Substituent Effects in the Naphthalene Ring System by ^{19}F NMR

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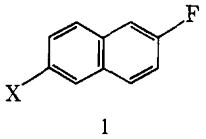
Abstract: More than 60 new substituted fluoronaphthalenes, and two new substituted fluorobiphenyls, have been synthesized and their ^{19}F chemical shifts measured. An analysis of the data provided the following conclusions. (1) Geometrical factors, as well as electronic interactions, appear to play a significant role in determining ^{19}F chemical shifts of peri-substituted fluoronaphthalenes. (2) The electronic effect of the trifluoromethyl substituent is a result of both a significant polar and π-electron effect. (3) A reexamination of ^{19}F chemical shifts in naphthalene in terms of Taft's DSP equation indicates that the precision of fit is not as good as previously reported. (4) ^{19}F substituent chemical shifts (SCS) from the 6β and 7β orientations can be confidently interpreted in terms of chemical reactivity parameters. Further, these two dispositions appear to have a number of advantages over the meta and para dispositions of fluorobenzene for estimating σ_I and $\sigma_R{}^0$ values of various substituents.

The fluorophenyl tag has been exploited extensively over the past decade as a sensitive probe for evaluating the electronic properties of substituents. Utilizing the precise linear relationships developed by Taft and co-workers[1] from the ^{19}F parameters[2] of meta- and para-substituted fluorobenzenes, many σ_I and σ_R values of a whole host of substituent types, varying in size and geometry, have been assigned.[1,3] The validity of the methodology is based essentially on two main assumptions. First, that the SCS is considered to be an exclusive manifestation of the electronic effect of the substituent. Since fluorine chemical shifts are considered to be dominated by the paramagnetic term of the Ramsey equation,[4] certain approximations are inevitable to reach this assumption, in particular, a constant average excitation energy term (ΔE) within a structurally similar series of compounds.[5] Second, that the meta SCS depended solely on inductive phenomena (σ_I), there being no resonance contribution by the substituent. Although the latter assumption has been criticized and shown to be highly questionable,[6] the first basic premise has remained virtually unchallenged with regards to the possibility that insertion of any substituent into a fluorinated aromatic produces a chemical shift merely by its presence, independent of any specific electronic effect. In terms of the usual treatment of chemical shifts, this would imply that ΔE is a function of the substituent.

However, recent studies of substituent effects in naphthalene and other model systems, where the substituent and fluorine probe are not proximate, have revealed that geometrical[7] and conformational factors,[8] as well as electronic factors, may be important in determining the fluorine chemical shifts of substituted aryl fluorides. In particular, our studies[7b] have shown that whereas ^{19}F SCS data derived from the fluorobenzene ring are likely to be complicated by substituent-induced structural distortions,[9] SCS formation from the 6β and 7β orientations[10] (**1** and **2**, respectively) of β(or 2)-fluoronaphthalene appear to be free of this phenomenon.



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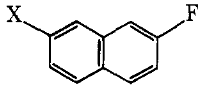

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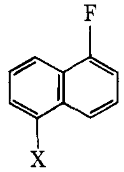

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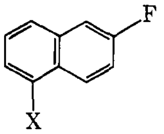

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As a result of this new insight into the factors governing the magnitude of ^{19}F SCS, we have extended our studies in naphthalene to include the two previously unknown series (5α and 5β,[10] **3** and **4**, respectively) of substituted fluoronaphthalenes as well as extending the range of substituent types (trifluoromethyl, methyl, onium, trimethylsilyl, and halogen substituents) in the other eight known dispositions.[6b,c,7b,11] In this paper we report on their synthesis and a study of their ^{19}F spectra.

Experimental Section

Synthesis. Although some compounds were available from previous studies,[7b,11] most of the naphthalene compounds described in this research are new.

Since the methods employed for converting a particular precursor to an appropriately substituted fluoronaphthalene (or fluorobiphenyl) are similar for most orientations, only a typical procedure for one of the orientations (mainly 4α) will be described. Twelve known meta- and para-substituted (SH, SCH_3, SO_2CH_3, $^+S(CH_3)_2$, and $P^+(CH_3)_3$) fluorobenzenes were prepared by the standard procedures outlined in the text for the correspondingly substituted fluoronaphthalenes. The analytical data for those naphthalene derivatives not described in the text are summarized in Table I together with the data for two new disubstituted biphenyls, namely 3′-fluoro-4-trifluoromethylbiphenyl (**23**) and 4′-fluoro-4-trifluoromethylbiphenyl (**24**). Molecular weight determinations (m/e) for all the compounds (table and in text) by mass spectrometry confirmed the indicated molecular formulas. ^{1}H NMR spectra for compounds **25–45**, as well as all compounds described in the text, were in accord with the assigned structures. Compounds **1–33** were shown to be homogeneous to GLC.

Spectra. The fluorine NMR spectra were measured with a Varian DP-60 spectrometer operating at 56.4 MHz, using solutions containing 15% (w/w) of the fluoro compound together with 5% (w/w) of 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFB) as internal standard. The Varian DP-60 instrument had been modified to obtain spectra in the HA mode which were calibrated using a Racal SA35 universal counter time. ^{1}H NMR spectra of all compounds were obtained using a Varian A-60 spectrometer; all spectra were integrated for the assigned structures.

1,4-Difluoronaphthalene. 1-Acetyl-4-fluoronaphthalene was prepared as described by Jacobs, Winstein, Ralls, and Robson.[12] Distillation of the crude product afforded a colorless oil, bp 102–108 °C (0.6–0.8 mm) (lit.[12] 138–140 °C (4.5 mm)). The ketone was converted to the oxime by treatment with hydroxylamine hydrochloride in the presence of pyridine. The oxime crystallized from aqueous ethanol in colorless needles, mp 123–124 °C. Treatment of the powdered oxime (68 g, 0.34 mol) with polyphosphoric acid

Table I. Analytical Data for the Substituted Fluoronaphthalenes

Compound	Orientation[a]	Precursor[b]	Mp or bp (mm), °C	nD (°C)	Calcd (Found) C, %	Calcd (Found) H, %
1 $FC_{10}H_6F$	3α	14	39–40 (0.02)	1.562 (23)	73.2 (73.2)	3.7 (3.9)
2	5α	*c*	63–64		73.2 (73.4)	3.7 (3.8)
3	6α	*c*	92 (15)	1.568 (25)	73.2 (73.4)	3.7 (3.8)
4	7α	14	46–50 (6)	1.564 (18)	73.2 (73.4)	3.7 (3.9)
5	6β	6c[d]	71.5–72.5		73.2 (73.3)	3.7 (3.8)
6	7β	6c	61–62		73.2 (73.2)	3.7 (3.6)
7 $FC_{10}H_6Cl$	6β	6c[d]	74–75		66.5 (66.7)	3.3 (3.4)
8	7β	6c	69.5–70.5		66.5 (66.1)	3.3 (3.3)
9	8β	14	60–62 (1)		66.5 (66.5)	3.3 (3.5)
10 $FC_{10}H_6Br$	5α	*c*	138–142 (2)	1.624 (25)	53.3 (54.1)	2.7 (3.1)
11	5β	*c*	42–43		53.3 (52.9)	2.7 (2.8)
12 $FC_{10}H_6I$	6β	6c[d]	81–82		44.1 (44.4)	2.2 (2.4)
13	7β	6c	84.5–85.5		44.1 (44.5)	2.2 (2.3)
14	8β	14	45–46		44.1 (44.0)	2.2 (2.3)
15 $FC_{10}H_6CF_3$	3α	14	28–30 (0.05)	1.515 (20)	61.7 (62.1)	2.8 (2.8)
16	5α	*c*	52–54 (2)	1.521 (19)	61.7 (61.8)	2.8 (3.0)
17	7α	14	34–35 (0.1)	1.514 (22)	61.7 (62.0)	2.8 (2.8)
18	4β	14	26–28 (0.05)	1.520 (21)	61.7 (61.5)	2.8 (2.8)
19	5β	*c*, 14	32–33 (0.07)	1.521 (21)	61.7 (62.0)	2.8 (2.8)
20	6β	14	37–38 (0.05)	1.514 (25)	61.7 (61.1)	2.8 (2.8)
21	7β	6c	34–35 (0.05)	1.514 (22)	61.7 (61.2)	2.8 (2.8)
22	8β	14	32–34 (0.05)	1.518 (22)	61.7 (60.8)	2.8 (2.9)
23 $FC_{12}H_8CF_3$	3′,4	6a	63–64 (0.2)	1.523 (19)	65.0 (65.0)	3.4 (3.4)
24	4′,4	6a	29–31		65.0 (64.5)	3.4 (3.6)
25 $FC_{10}H_6CH_3$	3α	14	34–36 (0.05)	1.589 (18)	82.5 (82.4)	5.7 (5.6)
26	4β	14	44–46 (0.03)	1.588 (21)	82.5 (82.6)	5.7 (5.8)
27	5β	*c*, 14	60 (1)	1.587 (21)	82.5 (82.4)	5.7 (5.7)
28 $FC_{10}H_6Si(CH_3)_3$	7α	14	68–71 (0.4)	1.557 (21)	71.5 (72.0)	6.9 (7.0)
29	5β	*c*	79–80 (0.03)	1.566 (25)	71.5 (72.2)	6.9 (7.3)
30	8β	14	64–67 (0.05)	1.566 (21)	71.5 (71.5)	6.9 (6.6)
31 $FC_{10}H_6N(CH_3)_2$	5α	*c*	90–91 (1)	1.591 (25)	76.2 (75.7)	6.4 (6.3)
32	6β	6c[d]	71–72		76.2 (75.5)	6.4 (6.4)
33	7β	6c	97–97.5		76.2 (76.2)	6.4 (6.6)
34 $FC_{10}H_6N^+(CH_3)_3$[e]	5α	*c*			51.5 (52.4)	5.0 (4.7)
35	6β	6c[d]			51.5 (51.2)	5.0 (4.7)
36	7β	6c			51.5 (51.2)	5.0 (5.2)
37 $FC_{10}H_6SH$	7β	6c	87–87.5		67.4 (67.5)	4.0 (4.0)
38 $FC_{10}H_6SCH_3$	6β	*c*	53–54		68.7 (68.8)	4.7 (4.7)
39	7β	*c*	53–54		68.7 (68.9)	4.7 (4.9)
40 $FC_{10}H_6SO_2CH_3$	6β	*c*	121–122		58.9 (59.5)	4.0 (4.2)
41	7β	*c*	107.5–108		58.9 (59.6)	4.0 (4.2)
42 $FC_{10}H_6S^+(CH_3)_2$[e]	6β	*c*			47.1 (47.4)	4.0 (3.8)
43	7β	*c*			47.1 (47.2)	4.0 (4.6)
44 $FC_{10}H_6P^+(CH_3)_3$[f]	6β	14			44.8 (45.3)	4.3 (4.4)
45	7β	6c			44.8 (45.3)	4.3 (4.5)

[a] See ref 10. [b] Reference to synthetic method employed. [c] This text. [d] 2-Amino-6-fluoronaphthalene was prepared from the corresponding naphthol as described for the 7β isomer. [e] Counterion, FSO_3^-. [f] Counterion, I^-.

