M. *Prog. Phys. Org. Chem.* **1971**, *8*, 235; Charton, M. *J. Am. Chem. Soc.* **1969**, *91*, 615; *ibid*, **1975**, *97*, 1552.

(74) Dewar, M. J. S. *Chem. Commun.*, **1968**, 547.

(75) CH_3 and $+NH_3$ are isoelectronic substituents; thus, ^{13}C and ^{19}F chemical shifts for ammonio-substituted derivatives relative to the corresponding shifts for the analogous methyl derivatives should provide SCS for remote sites, which are predominantly a manifestation of polar field effects. However, it should be noted that $\sigma_R^0 = 0.26$ for $^+NH_3$ (CF_3CO_2H) calculated from ^{19}F SCS data for 6- and 7-substituted 2-fluoronaphthalenes (Table VI) and the respective DSP correlative equations in DMF for these two dispositions.[2] σ_R^0 for $^+NH_3$ (D_2O) has been calculated to be −0.19.[12] σ_R^0 for CH_3 is −0.11.[10b] Thus, in strongly conjugated positions, there cannot be a perfect cancellation of resonance effects.

(76) Reynolds, W. F.; Peat, I. R.; Freedman, M. H.; Lyerla, J. R. *Can. J. Chem.* **1973**, *51*, 1857.

expected since solvation and ion-pair effects must be significant for this group ($^+NH_3$) in CF_3CO_2H as solvent. Thus, we have attempted to estimate a more realistic electronic charge for $^+NH_3$ in CF_3CO_2H by utilizing the appropriate ^{13}C and ^{19}F SCS for this group from the phenylbicyclooctyl (I, X = $^+NH_3$; + 1.02 ppm (C-4))[17b] and (*p*-fluorophenyl)bicyclooctyl systems ($^+NH_3$; +2.18 ppm)[17b] respectively. This was achieved by determining the F_D contribution (^{19}F SCS − F_π) to the ^{19}F SCS of the latter model system by using an averaged proportionality factor (1.40) to determine F_π (^{13}C SCS × 1.40 = 1.02 × 1.40 ppm) and then equating this value to the Buckingham equation[18] for the (*p*-fluorophenyl)bicyclooctyl system [SCS = AE_z, where $A = 31.0 \times 10^{-12}$ (esu) and $E_z = e/r^2$; r is the length of a line drawn between the midpoint of the CF bond and $^+NH_3$]. A value of 1.96×10^{-10} (esu) was obtained for the electronic charge which is substantially less than the value for full electron deficiency. F_D contributions to the ^{19}F SCS of $^+NH_3$ for benzene and naphthalene were calculated using this value and these are listed in Table X.

A cursory examination of the results listed in Table X clearly indicates that there are some significant differences in an absolute sense between the two sets of F_D calculations. This was to be expected given the obvious limitations of attempting electric field calculations in polar solvents.[65] However, it is also clear that the pattern of F_D effects between the two sets of calculations are very similar. The most important feature of the dissections (F_D and F_π) for $^+NH_3$ (Table X) is their overall similarity with the results for the $C(CN)_3$ group (Table IX). In particular, note the similar results for the 5α (relative to $C(CH_3)_3$ for $C(CN)_3$; vide supra) and 6α dispositions, the 7α and 8β dispositions, as well as the 4β orientation which were specifically alluded to above. One of the more noticeable differences between the two analyses (Tables IX and X) concerns the trends between the two sets of F_D calculations for the 5β and 8β dispositions. For the $C(CN)_3$ group, it can be seen (Table IX) that whereas in the 5β orientation the F_D contributions determined by factoring out F_π from the observed ^{19}F SCS are considerably smaller than those calculated using the Buckingham equation,[18] the converse situation is observed in the 8β disposition. Moreover, the calculations utilizing the Buckingham equation indicate that the F_D contribution in these two orientations should be similar. On the other hand, it can be seen from the analysis for the $^+NH_3$ group (Table X) that both types of calculations indicate that F_D effects should be similar for these two orientations.