(2000 g) according to the method outlined by Horning and Stromberg[13] afforded 1-acetamido-4-fluoronaphthalene crystallized from aqueous ethanol in colorless plates (60 g 88%), mp 172–174 °C (lit.[14] 182–183 °C). The acetamido derivative (12.5 g) was hydrolyzed by heating with 6 N hydrochloric acid (200 ml) and the amine, isolated via its hydrochloride salt, crystallized from petroleum ether in light pink plates (6.9 g, 65%), mp 50.5–51 °C (lit.[15] 48 °C). 1-Amino-4-fluoronaphthalene (1.61 g; 0.01 mol) was converted into the diazonium hexafluorophosphate salt (140 °C dec) as described by Adcock and Dewar[14] for the preparation of 2-fluoro-6-nitronaphthalene. The dried salt on decomposition (160 °C) and steam distillation give 1,4-difluoronaphthalene, crystallized from *n*-pentane in colorless plates (0.6 g, 37%), mp 31–32 °C (lit.[15] 31.5 °C).

1-Chloro-4-fluoronaphthalene. 1-Amino-4-fluoronaphthalene (1.61 g, 0.01 mol) was diazotized and the resulting solution was added slowly and cautiously to a solution of freshly prepared cuprous chloride (10 g) in hydrochloric acid (100 ml) at 60 °C. After maintaining the temperature for 60 min, the cooled solution was filtered and the crude residue sublimed to yield 1-chloro-4-fluoronaphthalene crystallized from *n*-pentane in colorless plates (0.4 g, 22%), mp 34–35 °C (lit.[16] 85 °C).

Anal. Calcd for $C_{10}H_6ClF$: C, 66.5; H, 3.3. Found: C, 66.5; H, 3.3.

1-Fluoro-4-iodonaphthalene was prepared by stirring the diazonium salt solution from 1-amino-4-fluoronaphthalene (2 g, 0.12 mol) into a concentrated potassium iodide solution. After 30 min the reaction mixture was extracted with petroleum ether (bp 40–60 °C). The petroleum ether extract was washed with aqueous sodium thiosulfate and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave an oily residue of crude 1-fluoro-4-iodonaphthalene which distilled as a light yellow oil (1.0 g, 29.6%), bp 73–74 °C (0.1 mm).

Anal. Calcd for $C_{10}H_6IF$: C, 44.1; H, 2.2. Found: C, 44.5; H, 2.4.

1-Fluoro-4-trifluoromethylnaphthalene. 4-Fluoro-1-naphthoic acid[12,14] (3.5 g) was treated with sulfur tetrafluoride (10 g)[17,18] in an autoclave at 135 °C for ca. 70 h. Excess sulfur tetrafluoride was vented from the bomb into a solution of sodium hydroxide. The residue in the autoclave was extracted with chloroform and sodium fluoride was added to the solution to remove any excess hydrogen fluoride. The suspension in chloroform was then filtered and the filtrate was washed with a 5% sodium hydroxide solution. The dried chloroform solution was then evaporated in vacuo and the residue steam was distilled to give crude 1-fluoro-4-trifluoromethylnaphthalene. Distillation afforded a colorless oil, bp 25–26 °C (0.03 mm) shown to be homogeneous to GLC.

Anal. Calcd for $C_{11}H_6F_4$: C, 61.7; H, 2.8. Found: C, 60.8; H, 2.8.

1-Fluoronaphthalene-4-trimethylammonium Fluorosulfonate. 1-

Amino-4-fluoronaphthalene (4.7 g, 0.03 mol) was treated with dimethyl sulfate (4 ml) as described by Hodgson et al.[19] for the preparation of 1-dimethylaminonaphthalene. 1-Dimethylamino-4-fluoronaphthalene distilled as a colorless oil (3.3 g, 62.5%), bp 92-96 °C (0.5 mm) (lit.[14] 96-98 °C (1 mm)).

A solution of 1-dimethylamino-4-fluoronaphthalene (0.6 g) in dry diethyl ether was treated with methyl fluorosulfonate[20] (1 g) and stirred for 30 min. The solid 1-fluoronaphthalene-4-trimethylammonium fluorosulfonate was collected and recrystallized from methanol. The salt formed light yellow needles (0.6 g, 60%).

Anal. Calcd for $C_{13}H_{15}FN$: C, 51.5; H, 5.0. Found: C, 51.6; H, 5.0.

1-Fluoro-4-methoxynaphthalene. A solution of 1-methoxy-4-nitronaphthalene[21] (20 g, 0.1 mol) in ethanol (200 ml) was reduced with hydrogen (50 psi) over palladized charcoal (5%). After reduction was complete the solution was filtered and evaporated in vacuo to give a reddish black oil of crude 4-methoxy-1-naphthylamine.

A solution of the crude amine (17.3 g, 0.1 mol) in tetrahydrofuran (150 ml) and fluoroboric acid (200 ml, 43%) at 0 °C was treated dropwise with stirring with a saturated solution of sodium nitrite (7.6 g, 0.11 mol).[22] The fluoroborate salt was collected and dried, mp 137-139 °C dec. Decomposition of the salt in cumene, followed by distillation, gave a light yellow oil of 1-fluoro-4-methoxynaphthalene (7.5 g, 43%): bp 77-80 °C (0.3 mm); n^{19}D 1.598.

Anal. Calcd for $C_{11}H_9FO$: C, 75.0; H, 5.1. Found: C, 75.5; H, 5.2.

A solution of 1-fluoro-4-methoxynaphthalene (3.52 g, 0.02 mol) in pyridinium chloride[23] (7.5 g) was refluxed for 20 min and then poured onto ice. The precipitate was collected, washed with water, dried, and recrystallized from light petroleum (bp 60-90 °C) giving 4-fluoro-1-naphthol as colorless plates (1.8 g, 55%), mp 127-128 °C (lit.[24] 115 °C).

4-Fluoro-1-thionaphthol. Reduction[25] of 1-chlorosulfonyl-4-fluoronaphthalene[15] (13 g) gave 4-fluoro-1-thionaphthol as a colorless oil (8.2 g, 87%), bp 100-102 °C (1 mm), which solidified, mp 29-30 °C.

Anal. Calcd for $C_{10}H_7FS$: C, 67.4; H, 4.0. Found: C, 67.2; H, 4.0.

1-Fluoro-4-naphthyl Methyl Thioether. Dimethyl sulfate (5 ml) was added dropwise to an aqueous solution of 4-fluoro-1-thionaphthol (5 g, 0.028 mol) and sodium hydroxide (20 ml, 10%). The reaction mixture was warmed on a steam bath for 30 min, made distinctly alkaline, and then warmed for an additional hour. The mixture was cooled and extracted with ether. Evaporation of the solvent from the dried ether extract afforded crude 1-fluoro-4-naphthyl methyl thioether; distillation gave a colorless (5.1 g, 96%): bp 107-108 °C (15 mm); n^{21}D 1.642.

Anal. Calcd for $C_{11}H_9FS$: C, 68.7; H, 4.7. Found: C, 69.1; H, 4.7.

1-Fluoro-4-naphthyl Methyl Sulfone. Oxidation[26] of the sulfide (1 g) gave 1-fluoro-4-naphthyl methyl sulfone, crystallized from methanol in colorless needles (0.7 g), mp 146-146.5 °C.

Anal. Calcd for $C_{11}H_9FO_2S$: C, 58.9; H, 4.0. Found: C, 58.9; H, 4.1.

1-Fluoronaphthyl-4-dimethylsulfonium fluorosulfonate was prepared from the above sulfide (0.5 g) compound in the same way as the corresponding ammonium salt and crystallized from water as colorless crystals (0.6 g).

Anal. Calcd for $C_{12}H_{12}SF$: C, 47.1; H, 4.0. Found: C, 47.0; H, 4.1.

6-Fluoro-2-thionaphthol. A solution of 6-fluoro-2-naphthol[6c] (10 g, 0.06 mol) and potassium hydroxide (5.0 g) in a tetrahydrofuran-water mixture (1:4, 125 ml) at 12 °C was treated with dimethylthiocarbamoyl chloride (13.64 g, 0.11 mol).[27] The reaction mixture was warmed to 35 °C stirred for 1.5 h, then cooled and made alkaline with potassium hydroxide (10%). The alkaline solution was then extracted with benzene and the benzene then evaporated to give crude *O*-6-fluoronaphthyl-2-dimethylthiocarbamate, which crystallized from methanol in pale yellow flakes (13.5 g, 88%), mp 121.5-123 °C.