These results highlight the fact that the ^{19}F SCS for CH_3 (Table VI) in the 5β and 8β orientations are unquestionably anomalous (too far *upfield* and *downfield* by at least 1 ppm, respectively) either from conventional electronic considerations[2] or expectations based on their correponding ^{13}C SCS (5β, 0.00 ppm; 8β, − 0.13 ppm).[14] Thus, by utilizing SCS determined relative to CH_3 rather than H as reference substituent to define the polar field effect of $^+NH_3$[75] but not $C(CN)_3$, substituent-induced ^{19}F NMR shifts which are not electronic in origin are apparently compensated for in the former but not the latter substituent. Interestingly, if the observed ^{19}F SCS for $C(CN)_3$ in these two orientations are approximately corrected for this phenomenon by using the appropriate ^{19}F SCS for CH_3 (Table VI) as the reference point, then the agreement between the two sets of F_D calculations (Table IX) become much more reasonable. We believe this result strengthens the proposal previously enunciated[2] that substituents in certain orientations, irrespective of their electronic behavior, can effect a perturbation of the ^{19}F chemical shift merely by their presence.

Table XI. Best Fit Parameters of DSP Equation[a] for Substituent ^{19}F NMR Shielding Effects in Naphthalene

disposition[b]	solvent	ρ_I	ρ_R	λ[c]	n[d]	SD[e]	f[f]
3α	DMF	7.69	1.85	0.24	8	0.86	0.27
3α[g]	DMF	9.50	0.57	0.06	7	0.86	0.20
4α	DMF	13.16	33.06	2.51	13	1.01	0.12
4α[h]	DMF	11.05	34.12	3.09	13	0.80	0.09
5α	DMF	5.36	0.51	0.10	9	0.80	0.37
5α[g]	DMF	3.15	2.10	0.67	7	0.41	0.28
6α	DMF	2.73	1.63	0.60	7	0.27	0.24
7α	DMF	3.56	4.78	1.35	9	0.27	0.16
4β	DMF	1.90	−2.91	−1.53	7	0.54	0.48
4β[g]	DMF	3.17	−4.09	−1.29	6	0.25	0.15
5β	DMF	3.75	3.40	0.91	7	0.59	0.34
5β[g]	DMF	5.75	0.74	0.13	6	0.41	0.15
6β	DMF	6.96	13.01	1.87	15	0.47	0.12
6β	C_6H_6	6.63	12.74	1.92	12	0.36	0.10
7β	DMF	4.55	2.31	0.51	15	0.24	0.14
7β	C_6H_6	4.46	1.97	0.44	13	0.22	0.12
8β	DMF	9.14	5.23	0.57	12	0.78	0.23
8β[g]	DMF	7.15	6.42	0.90	11	0.29	0.10

[a] SCS = $\rho_I\sigma_I + \rho_R\sigma_R^0$, where ρ_I and ρ_R are the polar and resonance susceptibility parameters, respectively. The sign convention for the SCS is opposite to that previously employed (ref 2). [b] See ref 3. [c] $\lambda \equiv \rho_R/\rho_I$. [d] The number of substituents in the data set. [e] The standard deviation of the fit. [f] The fit parameter, $f \equiv$ SD/RMS, where RMS is the root mean square of the data points. Correlations of excellent precision are those for which $f \leq 0.1$. [g] SCS calculated using CH_3 (SCS = 0) as the reference substituent rather than H. [h] SCS calculated using 1-fluoro-5-methylnaphthalene as the parent compound rather than 1-fluoronaphthalene.

In conclusion, it goes almost without saying that the results set out in Tables IX and X clearly invalidate our previous attempt to delineate ^{19}F NMR polar field effects for the various orientations of benzene and naphthalene. Most importantly, these dissections cogently demonstrate the two basic differences between polar effects monitored by aryl ^{19}F chemical shifts on the one hand, and chemical reactivity probes on the other.[77] (i) Whereas the latter arise predominantly from direct electrostatic interaction between the substituent and the reaction site, the former in many instances (Table IX and X) are dominated by the F_π polar mechanism (π polarization).[15] This must be the main reason for the observed variable ρ values when the FMMF empirical treatment of substituent effects[78] is applied to aryl ^{19}F SCS, but not chemical reactivity parameters, as the method treats only direct field effects (F_D). Unfortunately, because the pattern of F_π effects observed in the aryl rings (Tables IX and X) is not readily accommodated by a simple bond polarizability model,[79] it is difficult to see how they could be included in a general empirical treatment in a simple way. (ii) Whereas the direct field interaction for the latter is the result of a scalar field at the reaction site, F_D effects for the former depend on the component of the electric field acting along the CF bond (vector quantity). This distinction is clearly responsible for the dramatically different relative direct field effects at certain dispositions in naphthalene as monitored by each probe [chemical reactivity,[78,80] 7α > 8β; ^{19}F NMR

(77) (a) Reynolds, W. F. *Tetrahedron Lett.* **1977**, 675, and references cited therein. (b) Reynolds, W. F.; Mezey, P. G.; Hamer, G. K. *Can. J. Chem.* **1977**, *95*, 7242, and references cited therein.