Decomposition of the thiocarbamate in refluxing trigol (200 ml) under nitrogen for 1 h, followed by quenching with iced water and then filtration, gave *S*-6-fluoronaphthyl-2-dimethylthiocarbamate (8 g, 59%) crystallized from methanol as light yellow plates, mp 104-106 °C. Alkaline hydrolysis followed by acidification gave 6-fluoro-2-thionaphthol, which after recrystallization from light petroleum (bp 60-90 °C) gave white glistening plates (5 g, 88%), mp 89-89.5 °C.

Anal. Calcd for $C_{10}H_7FS$; C, 67.4; H, 4.0. Found: C, 67.6; H, 4.1.

1-Fluoronaphthyl-4-trimethylphosphonium Iodide. The Grignard reagent, prepared from 1-bromo-4-fluoronaphthalene[15] (4.5 g, 0.02 mol) and magnesium turnings (0.48 g, 0.02 g-atom) using dry tetrahydrofuran as solvent was carefully added at 0 °C to bis(diethylaminochlorophosphine) (5 ml).[28] The mixture was heated under reflux for 30 min and then allowed to stand overnight. Evaporation of the solvent under nitrogen afforded crude 1-fluoronaphthyl-4-bis(diethylaminophosphine) as a thick oil. The crude product was suspended in dry *n*-pentane (200 ml) and dry hydrogen chloride gas was passed through the solution at −70 °C. When no more diethylamine hydrochloride separated, the solution was allowed to come to room temperature and filtered, and the filtrate was carefully treated with a tetrahydrofuran solution of methylmagnesium chloride (20 ml, 3 M). The mixture was stirred for 30 min at room temperature and then filtered, and the solvent was evaporated in vacuo to afford a crude residue of 1-fluoronaphthyl-4-bis(dimethylphosphine). The crude product was dissolved in dry ether and excess methyl iodide added, and the resulting mixture was heated under reflux for 30 min. The precipitate of 1-fluoronaphthyl-4-trimethylphosphonium iodide was collected and recrystallized from methanol as white glistening plates (1.6 g, 23%).

Anal. Calcd for $C_{13}H_{15}FP$: C, 44.8; H, 4.3. Found: C, 44.6; H, 4.5.

1-Bromo-5-fluoronaphthalene. 5-Bromo-1-naphthoic acid (55 g)[29] was treated with sodium azide according to the procedure described by Adcock and Dewar[14] for the preparation of 1-amino-3-fluoronaphthalene. The solid obtained on basification with ammonium hydroxide was collected and recrystallized from aqueous ethanol to afford 1-amino-5-bromonaphthalene as pink plates (40 g, 90%), mp 59-60.5 °C (lit.[30] 69 °C). The amine (12 g) was converted into 1-bromo-5-fluoronaphthalene in the same way as the 2,6 isomer described by Adcock and Dewar.[14] The hexfluorophosphate salt (110 °C dec) was decomposed in the dry and the product was steam distilled to yield a dense yellow-brown oil (3.4 g, 28%): bp 138-142 °C (20 mm); n^{25}D 1.6242.

Anal. Calcd for $C_{10}H_6BrF$: C, 53.3; H, 2.7. Found: C, 54.1; H, 3.1.

1-Cyano-5-fluoronaphthalene was prepared from 1-bromo-5-fluoronaphthalene (3.4 g) in the same way as the 2,6 isomer described by Adcock and Dewar.[14] The nitrile crystallized from petroleum ether in colorless needles (1.2 g, 47%), mp 98.5-100 °C.

Anal. Calcd for $C_{11}H_6FN$: C, 77.2; H, 3.5. Found: C, 77.4; H, 3.6.

Acid hydrolysis[14] of the above nitrile (0.75 g) afforded 5-fluoro-1-naphthoic acid which crystallized from aqueous ethanol in golden brown needles (0.64 g, 69%), mp 210.5-212.5 °C. The acid was converted to 1-amino-5-fluoronaphthalene according to the method described by Adcock and Dewar[14] for the 1,3 isomer. The crude amine crystallized from petroleum ether as pink needles (1.8 g, 80%), mp 68-69 °C.

1-Fluoro-5-methylnaphthalene. 5-Fluoro-1-naphthoic acid (2.5 g, 0.013 mol) was reduced to 1-fluoro-5-methylnaphthalene according to the method outlined by Benkeser and co-workers.[31] Distillation afforded a colorless oil (0.5 g, 24%): bp 64 °C (0.7 mm); n^{25}D 1.5923. Shown to be homogeneous to GLC.

Anal. Calcd for $C_{11}H_9F$: C, 82.5; H, 5.7. Found: C, 82.7; H, 5.8.

1-Fluoro-5-trimethylsilylnaphthalene was prepared from 1-bromo-5-fluoronaphthalene (2.25 g, 0.01 mol) in the same way as the 2,6 isomer described by Adcock and co-workers.[11] Distillation of the crude product afforded a colorless oil (0.7 g, 32%): mp 110 °C (3 mm); n^{25}D 1.5636. Shown to be homogeneous to GLC.

Anal. Calcd for $C_{13}H_{15}FSi$: C, 72.5; H, 6.9. Found: C, 71.9; H, 7.1.

1-Bromo-6-fluoronaphthalene. 6-Fluoro-1-tetralone, prepared according to Allinger and Jones,[32] was converted to the oxime by treatment with hydroxylamine hydrochloride in the presence of sodium acetate. The oxime crystallized from aqueous ethanol in needles, mp 131-132 °C. A solution of the oxime (24 g) in glacial acetic acid (78 ml) and acetic anhydride (18 ml) was treated according to the procedure described by Adcock and Dewar[14] for the preparation of 1-amino-7-fluoronaphthalene. Work-up in the described manner afforded a dark brown oil. Distillation gave the amine as a pale yellow oil (8 g), bp 81–84 °C (0.01 mm).

The amine (7 g) was converted into 1-bromo-6-fluoronaphthalene via the diazonium mercuric bromide complex (mp 106–108 °C dec).[33] The product was recrystallized from *n*-pentane as long white needles (4.1 g, 41%), mp 42–43 °C.

Anal. Calcd for $C_{10}H_6BrF$: C, 53.3; H, 2.7. Found: C, 52.9; H, 2.8.

1-Cyano-6-fluoronaphthalene was prepared from 1-bromo-6-fluoronaphthalene (2.25 g) in the same way as the 2,6 isomer described by Adcock and Dewar.[14] The nitrile crystallized from petroleum ether in colorless needles (0.31 g, 34%), mp 98–99 °C.

Anal. Calcd for $C_{11}H_6FN$: C, 77.2; H, 3.5. Found: C, 77.3; H, 3.6.

1-Fluoro-7-methylnaphthalene. 7-Methyl-1-tetralone (23 g) was converted to the amine via the oxime (mp 92–93 °C) according to the method outlined above for 6-fluoro-1-tetralone. 1-Amino-7-methylnaphthalene crystallized from petroleum ether (bp 40–60 °C) as pink needles, mp 57–59 °C (lit.[34] 58–59 °C).

The amine (6.5 g) was diazotized[14] and the diazonium tetrafluoroborate salt was precipitated with sodium tetrafluoroborate. Decomposition of the salt (mp 97 °C dec), followed by steam distillation and then distillation, gave 1-fluoro-7-methylnaphthalene as a colorless oil (3.0 g, 43%): bp 63–65 °C (1 mm); n^{21}D 1.5885. The oil was shown to be homogeneous to GLC.

Anal. Calcd for $C_{11}H_9F$: C, 82.5; H, 5.7. Found: C, 81.8; H, 5.7.

Discussion

The basic objectives in this investigation were fourfold. First, we wanted to examine the ^{19}F SCS of the unknown 5α and 5β series of substituted fluoronaphthalenes (**3** and **4**, respectively). Although previous work[6b,6c] on the other dispositions had shed much light on substituent behavior in general, as well as the factors determining ^{19}F chemical shifts, we felt that the remaining unknown dispositions (5α and 5β) were of sufficient intrinsic interest to warrant detailed examination. According to simple MO theory (valence bond or PMO theory) the 5α disposition is a conjugative orientation in the naphthalene ring system. However, whereas the PMO method[35] indicates that mesomeric effects are transmitted as effectively in the 5α disposition as the 8β, formal charges calculated by a SCF-MO procedure[36] for the *amino* substituent indicate that mesomeric interactions should be greater in the 8β than the 5α disposition (+0.0027 vs. + +0.0013), the interactions in the latter being quite small. Further, chemical reactivity studies on side-chain derivatives of naphthalene where electron deficiency is generated in the ring suggested that direct mesomeric interactions in the 5α disposition are extremely small.[37] Thus it might be expected that with a neutral ground state measurement, such as ^{19}F NMR, direct mesomeric interaction in the 5α disposition should be negligible and that the ^{19}F SCS parameters will be predominantly a manifestation of field-inductive phenomena.[38] The unconjugated 5β disposition is of interest since it is the missing member of a disposition pair (6α and 5β).[39] The previous study[6b] of the other disposition pairs (3α and 4β; 7α and 8β) proved to be very informative when the ^{19}F SCS for each orientation within a pair were compared. In particular, the importance of charge alternation in the π system was clearly indicated by the apparently abnormal effects of +F +M substituents meta (3α and 4β) to the fluorine probe while the other pair (7α and 8β) showed that the magnitude of the field effect depends on the component of the electric field along the CF bond, rather than on the scalar potential in that region. The additional pair (6α and 5β) should also reflect the angular dependence of the field effect on ^{19}F SCS; the simple model adopted[6b] predicts that ^{19}F SCS for +F +M substituents should be approximately twice as large in the 5β than in the 6α orientation.

Second, we wanted to examine the electronic behavior of the trifluoromethyl substituent. The mode of interaction of this group has been the subject of considerable debate and has been reviewed recently by Holtz.[40a] Not only has the relative importance of the polar and π-electron effects been questioned[40b,c] but several interpretations have also been put forward regarding the origin of the latter interaction (π inductive[40a,e,f] fluorine hyperconjugation[3k,u,40d,h] and p-π electron interaction[40g]). Since there is a large number of nonproximate positional dependencies in the naphthalene ring system, it seemed to us that some additional insight might be provided from a study of the ^{19}F chemical shifts of a range of trifluoromethyl-substituted fluoronaphthalenes.

Third, we wanted to provide additional SCS information, mainly for methyl and halogen substituents, for all the nonproximate orientations. The need for additional data is partly determined by the stipulated basic set of substituents for a meaningful correlative analysis by the Taft dual substituent parameter (DSP) eq 1,[3s,t,41]

$$p^i = \sigma_I\rho_I{}^i + \sigma_R\rho_R{}^i = \rho_I{}^i(\sigma_I + \lambda\sigma_R) \qquad (1)$$

where p^i = the substituent effect property; σ_I and σ_R are the substituent polar and resonance effect parameters, respectively; ρ_I and ρ_R give the susceptibilities of the property to each of the substituent properties; the ratio or blend $\rho_R/\rho_I \equiv \lambda$. The index *i* refers to the position of the substituent relative to the probe or detector center.

Although a previous analysis[41a] showed that ^{19}F shielding effects in naphthalene follow eq 1 with good precision, the number and kind of substituents in many of the orientations were distinctly limited. The additional data should allow a more comprehensive and meaningful analysis. Further, the additional data should allow a useful comparison of ^{19}F and ^{13}C SCS[42] for a reasonable number of substituents in the naphthalene ring system.

Finally, we wanted to test our recent proposal[7b] that because of likely complications arising from substituent-induced structural distortions in the benzene ring system on ^{19}F chemical shifts, the electronic effects of substituents can be more reliably assessed from the 6β and 7β orientations of β-fluoronaphthalene. We have thus examined in these two dispositions of naphthalene a series of relatively large substituents (SH, SCH_3, SO_2CH_3, $S^+(CH_3)_2$, $N^+(CH_3)_3$, $P^+(CH_3)_3$) which have been previously investigated employing the fluorophenyl tag.[1,3d,f,g] New σ_I and $\sigma_R{}^0$ values for these substituents can be calculated utilizing the derived DSP equations for the 6β and 7β orientations. It is important to note that besides avoiding geometrical complications, employing the 6β and 7β orientations of β-fluoronaphthalene for calculating polar and resonance parameters should circumvent most of the problems (σ[43] and π[44] electron effects and substituent-probe interactions[45]) associated with the fluorophenyl tag.

^{19}F NMR Spectra of 5α- and 5β-Fluoronaphthalenes. The ^{19}F substituent chemical shifts for the 5α- and 5β-fluoronaphthalenes in DMF are listed in Table II. A cursory examination of the data indicates immediately that something unusual is happening in these two dispositions. In the first place, the SCS for the methyl substituent in the conjugated 5α disposition is *negative*, implying net *electron withdrawal!* This observation is in total disagreement with the generally accepted electron-donating behavior of this substituent.[46] Second, based on the magnitude of the SCS for the methyl substituent in the "normal" unconjugated 7β orientation (+0.25 ppm),[11] the magnitude of the SCS for this substituent in the unconjugated 5β disposition appears far too large. We believe that substituent-induced structural factors, which were previously suggested as the origin of the

Table II. Substituent Chemical Shifts (ppm) of 5α- and 5β-Substituted Fluoronaphthalenes in Dimethylformamide

	Orientation	
Substituent	5α	5β
NO_2	−3.47[a]	−2.34[a]
CN	−2.41	−2.70
COOH	−1.80	−0.16
F	−2.15 (−1.72)[b]	−1.74
Br	−1.88	−0.91
NH_2	−1.09 (−4.79)[c]	+1.78
$N(CH_3)_2$	−1.19	
CH_3	−1.03	+1.09
$Si(CH_3)_3$	−1.53	+0.92
$^+N(CH_3)_3$	−6.02 (−8.52)[c]	

[a] J. P. Bechner, Ph.D. Thesis, Iowa State University, 1969. [b] Solvent, benzene. [c] Solvent, CF_3CO_2H.

Table III. Comparison of SCS Values Calculated by the FM Method for 5α- and 5β-Substituted Fluoronaphthalenes with Observed Values

	Orientation			
	5α		5β	
Substituent	Obsd	Calcd	Obsd	Calcd
NO_2	−3.47	−5.36 (−2.97)[a]	−2.34	−3.19
CN	−2.41	−5.01 (−2.61)[a]	−2.70	−2.54
COOH	−1.80	−2.81 (−0.90)[a]	−0.16	−0.78

[a] Calculated value neglecting mesomeric interactions.

Table IV. Substituent Chemical Shifts (ppm) of Trifluoromethyl-Substituted Fluoronaphthalenes and Fluorobiphenyls

Compound	Obsd SCS in DMF[a]	Calcd SCS
3α	−3.70 (−3.26)	−2.57
4α	−8.28 (−7.24)	−6.56
5α	−3.03 (−2.20)	−3.17
7α	−1.71 (−1.90)	−1.49
4β	−0.09 (0.00)	−1.70
5β	−1.67 (−1.42)	−1.99
6β	−3.99[b] (−3.67)	−3.03
7β	−2.37 (−2.15)	−1.91
8β	−4.72 (−4.80)	−3.85
3′-CF_3-4-fluorobiphenyl	−1.35 (−1.37)	−1.84
4′-CF_3-4-fluorobiphenyl	−1.65 (−1.68)	−2.05

[a] Values in parentheses are for benzene as solvent. [b] In CF_3CO_2H the SCS is −3.75 ppm.

observed *negative* SCS for the alkyl groups in the 8β disposition,[7b] are indeed responsible for the apparent anomalies in the 5α and 5β disposition. Recent studies by Mallory and co-workers[47] strongly support this proposition. They concluded from a substituent effect study on J_{FF} in 4-substituted 1,8-difluoronaphthalene that the variation of J_{FF} reflects primarily a steric effect of the *peri* substituent. X-ray crystallographic studies of model systems were presented which showed that in peri-substituted naphthalenes the crowding strain leads to an increase in the adjacent peri angle and a decrease in the remote peri angle relative to the angles in naphthalene itself. Thus the anomalous SCS for the methyl substituent in the 5α- and 5β-fluoronaphthalenes, as well as the 8β orientation,[7b] probably reflects a variation in the distance of separation between the fluorine and adjacent *peri* hydrogen, relative to 1- and 2-fluoronaphthalene, as a result of substituent-induced structural distortions. Similar factors probably affect the SCS in the other peri substituted fluoronaphthalenes: 4α (downfield)[6b,7b] and 4β (upfield).[6b,7b] It seems relatively clear then that ^{19}F SCS from peri substituted orientations (4α, 5α, 4β, 5β, and 8β) reflect geometric as well as electronic factors, the relative importance of the former being variable since it is dependent on substituent size.[48] However, it is important to note that this geometrical factor would not be large enough to account for the anomalous results of +F +M substituents in the 4β orientation.[6b,6e] The calculated energies of *peri* crowding in units of kcal/mol determined by Mallory and co-workers[47] are as follows: 0.2 for H, 0.8 for CN, 1.4 for Cl, 1.9 for CH_3, 2.0 for NH_2 and $NH\cdot COCH_3$, and 3.0 for NO_2. This pattern suggests that any upfield shift in the 4β disposition for the CN substituent due to molecular distortions should be much less than that for the methyl group. However, whereas the ^{19}F SCS difference for the CN substituent in the meta orientations (3α and 4β) is 2.88 ppm (Table V), the difference for the methyl group is only 0.28 ppm (Table VI).

A number of other important conclusions follow from the results set out in Tables II and III. First, it can be seen that the SCS of the strong mesomeric electron-donating substituent in the conjugated 5α disposition is *negative*. Further, by replacing the hydrogens of the NH_2 groups with CH_3 substituents, a structural manipulation, known to strongly inhibit mesomerism in the 4α and 8β dispositions,[6b] leads to a negligible perturbation of the SCS. We believe that this is good evidence to suggest that in the neutral ground state the transmission of mesomeric effects (direct and indirect) in the 5α orientation is virtually nonexistent. Thus, the ^{19}F SCS in this orientation must reflect essentially field effects, and depending on substituent size, steric crowding. The relatively large negative SCS for the small *cyano* and *fluoro* substituents (steric effects should be relatively small) confirm recent conclusions from other model systems regarding the importance of field effects in determining the magnitude of ^{19}F chemical shifts in aryl fluorides.[38] It is of interest to note that for the same reasons enunciated for the CH_3 group, the relatively large positive SCS for the NH_2 substituent (approximately the same size as CH_3) in the 5β disposition must be largely a reflection of geometry changes.