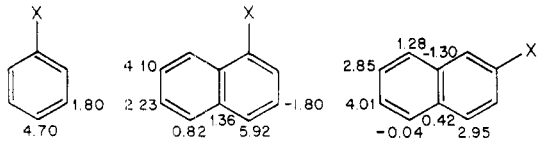
(78) Dewar, M. J. S.; Golden, R.; Harris, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 4187.

(79) Batchelor, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 3411.

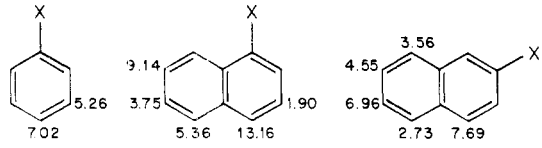
(80) (a) Dewar, M. J. S.; Grisdale, P. J. *J. Am. Chem. Soc.* **1962**, *84*, 3548. (b) Wells, P. R.; Adcock, W. *Aust. J. Chem.* **1965**, *18*, 1365.

Chart III

ρ_I values (^{13}C SCS)



ρ_I values (^{19}F SCS)



(Tables IX and X), $8\beta > 7\alpha$].

DSP Correlative Analyses. The dual substituent parameter (DSP) equation[10] embodies the idea that the electronic effect of a substituent may be considered an additive blend of effects due entirely to polar (σ_I) and resonance or mesomeric (σ_R) phenomena and that, since σ_I and σ_R are quantities independent of one another, regression analysis of data using the equation (see footnote *a* to Table XI) is able to distinguish and meaningfully separate them. It is important to note, however, that the efficacy of the methodology hinges critically on a minimum basis set of substituents,[10b] embracing a wide range of electronic behavior, for which there are nonlinear relationships between the σ_I and σ_R values of both the –R and +R substituents. Although the validity of this free fitting statistical procedure has been strongly questioned,[81] some experimental support for it has recently been presented[14,16] based on the observation that the pattern of ρ_I values from a DSP analysis of the ^{13}C SCS for 4-substituted biphenyls and 1- and 2-substituted naphthalenes (Chart III) is very similar to the ^{13}C SCS for 4-ammoniobiphenyl and 1- and 2-ammonionaphthalene (Chart II), respectively. A similar comparison of the ^{13}C and ^{19}F SCS for $C(CN)_3$ (Chart I) as well as the ^{19}F SCS (relative to CH_3)[75] for $+NH_3$ in benzene and naphthalene (Chart II) with the corresponding ρ_I values (Chart III) offers further corroboration of the basic correctness of the separation of polar and resonance effect contributions to the ^{13}C and ^{19}F SCS for substituted benzenes and naphthalenes by the DSP equation. The ρ_I values for the ^{13}C SCS ($DCCl_3$) of naphthalene displayed in Chart III were taken from our recent work[14] while those for benzene ($DCCl_3$) were kindly provided by Professor R. W. Taft. The ρ_I values for the ^{19}F SCS in benzene (Chart III) are for CCl_4 as solvent,[66] while the corresponding values for naphthalene (Chart III) were obtained from a new DSP analysis of the appropriate ^{19}F SCS[2] since the data set for some orientations, in particular 5α[72c] and 6α (this study), have been expanded. Table XI summarizes these latter results for the various orientations.