Second, Table III shows the SCS values calculated by the FM method[6b] compared with the experimental values for the +F +M substituents (NO_2, CN, and COOH). The values in parentheses for the 5α orientation are the calculated values neglecting mesomeric interactions. The agreement between the calculated and observed values is satisfactory provided the mesomeric component in the 5α orientation is ignored. It is important to note that the agreement is particularly good for the small CN substituent, the substituent least likely to introduce geometrical complications. A corollary of the success of the FM method for predicting SCS in aromatic systems is that long-range interactions of +F +M substituents are conveyed predominantly by a field effect and a mesomeric effect. Third, the importance of angular factors is strongly supported by the fact that the SCS for the CN group in the 5β disposition (−2.70 ppm) is more than twice as large as the value in the 6α orientation (−1.29 ppm),[6b] a result completely in accord with predictions from the simple model.[6b]

The Electrical Effect of the CF_3 Substituent. The substituent chemical shifts (SCS) for the trifluoromethyl-substituted fluoronaphthalenes and fluorobiphenyls are listed in Table IV together with the SCS calculated by the FM method.[6b] The SCS for +F +M substituents (NO_2, CN, and COOH), which have been previously reported,[6a c] are listed in Table V for comparison. An examination of the data (Table IV) provides decisive confirmation of the generally accepted electrical behavior of the CF_3 substituent,[3u,40a] namely, that the relatively large net electron-withdrawing effect of this group is a result of both a signifi-

Table V. Substituent Chemical Shifts (ppm) of +F +M (NO_2, CN, and COOH) Substituted Fluoronaphthalenes and Fluorobiphenyls in DMF

	Orientation										
Substituent	3α[a]	4α[a]	5α[b]	7α[a]	4β[a]	5β[b]	6β[a]	7β[c]	8β[a]	3′,4[d]	4′,4[d]
NO_2	−4.87	−12.77	−3.47	−3.39	−0.79	−2.34	−6.54	−3.25	−6.76	−2.08	−2.74
CN	−3.68	−11.34	−2.41	−2.35	−0.80	−2.70	−5.45	−3.05	−5.32	−1.80	−2.24
COOH	−1.01	−8.19	−1.80	−1.52	+0.72	−0.16	−3.26	−1.24	−3.46	−0.80	−1.40

[a] Reference 6b. [b] This work. [c] Reference 6c. [d] Reference 6a.

Table VI. Substituent Chemical Shifts (ppm) of Halogen-, Trimethylsilyl-, and Methyl-Substituted Fluoronaphthalenes in DMF (Benzene)

Substituent	Orientation	SCS
F	3α	−4.90 (−4.52)
F	4α	+3.93 (+4.57)
F	6α	−1.22
F	7α	−0.60 (−0.56)
F	4β	−2.52 (−2.30)
F	6β	+1.04 (+1.16)
F	7β	−1.31 (−1.29)
F	8β	−2.19 (−2.06)
Cl	4α	−0.19 (+0.56)
Cl	6β	−0.91 (−0.63)
Cl	7β	−1.74 (−1.72)
Cl	8β	−3.20 (−2.99)
I	4α	−1.08 (−0.67)
I	6β	−1.51 (−1.41)
I	7β	−1.81 (−1.82)
I	8β	−3.05 (−3.08)
$Si(CH_3)_3$	7α	+0.23
$Si(CH_3)_3$	8β	−1.22
CH_3	3α	+0.96 (+1.18)
CH_3	7α	+0.60
CH_3	4β	+0.68

cant polar (field inductive) and π-electron effect (mesomeric or π inductive).[49] First, it can be seen that there is a large difference between the SCS in the 7α and 8β dispositions. This difference was previously noted for +F +M substituents (Table V) and was rationalized in terms of angular factors associated with a significant field effect.[6b,50]

Second, it can also be seen that there is a large difference between the SCS in the meta disposition pair (3α and 4β). Note that in the 4β orientation the SCS in benzene is *zero!* We believe the only possible explanation for this apparent "anomaly" is that the π-electron effect (mesomeric or π-inductive) of the CF_3 substituent induces a marked alternation of π-electron density around the aromatic ring.[6b,e,7b] Apparently the negative π charge density on the carbon in the 4β disposition is large enough to completely cancel out the perturbation by the field effect. Third, the agreement between the SCS values calculated by the FM method[6b] and the observed values for most of the orientations is reasonable. However, it should be noted that the result for the 5α disposition must be fortuitous since this orientation clearly provides a SCS which is a manifestation of both electrical and geometrical factors. Because the covalent diameter of the trifluoromethyl group (3.3 Å) is only slightly larger than that of the methyl group (2.8 Å),[51] an estimate for the SCS in this orientation in the absence of steric crowding can be made by determining the shift relative to CH_3 rather than H. The SCS determined in this way (−2.0 ppm) compares favorably with the FM calculated value (−1.97) assuming only field effects to be operative.

Fourth, a comparison of the data in Table IV with the SCS for the +F +M substituents listed in Table V indicates that in all orientations where field-inductive effects predominate (3α; 5α; 7α; 5β; 7β; 8β; 3′,4; and 4′,4) the CF_3 group parallels the CN substituent, while in those orientations where π-electron effects are important (4α, 4β, and 6β) the parallel is with the COOH group. This result demonstrates qualitatively that the field effect of the CF_3 group is much greater than that of the COOH, being only slightly less than that for the CN. Further, the π-electron effect of the CF_3 group must be less than that for either the CN or COOH substituents. It is of interest to note that this qualitative conclusion is in agreement with σ_I[3t] or $\mathcal{F}$[52] as a quantitative measure of the field effect. However, whereas the qualitative order of π-electron effects is in line with σ_R^0 [3t] it is not in agreement with $\mathcal{R}$[52] (vide infra).

Fifth, it can be seen that changing the solvent from benzene to DMF in most of the orientations leads to an increase in the electron-withdrawing power of the CF_3 substituent, an observation in line with expectations.[53] However, in the 7α and 8β dispositions the converse is observed. We believe the latter result can be rationalized only in terms of a direct electrostatic interaction which is attenuated by polar solvents, as a result of their greater effective dielectric constants.[6c,38] Apparently solvent intrusion into the cavity is important where the major lines of force traverse the periphery of the molecule. The fact that the solvent effect in the 5α orientation (π-electron effects negligible) is almost the same magnitude as that observed in the 4α disposition suggests that the enhanced electron-withdrawing power of the CF_3 groups in polar solvents can be attributed to the field effect.[53]

Finally, although the SCS data in Table IV do not allow an unequivocal decision regarding the origin of the substantial π-electron effect of the CF_3 group, we favor the π-inductive mechanism[40a,e,f] rather than a mesomeric one[3k,u,40d,h] for the following reason. The ^{19}F chemical shifts of substituted benzotrifluorides, in contrast to aryl fluorides, have been shown to be virtually insensitive to the electronic behavior of the substituent.[54] In terms of the usual perturbation treatment of chemical shifts[4,5] this implies that whereas there are relatively low-lying excited states involving the fluorine electrons in aromatic fluorides, the corresponding excitation energies in benzotrifluorides must be much larger. An obvious corollary is that σ–π interactions involving the CF_3 group are energetically inaccessible. However, it is of interest to note that recent experimental evidence[38] strongly suggests that mono-substituted methyl groups engage in hyperconjugative electron withdrawal in the neutral ground state. An important consequence of this is that ^{19}F chemical shifts of substituted benzylfluorides are extremely sensitive to the electrical effects of substituents.[55]

Correlative Analyses. Some additional data, which were determined for a reexamination of ^{19}F chemical shifts in naphthalene in terms of Taft's DSP equation, are listed in Table VI. These data together with that listed in Tables II and IV were combined with previously published results[6b,c,7b,11] in order to provide the best possible basic set of substituents for each orientation. Because of synthetic complications, it is unfortunate that SCS for CH_3 and CF_3 substituents are unavailable in the 6α orientation. Table VII summarizes the DSP (eq 1) results for the various orientations.[56] The best fit parameters to σ_R^0 are listed together with the fit parameter, $f \equiv$ SD/RMS, previously determi-

Table VII. Best Fit Parameters of Equation 1 for Substituent ^{19}F NMR Shielding Effects in Naphthalene

Disposition	Type	Solvent	ρ_I	ρ_R	λ	n	SD	f	f^a
3α	σ_R^0	DMF	−7.728	−1.141	0.148	7	0.800	0.227	0.102
4α	σ_R^0	DMF	−13.628	−31.423	2.306	11	0.863	0.109	0.068
5α	σ_R^0	DMF	−4.827	0.096	−0.02	8	0.926	0.415	
6α	σ_R^0	DMF	−2.672	−1.864	0.698	5	0.374	0.275	0.207
7α	σ_R^0	DMF	−3.626	−4.431	1.222	10	0.291	0.172	0.153
4β	σ_R^0	DMF	−1.879	1.792	−0.954	7	0.583	0.503	0.200
5β	σ_R^0	DMF	−3.772	−3.138	0.832	8	0.585	0.333	
6β	σ_R^0	DMF	−7.299	−12.536	1.717	12	0.383	0.106	0.100
7β	σ_R^0	DMF	−4.676	−2.255	0.482	12	0.253	0.140	
8β	σ_R^0	DMF	−8.975	−4.747	0.529	12	0.833	0.235	0.079
4α	σ_R^0	Benzene	−11.800	−28.332	2.401	5	0.548	0.142	
7α	σ_R^0	Benzene	−3.944	−4.905	1.244	8	0.257	0.126	
6β	σ_R^0	Benzene	−7.015	−12.124	1.728	10	0.370	0.109	
7β	σ_R^0	Benzene	−4.486	−2.060	0.459	10	0.252	0.133	
8β	σ_R^0	Benzene	−9.293	−5.404	0.581	10	0.434	0.111	

[a] Taken from ref 41a.

ned.[41a] Fits to other resonance scales[3t] are in general appreciably poorer and are not given. The most noticeable feature about the new analysis is that the precision of fits achieved by the DSP equation is significantly worse than those previously reported, being most pronounced for the unconjugated 3α, 6α, and 4β dispositions as well as the conjugated 8β[57a] orientation. Thus the need for a proper range of substituent types in carrying out a DSP type correlative analysis is exemplified.