It should be noted, however, that in making these comparisons several important facts should be borne in mind. First, there may not be an exact cancellation of resonance effects in strongly conjugated positions (para, 4α, 7α, 6β, 8β) when monitoring pure polar contributions to SCS with $^+NH_3$ (relative to CH_3)[75] in CF_3CO_2H. On the other hand, the polar parameters provided by the SCS of $C(CN)_3$ definitely need correcting for a weak electron-donating resonance influence ($\sigma_R^0 = -0.04$) in similar orientations. Based on the appropriate ρ_R values, the following approximate correction values for resonance emerge: ^{13}C SCS (ppm), para, 0.80; 4α, 0.80; 7α, 0.20; 6β, 0.30; 8β, 0.20; ^{19}F SCS (ppm), para, 1.20; 4α, 1.20; 7α, 0.20; 6β, 0.50; 8β, 0.20). As mentioned above, however, the resonance correction factor (^{13}C and ^{19}F SCS) in the 4α orientation for the $C(CN)_3$ group is probably more than cancelled out by a corresponding substituent-induced structural factor (downfield shift). Second, in certain orientations in naphthalene both ^{13}C (4α and 5α) and ^{19}F SCS (4α, 5α, 5β and 8β) are manifested by factors (probably structural) not necessarily electronic in origin.[2,14] Thus, appropriate corrections (vide supra) are probably necessary for the SCS of $C(CN)_3$ but not those for $^+NH_3$ since these are relative to a group (CH_3) of similar size. Although it is impossible to predict into which term ($\rho_I\sigma_I$ or $\rho_R\sigma_R^0$) these extraneous factors will be "shunted" by the DSP analysis, it is of interest to note that the ρ_I value for ^{19}F SCS is significantly altered (sometimes the precision of fit as well) in these problem orientations when CH_3 is employed as the reference substituent rather than H (see Table XI: 3α, 4α, 5α, 4β, 5β, 8β). Third, the precision of fit of the data (relative to H) by the DSP equation is very poor indeed for some orientations [^{13}C SCS:[14] 5α, 7α, and 4β; ^{19}F SCS: 4β (Table XI)] and is not likely to be improved by an expanded and more stringent basis data set. Fourth, the electronic effect of the $C(CN)_3$ group is markedly influenced by the nature of the solvent (Table VI; vide infra), thus, it is appropriate to employ the CH_2Cl_2 and c-C_6H_{12} ^{19}F SCS in naphthalene for this group (Chart I) when making comparisons with the appropriate ρ_I values (DMF). Finally, although ^{13}C SCS data from system I (C-4) clearly indicate that the polar field effect of $^+NH_3$ in CF_3CO_2H (+ 1.02 ppm)[17b] is very similar to that for $C(CN)_3$ ($DCCl_3$, 1.18 ppm), solvent effects may cause more significant differentials in certain orientations of benzene and naphthalene.

In conclusion, although there are some fairly obvious problems of interpretation and of reconciliation of discordant observations that remain to be resolved on comparing the SCS data for $C(CN)_3$ and $+NH_3$ (Chart I and II) with the appropriate DSP derived ρ_I values (Chart III), it is quite apparent again (vide supra) that the 6β and 7β dispositions of naphthalene are the most well behaved. Note for these two dispositions the excellent accord between the various polar parameters as monitored by $^+NH_3$, $C(CN)_3$, and DSP ρ_I values. This contrasts significantly with the less satisfactory situation for the meta and para orientations of the benzene ring, particularly when fluorine is the probe. Interestingly, the ^{19}F SCS results for both the $C(CN)_3$ and $^+NH_3$ group (Charts I and II, respectively) clearly indicate that the DSP analysis significantly underestimates the polar susceptibility parameter (ρ_I; ^{19}F SCS) for the strongly conjugated para disposition in benzene. This is contrary to recent evidence which has emerged from more refined multiparameter regression analyses (DSP-2).[10c] One of the main factors which can complicate the use of fluorine as an electronic probe is the possibility of direct conjugative interactions between the substituent and the probe. That this is important in the para orientation of benzene is evident from the apparent bilinear relationship which exists between ^{19}F and ^{13}C SCS in this orientation,[66] and is further corroborated by a similar relationship for the plot between the appropriate theoretical parameters (Δq_π^F vs. Δq_π^C).[66] Note, however, that this phenomenon is not apparent in the conjugated 6β disposition of naphthalene as there is a good linear relationship here between ^{19}F SCS[2,25,67] and the corre-

(81) (a) Ager, I. R.; Phillips, L.; Tewson, T. J.; Wray, V. *J. Chem. Soc. Perkin Trans 2*, **1972**, 1980. (b) Mitchell, P. J.; Phillips, L. *ibid.* **1974**, 109. (c) Johnson, C. D.; Roberts, I.; Taylor, P. G. *J. Chem. Soc., Chem. Commun.*, **1977**, 897.