Although the present results do not invalidate much of the detailed discussion of the previous analysis, the poorer precision of fit observed plus the new date for the 5α, 5β, and 7β orientations deserve some comment. First, except for the 7β orientation the precision of fit for the unconjugated positions (3α, 6α, 4β, and 5β) is not comparable to that for the naphthalene reactivities.[41a] This suggests that ^{19}F chemical shifts involve factors not encountered in the study of substituent effects on conventional chemical properties. Part of the problem seems to be the apparent sensitivity of ^{19}F chemical shifts to geometrical factors and π-charge alternation effects. Second, the correlation for the conjugated 5α orientation[57b] is not only poor but ρ_R is almost *zero*. This result strongly supports our conclusions that ^{19}F SCS in this orientation are essentially a manifestation of field-inductive effects and complicating geometrical factors. Finally, it can be seen that ρ_I for the 6β orientation is almost twice as large as that for the 7β disposition. Since the $\sigma_I\rho_I$ term is considered to arise from field and π-inductive effects,[41a] and because a consideration of angular, distance and dielectric factors suggests a similar field effect from both orientations,[58] this result supports the importance of a π-inductive mechanism. It is of interest to note that Stock and co-workers[59] have come to a similar conclusion from reactivity and ^{19}F NMR studies of meso-substituted anthracene derivatives. However, recent ^{13}C NMR studies[42c] of mono-substituted naphthalene and anthracene derivatives do not unequivocally support this proposal as a completely satisfactory explanation of the ^{19}F SCS difference between systems of different structural type.

Adcock and co-workers[42c] previously showed that a comparison of ^{13}C SCS values with the corresponding ^{19}F SCS gave a reasonable linear correspondence for the 4α orientation in naphthalene as well as the para and meso disposition of benzene and anthracene, respectively, the correlation coefficients being r = 0.96, 0.97, and 0.94, respectively. Correlations performed during this work by least-squares procedures of the ^{13}C SCS[42] vs. ^{19}F SCS for the remaining orientations in naphthalene gave poor correlations (0.21–0.81) except for the 6β and 8β dispositions (r = 0.97 and 0.97, respectively). Since the determining balance between mesomeric and field-inductive effects of substituents for both probes is completely different,[60] the results of the analysis are not entirely unexpected. Reasonable correlations should occur where conjugative interactions are strong (4α and 6β). However, the reasonable correlation for the 8β disposition where ^{19}F SCS are believed to be largely determined by field effects is inexplicable.

Table VIII. Substituent Chemical Shifts (ppm) of SH-, SCH_3-, SO_2CH_3-, $S^+(CH_3)_2$-, and $P^+(CH_3)_3$-Substituted Fluorobenzenes

	Orientation			
	Meta		Para	
Substituent	Benzene	DMF	Benzene	DMF
SH	−0.66	−0.13	+4.00	+5.01
SCH_3	−0.27	−0.27	+4.82	+4.86
SO_2CH_3	−3.14	−2.96	−7.73	−7.80
$S^+(CH_3)_2$[a]		−4.63		−8.46
$P^+(CH_3)_3$[b]		−2.20		−8.20

[a] Counterion, FSO_3^-. [b] Counterion, I^-.

Calculation of Substituent Parameters. The ^{19}F substituent chemical shifts for a number of sulfur and onium substituents in fluorobenzene and fluoronaphthalene (4α, 6β and 7β) are listed in Tables VIII and X, respectively. The substituted fluorobenzenes were reexamined in benzene and DMF in order to check previously reported data on these groups.[3d-g] Substituent parameters (σ_I and σ_R^0) for these groups were derived from the data in Table VIII employing Taft's methodology. A comparison of these values (Table IX) with the previously determined parameters indicates satisfactory agreement.

Substituent parameters derived from the data in naphthalene (Table X) by employing eq 2 and 3 (DMF) and eq 4 and 5 (benzene), the DSP equations for the 6β and 7β orientations respectively (Table VII), are listed in Table XI together with the values computed for the metalloidal substituents (^{19}F SCS data previously published[11]).

$$\text{SCS} = -7.299\sigma_I - 12.536\sigma_R^0 \quad (6\beta, \text{DMF}) \tag{2}$$

$$\text{SCS} = -4.676\sigma_I - 2.255\sigma_R^0 \quad (7\beta, \text{DMF}) \tag{3}$$

$$\text{SCS} = -7.015\sigma_I - 12.124\sigma_R^0 \quad (6\beta, \text{benzene}) \tag{4}$$

$$\text{SCS} = -4.486\sigma_I - 2.060\sigma_R^0 \quad (7\beta, \text{benzene}) \tag{5}$$

The DSP correlative analysis for both these orientations in naphthalene indicated (Table VII) a good precision fit of the ^{19}F SCS. The σ_R^0 values derived by ir and ^{19}F NMR methods are listed in Table XII. An examination of the data listed in Tables IX, XI, and XII brings to light a number of significant features. First, it can be seen that the σ_R^0

Table IX. Comparison of Substituent Parameters (σ_I and σ_R^0) Derived from ^{19}F SCS of Substituted Fluorobenzenes

	Substituent parameters			
Substituent	σ_I[a]	σ_I[b]	σ_R^0[a]	σ_R^0[b]
SH	0.19 (CCl_4)	0.18 (benzene)[c]	−0.15 (CCl_4)	−0.16 (benzene)[d]
SCH_3	0.13 (CCl_4)	0.12 (benzene)[e]	−0.16 (CCl_4)	−0.17 (benzene)[e]
SO_2CH_3	0.55 (CCl_4)	0.53 (benzene)[f]	0.16 (CCl_4)	0.16 (benzene)[e]
$^{+}S(CH_3)_2$	0.89 (CH_3CN)[g]	0.74 (DMF)	0.17 (CH_3CN)[g]	0.13 (DMF)
$^{+}P(CH_3)_3$	0.43 (DMSO)[h]	0.40 (DMF)	0.20 (DMSO)[h]	0.20 (DMF)

[a] See ref 3g. [b] This study. [c] 0.10 (DMF). [d] −0.17 (DMF). [e] Same value in DMF as solvent. [f] 0.50 (DMF). [g] Counterion, ClO_4^-. [h] Counterion, BF_4^-. See ref 3e.

Table X. Substituent Chemical Shifts (ppm) of SH-, SCH_3-, SO_2CH_3-, $^{+}N(CH_3)_3$-, $^{+}S(CH_3)_2$-, and $^{+}P(CH_3)_3$-Substituted Fluoronaphthalenes

	Orientation					
	4α		6β		7β	
Substituent	Benzene	DMF	Benzene	DMF	Benzene	DMF
SH	+0.74	+4.30	+0.30	+0.75	−1.17	−0.95
SCH_3	+2.23	+2.87	+0.87	+1.01	−0.76	−0.72
SO_2CH_3	−10.69	−11.12	−5.37	−5.22	−2.96	−2.82
$^{+}NH_3$		−1.82[a]		−1.24[a] (−4.56)[b]		−1.58[a] (−4.47)[b]
$^{+}N(CH_3)_3$		−6.44 (−10.02)[b]		−3.40 (−6.13)[b]		−2.69 (−5.44)[b]
$^{+}S(CH_3)_2$		−10.91 (−15.98)[b]		−6.00 (−9.47)[b]		−3.41
$^{+}P(CH_3)_3$		−11.25 (−15.90)[b]		−5.55 (−8.67)[b]		−2.89 (−5.51)[b]

[a] Taken from ref 6b and 6c. [b] Solvent, CF_3CO_2H.

Table XI. Substituent Parameters (σ_I and σ_R^0) Derived from ^{19}F SCS of Substituted Fluoronaphthalenes

	σ_I		σ_R^0	
Substituent	Benzene	DMF	Benzene	DMF
SH	0.37	0.32	−0.24	−0.25
SCH_3	0.28	0.27	−0.23	−0.24
SO_2CH_3	0.62	0.56	0.08	0.09
$^{+}NH_3$		0.40		−0.14
$^{+}N(CH_3)_3$		0.62		−0.09
$^{+}S(CH_3)_2$		0.69		0.08
$^{+}P(CH_3)_3$		0.56		0.12
$Si(CH_3)_3$[a]	0.02	0.03	0.05	0.04
$Ge(CH_3)_3$[a]	0.06	0.06	0.01	−0.02
$Sn(CH_3)_3$[a]	0.09	0.06	−0.02	−0.03
$Pb(CH_3)_3$[a]	0.16	0.12	−0.10	−0.09

[a] ^{19}F SCS data taken from ref 11.

Table XII. Comparison of Ir and ^{19}F NMR Derived σ_R^0 Values

Substituent	σ_R^0 (ir)	σ_R^0 (NMR; fluorobenzene)	σ_R^0 (NMR; fluoronaphthalene)
SH	−0.19[a]	−0.15	−0.24
SCH_3	−0.25[a]	−0.16	−0.23
SO_2CH_3	0.06[b]	0.16	0.08
$^{+}NH_3$	−0.19 (D_2O)[c]		−0.14
$^{+}N(CH_3)_3$	−0.15 (D_2O)[c]	−0.08[d]	−0.09
$^{+}S(CH_3)_2$	−0.09[e]	0.17	0.08
$^{+}P(CH_3)_3$	0.08[e] (D_2O)[h]	0.20	0.12
$Si(CH_3)_3$	0.02[f]	0.04[f]	0.05
$Ge(CH_3)_3$	±0.05[f] (−0.08)[e]	0.01[f]	0.01
$Sn(CH_3)_3$	±0.07[f] (−0.10)[e]	0.01[f]	−0.02
$Pb(CH_3)_3$		0.007[g]	−0.10

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values for the $^{+}N(CH_3)_3$ substituent (Table XII) derived from the benzene and naphthalene systems by the ^{19}F NMR method are in good agreement. This result is a surprising one since this substituent is isoelectronic with the $C(CH_3)_3$ group, and also similar in size, which has been shown to effect an "anomalous" *upfield* ^{19}F chemical shift when located in the para position of fluorobenzene but not in the 6β orientation of β-fluoronaphthalene.[7b,9] We believe that the correspondence in σ_R^0 values between the two systems indicates that a compensating *downfield* shift due to geometrical factors must also occur when the $^{+}N(CH_3)_3$ substituent is meta disposed. The fact that the meta SCS for $C(CH_3)_3$ is much less positive than CH_3,[8b,61] which is contrary to expectations based on inductive phenomena,[8b] appears to strongly support this supposition. Thus, although ^{19}F SCS data from fluorobenzene for substituents which inflict structural distortions by unfavorable steric interactions with the orthohydrogens[9] lead to incorrect σ_I values, an apparent fortuitous cancelation of the geometrical factor in the Taft methodology allows computation of a reliable σ_R^0 value.