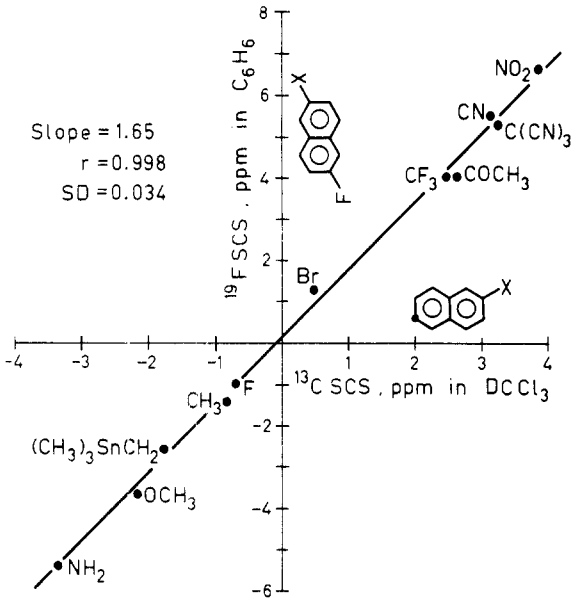


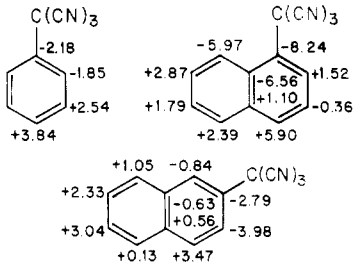
Figure 3. Plot of ^{19}F SCS (benzene) of 6-substituted 2-fluoronaphthalenes (6β) vs. ^{13}C SCS ($DCCl_3$) of C6 in 2-substituted naphthalenes.

sponding ^{13}C NMR parameters[14,25] (Figure 3). Interestingly, a DSP-2 analysis [10c] of the 6β (fluoronaphthyl) ^{19}F SCS data yield ρ_I values of 6.32 (DMF) and 6.04 (benzene), respectively, which are in slightly better agreement with the magnitude of ρ_I suggested by the ^{19}F SCS for $C(CN)_3$ (Chart I) and $^+NH_3$ (Chart II) than the ρ_I values (Chart III) derived by the more conventional DSP treatment.[10a,b] This suggests that conjugative substituent–probe interactions may be slightly influencing ^{19}F SCS in this orientation.

Solvent Effects. The large solvent effects displayed by the electronic effect of the $C(CN)_3$ group as monitored by the fluorine probe (Table VI) are of interest since, although extremely complex, some qualitative appreciation of the broad trends can be achieved by consideration of the following facts. (i) Aryl ^{19}F NMR polar shifts are the net result of two distinct polar mechanisms ($F_D + F_\pi$).[15] Moreover, as seen from this study, the actual blend or relative importance of these mechanisms is highly dependent on the geometrical relationship between the substituent and fluorine probe. Thus, according to the simple Dayal–Taft model[82] for ^{19}F NMR polar solvent shifts, an increase in both F_D and F_π is to be expected in polar solvents due to enhanced substituent polarity as a result of solvation. In addition, the possibility also arises that the F_D contribution may be attenuated by an increase in the effective dielectric constant[83] due to intrusion of the polar solvent into the cavity (dependent on the orientation) through which the major lines of force must pass. The effect of this factor on F_π is impossible to qualitatively assess on an a priori basis. (ii) Unlike most conventional dipolar substituents employed in substituent effect studies, the $C(CN)_3$ group is a highly pendant substituent and, thus, the major lines of force of its electric field traverse the periphery rather than the internal region of the molecule.[4] As a result, this is likely to lead to an abnormally pronounced dependence of its polar effect on the effective dielectric term. (iii) It has been shown that the efficiency of transmission of ^{19}F NMR polar effects in the (fluorophenyl)bicyclooctyl[17b] (rod-shaped) and fluorophenyl[81] (disk-shaped) systems for conventional substituents are in the order c-C_6H_{12} > CH_2Cl_2 > C_6H_6 ~ MeOH > DMF and DMF ~ MeOH > C_6H_6 > c-C_6H_{12}, respectively. These results highlight the relative importance of the effective dielectric term and enhanced substituent polarity as a function of the shape of the molecule and the blend of the two polar mechanisms ($F_D + F_\pi$).

Chart IV

^{13}C SCS [$(CD_3)_2CO$]



Based on the assumption that a solvent differential greater than 0.1 ppm is significant, then the solvent effects in the various orientations of naphthalene as displayed by the ^{19}F SCS of the $C(CN)_3$ group (Table VI) may be summarized as follows: 3α, CH_2Cl_2 > C_6H_6 ~ c-C_6H_{12} > MeOH > DMF; 4α, CH_2Cl_2 > MeOH ~ c-C_6H_{12} > C_6H_6 ~ DMF; 5α CH_2Cl_2 > MeOH > DMF > c-C_6H_{12} > C_6H_6; 6α, CH_2Cl_2 > c-C_6H_{12} > MeOH > DMF ~ C_6H_6; 7α, c-C_6H_{12} ~ CH_2Cl_2 ~ C_6H_6 > MeOH > DMF; 4β, c-C_6H_{12} ~ C_6H_6 > CH_2Cl_2 ~ MeOH > DMF; 5β, c-C_6H_{12} > CH_2Cl_2 > MeOH ~ C_6H_6 > DMF; 6β c-C_6H_{12} > CH_2Cl_2 > C_6H_6 ~ MeOH > DMF; 7β, c-C_6H_{12} > CH_2Cl_2 > MeOH > C_6H_6 > DMF; 8β, CH_2Cl_2 ~ C_6H_6 > MeOH > DMF. Note that in all orientations except 5α the efficiency of transmission of the polar effect is at a minimum in DMF, which is the solvent with the largest bulk dielectric constant. Furthermore, it should be noted that whereas the overall trend for the 6β disposition (elliptoid-shaped) is identical with that observed in the (fluorophenyl)bicyclooctyl system (vide supra), the situation in the 4α orientation (disk-shaped) is quite different to that observed in the fluorophenyl system (vide supra) for conventional substituents. Note also that for the latter substituents in the 6β disposition, the efficiency of transmission of polar effects in DMF is greater than that in benzene as solvent [Table XI; ρ_I = 6.96 (DMF) and 6.63 (C_6H_6)]. These results clearly exemplify that the effective dielectric term impinges importantly on polar ^{19}F SCS as determined by the $C(CN)_3$ group. Although this is probably manifested more in the F_D component, it is apparent from a comparison of the ^{13}C SCS for $C(CN)_3$ in acetone (Chart IV) with those in $DCCl_3$ (Chart I) that the F_π contribution is also slightly attenuated. This latter observation contrasts with the results for conventional polar substituents for a similar solvent change.[14]

Finally, it should be pointed out that the relative trends for c-C_6H_{12} and CH_2Cl_2 in each orientation highlight the subtle interplay of the effective dielectric term and enhanced substituent polarity on both F_D and F_π contributions to the polar shift. Although the reason why ^{19}F NMR polar field effects in some orientations are markedly attenuated in benzene ($\epsilon \simeq 2.3$) compared to cyclohexane ($\epsilon \approx 2.0$) is not immediately apparent, it may be due to polarizability, size, and shape factors impinging on the effective dielectric term.[83]

Acknowledgments. We thank Monash University and the University of Adelaide for the use of their NMR facilities as well as the Australian Research Grants Com-

(82) Dayal, S. K.; Taft, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 5595.
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mittee for providing access to the National NMR Center (Director: Dr. Alan Jones). We are indebted to Professor R. D. Topsom for the infrared intensity measurements, and to Professor R. W. Taft and Dr. R. T. C. Brownlee for a copy of the DSP computer program.