The *negative* sign for the σ_R^0 of $^{+}N(CH_3)_3$ indicates that the nitrogen pole can act as an electron-donating group by hyperconjugation involving the N-C bond. This result strongly supports the evidence from secondary isotope effects[62] and infrared intensities.[63] It is important to note that since Swain's $\mathcal{R}$ scale[52] is based on the assumption that the resonance effect of the trimethylammonium group is *zero*, the parameter $\mathcal{R}$ may not be a good measure of the mesomeric component of a substituent[6d] (note discussion on the CF_3 group).

A further consequence of N-C hyperconjugative electron donation and C-N electron withdrawal,[38] as well as geometrical factors, is the large chemical shift differential for $^{+}N(CH_3)_3$ when a methylene group is interposed between the group and the phenyl ring (p-$FC_6H_4N^+(CH_3)_3$ relative to C_6H_5F is −3.10 ppm (MeOH)[1] and −1.03 ppm (DMF);[6d] p-$FC_6H_4CH_2N^+(CH_3)_3$ relative to p-$FC_6H_4CH_3$ is −7.70 ppm (DMF)[38]). Assuming that the $N^+(CH_3)_3$ group acts only by a field-inductive effect, the results suggest that the electron-withdrawing effect of $N^+(CH_3)_3$ increases as it is moved further from the ring system! It should be noted that Reynolds and co-workers[64] noted a similar discrepancy in the ^{13}C chemical shifts of C4 in anilinium trifluoroacetate and benzylammonium trifluoroacetate but were unable to provide a satisfactory explanation.

Second, a comparison of the data in Table IX with the appropriate parameters listed in Table XI indicates that although the signs of the parameters are in general agreement there are significant differences in their magnitude. Clearly, the σ_R^0 values for the conjugatively net electron-withdrawing groups (SO_2CH_3, $^+S(CH_3)_2$, and $^+P(CH_3)_3$) from the naphthalene data are smaller than those derived from the benzene system. Note that the former σ_R^0 values are more in line with those determined by the ir method (Table XII), given that the sign for the dimethylsulfonium substituent (ir method) is undoubtedly spurious.[65] This parallel suggests that the discrepancies between the σ_R^0 values (^{19}F NMR) from the benzene and naphthalene systems are a result of much larger substituent-probe interactions in para-substituted fluorobenzenes compared with 6-substituted 2-fluoronaphthalenes.[45] It follows then that the significantly smaller σ_R^0 values for the divalent sulfur substituents in the benzene system (Table IX) compared to the naphthalene derived results strongly supports the d-orbital acceptance capacity of these groups, a concept of much controversial debate.[66] It is of interest to note that the p–d nature of the π conjugation (not susceptible to twisting effects) of the SO_2CH_3, $^+S(CH_3)_2$, and $^+P(CH_3)_3$ substituents is exemplified by the good agreement between the calculated SCS (DMF: −10.46, −11.80, and −11.29 ppm, respectively) for the sterically hindered 4α orientation (utilizing DSP parameters listed in Table XI) and the observed ^{19}F SCS (Table X). However, the calculated SCS (DMF) for the unsymmetrical SCH_3 substituent (+3.78 ppm) in the 4α orientation is considerably more positive than the observed SCS (+2.87 ppm; Table X), possibly indicating some steric inhibition of mesomerism (π (p–p) conjugation) for this group.[67] The substantial differences between σ_I for the unsymmetrical divalent sulfur substituents determined from the benzene (Table IX) and naphthalene (Table XI) systems may reflect a manifestation of geometrical factors in the former system.

Third, it can be seen that there is a reasonable parallel between the ^{19}F NMR derived σ_R^0 values (Table XII) for the metalloidal substituents except for the $Pb(CH_3)_3$ group. The relatively large *negative* value for this substituent implies mesomeric electron donation, presumably by a hyperconjugative mechanism involving the C–Pb bond. It is important to note that the naphthalene derived σ_R^0 values for the metalloidal substituents are in accord with ^{13}C NMR derived parameters which indicate significant net electron withdrawal and electron donation for the $Si(CH_3)_3$ and $Pb(CH_3)_3$ substituents respectively but no significant net π-electron effects for $Ge(CH_3)_3$ and $Sn(CH_3)_3$.[68] Interestingly, the infrared method of Katritzky and co-workers[3p] yields significant *negative* σ_R^0 values for $Ge(CH_3)_3$ and $Sn(CH_3)_3$. However, this may be due to the considerable uncertainties in the ir data for weakly interacting substituents. Note also that the σ_I values (Table XI) for $Ge(CH_3)_3$, $Sn(CH_3)_3$, and $Pb(CH_3)_3$ are significantly *positive* and that these are different to those determined by the fluorophenyl tag ($(CH_3)_3Si$, −0.03; $(CH_3)_3Ge$, −0.01; $(CH_3)_3Sn$, 0.00; $(CH_3)_3Pb$, 0.03).[69] If the results are accepted at their face value, they imply that the metalloidal substituents, particularly $Pb(CH_3)_3$, *withdraw* electrons by an inductive mechanism! Although this result is contrary to conclusions reported in a recent study on the electronic effect of $Sn(CH_3)_3$,[70] evidence has been presented[71] to suggest that the electronegativity of lead in PbR_4 is greater than the other metalloids and even that of H and C. It should also be pointed out that from ^{19}F NMR studies on the electronic effect of $CH_2M(CH_3)_3$ substituents,[61] the metalloids were inferred to be electropositive (Sn > Ge > Si). However, this conclusion is now in jeopardy since Eaborn and co-workers[71b] have recently proposed that the relative magnitude of σ–π interactions for these groups is determined largely by their C–M bond strengths rather than their respective electronegativities.[72] It is amusing to note that essentially the same substituent parameters listed for the metalloidal substituents (Table XI) can be computed from the naphthalene system by solving the appropriate DSP equations for the 4α and 6β orientations (benzene as solvent) rather than the two equations for the 6β and 7β dispositions.

Table XIII. Comparison of SCS Values Calculated by by DSP Parameters

Substituent	Orientation	Solvent	SCS Obsd	SCS Calcd
OH	4α	Benzene	+9.61	+9.23
OH	4α	DMF	+13.40	+10.10
OCH_3	4α	Benzene	+10.35	+9.56
OCH_3	4α	DMF	+11.82	+10.46
$COCH_3$	4α	DMF	−8.46	−8.84
$COCH_3$	6β	DMF	−4.00	−4.05
$COCH_3$	8β	DMF	−3.40	−3.27
$N(CH_3)_2$	6β	DMF	+5.92	+6.08
$N(CH_3)_2$	7β	DMF	+0.77	+0.89

Fourth, the solvent effect on the ^{19}F SCS of the positive poles (Table X) is worthy of comment. Note the dramatic increase in the electron-withdrawing power of the groups when the solvent is changed from DMF to CF_3CO_2H. This effect had been previously observed for the phosphonium[3e]- and sulfonium[3g]-substituted fluorobenzenes on changing the solvent from DMSO to CF_3CO_2H[3e] and CF_3CO_2H to CH_3CN (and HMPA).[3g] It was suggested[3e] that the lower inductive effect (σ_I) of the $^+P(CH_3)_3$ group in DMSO may be due to complexation between the oxygen anionic site of the solvent and the phosphorus cationic site of the solute decreasing the net positive charge on phosphorus. Although it was not suggested, this strong co-ordination would also reduce the requirements for $\pi \rightarrow$ d bonding and lead to a reduction in σ_R^0. It was noted[3e] that the solvent effect did influence σ_R^0 in the same direction as σ_I but the effect was much smaller. However, it can be seen from the data (Table X) that the effect is just as pronounced with the nitrogen pole which clearly does not engage in $\pi \rightarrow$ d electron withdrawal. Further, the nitrogen cationic site would not be very accessible to complexation with the solvent due to effective steric protection of the relatively small nitrogen by the methyl groups. Thus, we believe that the observed solvent effect for these groups can be more readily attributed to a decrease in ion-pair interactions[73] as the ionizing power of the solvent increases. Low nucleophilicity and hydrogen-bonding effects are probably also significant with CF_3CO_2H.

Finally, we would like to draw attention to the fact that the DSP parameters listed in Table VII may be useful for estimating ^{19}F SCS parameters in 1- and 2-fluoronaphthalene for any substituent whose σ_I and σ_R^0 values are known. This point is exemplified by the results listed in Table XIII for some miscellaneous ^{19}F SCS data. The considerable difference between the observed and calculated values for the OH substituent in DMF can be attributed to strong substituent–solvent interactions.

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(43) R. T. C. Brownlee and R. W. Taft, *J. Am. Chem. Soc.*, **92**, 7007 (1970). CNDO/2 calculations suggest that σ-electron effects are dominant at fluorine in meta-substituted fluorobenzenes. However, because the interacting groups in the 6β and 7β orientations of naphthalene are so far apart, σ-electron effects should be negligible; MO calculations suggest that attenuation of substituent effects upon electronic distribution in orbitals of σ symmetry is much more rapid than in orbitals of π symmetry (W. J. Hehre, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 1496 (1972)).

(44) SCF–MO calculations on the *amino* and *formyl* substituents (see ref 36) indicate that charge alternation in the π system is much less pronounced in the ring bearing the fluorine for the 6β and 7β orientations of naphthalene than for fluorobenzene. Thus π-electron effects of the type previously described (see ref 6b) should be relatively unimportant.