Registry No. I (X = H), 23062-62-6; I (X = CH_2OH), 23760-80-7; I (X = CH_2Cl), 70631-55-9; I (X = CH_2CN), 70631-56-0; I (X = CH_2COOH), 70631-57-1; I (X = CH_2COOCH_3), 70631-58-2; I (X = $CH(CN)_2$), 70631-59-3; I (X = $C(CN)_3$), 70631-60-6; 1-fluoro-3-(bromomethyl)naphthalene, 34236-55-0; 1-fluoro-3-(cyanomethyl)-naphthalene, 70631-33-3; 1-fluoro-3-(tricyanomethyl)naphthalene, 70631-34-4; 1-fluoro-4-(bromomethyl)naphthalene, 6905-05-1; 1-fluoro-4-(cyanomethyl)naphthalene, 3832-87-9; 1-fluoro-4-(tricyanomethyl)naphthalene, 61653-16-5; 1-fluoro-5-(bromomethyl)-naphthalene, 70631-35-5; 1-fluoro-5-(cyanomethyl)naphthalene, 70631-36-6; 1-fluoro-5-(tricyanomethyl)naphthalene, 70631-37-7; 1-fluoro-6-(bromomethyl)naphthalene, 70631-38-8; 1-fluoro-6-(cyanomethyl)naphthalene, 70631-39-9; 1-fluoro-6-(tricyanomethyl)-naphthalene, 70631-40-2; 1-fluoro-7-(bromomethyl)naphthalene, 70631-41-3; 1-fluoro-7-(cyanomethyl)naphthalene, 70631-42-4; 1-fluoro-7-(tricyanomethyl)naphthalene, 70631-43-5; 2-fluoro-4-(bromomethyl)naphthalene, 70631-44-6; 2-fluoro-4-(cyanomethyl)-naphthalene, 70631-45-7; 2-fluoro-4-(tricyanomethyl)naphthalene, 70631-46-8; 2-fluoro-5-(bromomethyl)naphthalene, 70631-47-9; 2-fluoro-5-(cyanomethyl)naphthalene, 70631-48-0; 2-fluoro-5-(tricyanomethyl)naphthalene, 70631-49-1; 2-fluoro-6-(bromomethyl)-naphthalene, 581-72-6; 2-fluoro-6-(cyanomethyl)naphthalene, 66922-61-0; 2-fluoro-6-(tricyanomethyl)naphthalene, 61653-14-3; 2-fluoro-7-(bromomethyl)naphthalene, 64168-12-3; 2-fluoro-7-(cyanomethyl)naphthalene, 66922-65-4; 2-fluoro-2-(tricyanomethyl)-naphthalene, 61653-15-4; 2-fluoro-8-(bromomethyl)naphthalene, 70631-50-4; 2-fluoro-8-(cyanomethyl)naphthalene, 70631-51-5; 2-fluoro-8-(tricyanomethyl)naphthalene, 70631-52-6; (tricyanomethyl)benzene, 5247-17-6; 1-(tricyanomethyl)naphthalene, 5247-21-2; 2-(cyanomethyl)naphthalene, 7498-57-9; 2-(dicyanomethyl)-naphthalene, 32122-61-5; 2-(tricyanomethyl)naphthalene, 70631-53-7; *m*-fluoro(tricyanomethyl)benzene, 5247-19-8; 2-(dicyanomethyl)-6-fluoronaphthalene, 70631-54-8; 1-fluoro-3-ammonionaphthalene, 70631-61-7; 1-fluoro-4-ammonionaphthalene, 70631-62-8; 1-fluoro-5-ammonionaphthalene, 70631-63-9; 1-fluoro-6-ammonionaphthalene, 70631-64-0; 1-fluoro-7-ammonionaphthalene, 70631-65-1; 2-fluoro-4-ammonionaphthalene, 70631-66-2; 2-fluoro-5-ammonionaphthalene, 70631-67-3; 2-fluoro-6-ammonionaphthalene, 70631-68-4; 2-fluoro-7-ammonionaphthalene, 70631-69-5; 2-fluoro-8-ammonionaphthalene, 70631-70-8; 1-fluoro-3-methylnaphthalene, 319-15-3; 1-fluoro-4-methylnaphthalene, 315-50-4; 1-fluoro-5-methylnaphthalene, 51010-55-0; 1-fluoro-6-methylnaphthalene, 70631-71-9; 1-fluoro-7-methylnaphthalene, 59080-31-8; 2-fluoro-4-methylnaphthalene, 59079-88-8; 2-fluoro-5-methylnaphthalene, 59079-89-9; 2-fluoro-6-methylnaphthalene, 324-42-5; 2-fluoro-7-methylnaphthalene, 29885-92-5; 2-fluoro-8-methylnaphthalene, 70631-72-0; 1-fluoro-4-(dibromomethyl)naphthalene, 70631-73-1; 1-fluoro-7-(dibromomethyl)naphthalene, 70631-74-2; 2-fluoro-6-(dibromomethyl)-naphthalene, 70631-75-3; 2-fluoro-7-(dibromomethyl)naphthalene, 70631-76-4; 2-fluoro-7-(dicyanomethyl)naphthalene, 70631-77-5; 1-fluoro-4-(tribromomethyl)naphthalene, 70631-78-6; 2-fluoro-6-(tribromomethyl)naphthalene, 70631-79-7; 2-fluoro-7-(tribromomethyl)naphthalene, 70631-80-0; 1-fluoro-6-formylnaphthalene, 70631-81-1; 1-fluoro-6-aminonaphthalene, 13720-50-8; 1-fluoro-6-carboxynaphthalene, 70631-82-2; *p*-fluoro(tricyanomethyl)benzene, 5247-20-1; *m*-fluoroammoniobenzene, 28966-00-9; *p*-fluoroammoniobenzene, 29131-39-3; phenylacetone, 103-79-7; 3-methyl-4-phenylbutanoic acid, 7315-68-6; 3-methyl-1-tetralone, 14944-23-1; 3-methyl-1-tetralone oxime, 70631-83-3; 3-methyl-1-naphthylamine hydrochloride, 13615-39-9; 3-methyl-1-naphthyldiazonium hexafluorophosphate, 70631-85-5; 5-fluoro-1-naphthylmagnesium bromide, 70631-86-6; 3-methylbenzyl chloride, 620-19-9; 4-(*m*-tolyl)butanoic acid, 22156-45-2; 6-methyl-1-tetralone, 51015-29-3; 6-methyl-1-tetralone oxime, 70631-87-7; *o*-fluorobenzyl chloride, 345-35-7; 4,4-dimethoxybutan-2-one, 5436-21-5; β-(*m*-fluorophenyl)propionic acid, 458-45-7; 4-(*m*-fluorophenyl)butanoic acid, 70631-88-8; 6-fluoro-1-tetralone, 703-67-3; 6-fluoro-1-methyl-1-tetralol, 70631-89-9; 6-fluoro-1-methyl-3,4-dihydronaphthalene, 70631-90-2; 7-fluoro-1-tetralone, 2840-44-0; 4-phenyl-1-bicyclo[2.2.2]octylcarboxylic acid, 953-69-5; 4-phenyl-1-bicyclo[2.2.2]octylmalonamide, 70631-91-3; 2-(*o*-fluorobenzyl)-4,4-dimethoxy-2-butanol, 70631-92-4; methyl bromide, 74-83-9.

Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy. Natural-Abundance Nitrogen-15 Chemical Shifts of Alkyl- and Aryl-Substituted Ureas[1]

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^{15}N chemical shifts of urea and several alkyl- and arylureas have been determined at the natural-abundance level in DMF and Me_2SO. Dilution has very little effect on the chemical shifts. N-Methylation at nitrogen induces systematic upfield shifts which contrast with expected downfield shifts. Alkyl substitution at positions β, γ, and δ to the nitrogen induces shifts in the expected order based on aliphatic amines. Multiple regression analysis gives appropriate α, β, γ, and δ substituent parameters. The shifts of urea and the methylureas can be correlated with ionization potential differences between lone-pair molecular orbitals. Activation energy barriers for rotation around the C–N bond have been estimated using equations derived for substituted amides; the appropriateness of this method is discussed. ^{13}C chemical shifts of the ureas have also been determined.

As a class of compounds, ureas are chemically and pharmacologically important because they are effective protein denaturants and because the urea moiety is a structural element in biologically active compounds such as barbiturates and purine bases. To the extent that nitrogen nuclear magnetic resonance (NMR) spectroscopy is useful in probing the structures and interactions of these types of compounds, a knowledge of the factors influencing their chemical shifts is useful. Some early results using ^{14}N NMR have been reported,[2,3] but identification of resonances of unsymetrically substituted ureas is hampered by the inherently broad signals arising from ^{14}N quadrupolar relaxation. ^{15}N data for urea and tetramethylurea

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