(45) R. T. C. Brownlee, D. G. Cameron, R. D. Topsom, A. R. Katritzky, and A. F. Pozharsky, *J. Chem. Soc., Perkin Trans. 2*, **247** (1974), and references therein. Electromeric interactions have been demonstrated to be important between fluorine (resonance donor) and strong resonance acceptors. Thus, $\sigma_R{}^0$ values for resonance-accepting substituents determined from meta- and para-substituted fluorobenzenes are enhanced compared with those obtained by ir studies on monosubstituted benzenes. However, in valence bond terminology whereas the ratio of mesomeric to electromeric canonical structures contributing to the resonance hybrid description of the electronic ground state of a para-substituted fluorobenzene is three to one, the ratio for a 6-substituted 2-fluoronaphthalene is five to one. Therefore, the effect of substituent-probe interactions on $\sigma_R{}^0$ values should be minimized by employing the 6β and 7β orientations of β-fluoronaphthalene for computing the substituent parameters rather than the fluorophenyl tag.

(46) L. Libit and R. Hoffman, *J. Am. Chem. Soc.*, **96**, 1370 (1974), and references therein.

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(49) Dewar (ref 40b) and Stock (ref 40c) have suggested that the trifluoromethyl group operates mainly by a field effect.

(50) Substituent chemical shifts in aryl fluorides arise primarily by π polarization, rather than by polarization of the CF σ bond: M. J. S. Dewar and T. G. Squires, *J. Am. Chem. Soc.*, **90**, 210 (1968).

(51) H. C. Clark, *Adv. Fluorine Chem.*, **3**, 21 (1963).

(52) C. F. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, **90**, 4328 (1968). CN: $\sigma_I = 0.56$; $\sigma_R{}^0 = 0.13$. CF_3: $\sigma_I = 0.45$; $\sigma_R{}^0 = 0.08$. COOR: $\sigma_I = 0.30$; $\sigma_R{}^0 = 0.14$. CN: $\mathcal{F} = 0.847$; $\mathcal{R} = 0.184$. CF_3: $\mathcal{F} = 0.631$; $\mathcal{R} = 0.186$. COOR: $\mathcal{F} = 0.552$; $\mathcal{R} = 0.140$.

(53) R. T. C. Brownlee, S. K. Dayal, J. L. Lyle, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 7208 (1972), and references therein.

(54) C. L. Bumgardner, *J. Org. Chem.*, **28**, 3225 (1963).

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(56) We are grateful to Professor R. W. Taft for the calculations.

(57) (*a*) The precision of fit for the 8β disposition (DMF) is greatly improved

if the CH_3 and $Si(CH)_3$ substituents are deleted from the correlation: $\rho_1 = -9.147$; $\rho_R = -4.958$; $\lambda = 0.542$; $f = 0.101$. (b) Deletion of the CH_3 and $Si(CH_3)_3$ substituents from the 5α correlation leads to an improved correlation; $\rho_1 = -5.012$; $\rho_R = 0.021$; $\lambda = -0.004$; $f = 0.187$.

(58) Field effects from similar orientations in other model systems, 6-fluoro- and 7-fluoro-2-tetralone, have been shown to be the same (see ref 6c).

(59) G. L. Anderson, R. C. Parish, and L. M. Stock, *J. Am. Chem. Soc.*, **93,** 6984 (1971).

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(61) See footnote *g* to Table XII.

(62) S. R. Hartshorn and J. H. Ridd, *J. Chem. Soc. B*, 1063 (1968).

(63) (a) P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Am. Chem. Soc.*, **90,** 1767 (1968); (b) N. C. Cutress, T. B. Grindley, A. R. Katritzky, M. V. Sinnott, and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2,* 2255 (1972).

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

(65) Electrophilic aromatic substitution studies have indicated that the dimethylsulfonium substituent is predominantly meta directing (90.4% meta). This observation is in line with a *net* electron-withdrawing mesomeric component (see H. M. Gislow and G. L. Walker, *J. Org. Chem.,* **32,** 2580 (1967)).

(66) (a) N. C. Cutress, T. B. Grindley, A. R. Katritzky, and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2,* 263 (1974), and references therein. (b) Recent studies suggest that this may be the result of polarization rather than p → d orbital conjugation: A. Streitwieser and S. P. Ewing, *J. Am. Chem. Soc.*, **97,** 190 (1975); A. Streitwieser and J. E. Williams, *ibid.*, **97,** 191 (1975).

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(68) (a) C. D. Schaeffer, Jr., and J. J. Zuckerman, *J. Organomet. Chem.,* **55,** 97 (1973). The para (C_4) SCS for $Sn(CH_3)_3$ in $C_6H_5Sn(CH_3)_3$ is −0.1 ppm (*negative* sign implies upfield from internal benzene) and the shift separation of the meta and para carbons is zero. (b) D. Doddrell, K. G. Lewis, C. E. Mulquiney, W. Adcock, W. Kitching, and M. Bullpitt, *Aust. J. Chem.*, **27,** 417 (1974). Unfortunately, the ^{13}C chemical shifts for the metalloidal substituted benzenes in this study were not determined with respect to internal benzene as a standard. However, using the (C_4) SCS for $Sn(CH_3)_3$ determined by Schaeffer and Zuckerman and the ^{13}C chemical shift relative to TMS of C_4 in $C_6H_4Sn(CH_3)_3$, a chemical shift of 128.6 ppm (TMS) for benzene can be determined. This leads to the following (C_4) ^{13}C SCS (ppm): $Si(CH_3)_3$, 0.4; $Ge(CH_3)_3$, 0.1; $Sn(CH_3)_3$, −0.1; $Pb(CH_3)_3$, −0.9. It should also be noted that the shift separation of the meta and para carbons is only significant for $Si(CH_3)_3$ and $Pb(CH_3)_3$.

(69) ^{19}F SCS data taken from reference listed as footnote *g* to Table XII.

(70) C. D. Schaeffer, Jr., and J. J. Zuckerman, *J. Organomet. Chem.*, **78,** 373 (1974), and references therein.

(71) (a) C. Eaborn and K. C. Pande, *J. Chem. Soc.,* 1566, (1960), and references therein; (b) C. Eaborn, T. A. Emokpae, V. I. Sidorov, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2,* 1454 (1974).

(72) P. K. Bischof, M. J. S. Dewar, D. W. Goodman, and T. B. Jones, *J. Organomet. Chem.,* **82,** 89 (1974). An analysis of the photoelectron spectral data for compounds $(CH_3)_3MPh$ and $(CH_3)_3MCH_2Ph$ (M = C, Si, Ge, and Sn) suggests a constant inductive contribution by Si, Ge, and Sn. Further, that p_π–d_π conjugation is important for Si and Ge. However, the conclusions are not unequivocal because many of the spectra were poorly resolved and it is therefore difficult to estimate the various ionization energies accurately.

(73) (a) G. Fraenkel, *J. Chem. Phys.*, **39,** 1614 (1963); (b) G. Fraenkel and J. P. Kim, *J. Am. Chem. Soc.*, **88,** 4203 (1966).

ESR and X-Ray Study of the Structure of Diquat (6,7-Dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium) Cation Radical and Dication

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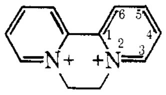
Received July 25, 1975

Abstract: The x-ray structure of diquat (6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium dication) has been redetermined. The diheral angle between the rings is found to be ca. 20°. ESR studies on the diquat cation radical have been interpreted in terms of an intermediate rate of ring inversion. From the ESR spectra an upper limit can be estimated for the barrier to inversion. Molecular orbital calculations (HMO and INDO) are consistent with this interpretation and also provide some insight into the herbicidal action of diquat.

Diquat **1** (6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium dication) and paraquat **2** (*N,N*′-dimethyl-4,4′-dipyridylium dication) are powerful herbicides.[1] Their herbicidal mode of action has been related to the relative ease with which these compounds may be photolytically and reversibly reduced to their cation radical.[2] The structure of the dications and cation radicals is also believed important to the herbicidal activity of these compounds.[3] The structure of the paraquat dication has been investigated by x-ray methods[4] and is found to be planar. The planar structure of the paraquat cation radical has been inferred from ESR studies.[5] The diquat molecule has been less thoroughly studied, a preliminary x-ray study of the dication has appeared[6] and an unresolved ESR spectrum of the cation radical has been reported.[7] It is the purpose of this paper to present an analysis of the ESR spectrum of the diquat cation radical and to rationalize this spectrum in terms of the probable structure of the cation radical. This is done by analogy to the structure of diquat dication which has been redetermined by x-ray methods. INDO calculations on the cation radical have also been used to aid in our analysis.



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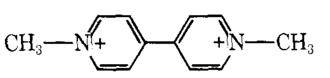

2

Experimental Section

Diquat dibromide was prepared by refluxing 2,2′-bipyridyl in excess 1,2-dibromoethane following previously described methods.[7] A deuterated derivative of diquat was prepared in a similar manner using 2,2′-bipyridyl and excess deuterated 1,2-dibromoethane-d_4 (99.9% from Stohler Chemical Co.). The cation radical of diquat was prepared by chemical reduction with zinc dust in ethanol, acetonitrile, or trifluoroacetic acid (TFA). The best resolved ESR spectra were obtained by zinc reduction in TFA of solutions approximately 2×10^{-4} M in diquat. The samples were submitted to several freeze–pump–thaw cycles before ESR observation. The ESR spectra were recorded on a Varian E-15 spectrometer in a dual cavity, the spectral analyses were carried out using the perylene radical anion as a secondary standard, and the splitting constants were obtained from a least-squares analysis.[8]

A purified crystal of diquat dibromide of approximate dimensions 0.4 × 0.15 × 0.1 mm was used for the x-ray analysis. Survey