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Carbon-13 Nuclear Magnetic Resonance Examination of Naphthalene Derivatives. Assignments and Analysis of Substituent Chemical Shifts

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The natural abundance ^{13}C NMR spectra of a number of substituted naphthalenes have been obtained and assigned by utilization of some or all of the following criteria: (a) specific ^{2}H incorporation and spectral consequences thereof, (b) fully proton coupled spectra, (c) fluoro substitution, and (d) approximate additivity of substituent effects on chemical shifts for certain dispositions. For crucial sets of 1- and 2-substituted naphthalenes, spectra have been obtained under dilute conditions in chloroform and acetone, and the substituent chemical shifts have been treated by the dual substituent parameter equation (DSP analysis) to provide further insight into the transmission of substituent effects in the naphthyl system.

Recently we reported[1,2] some initial studies of the ^{13}C spectra of substituted naphthalenes, and emphasized the beneficial effects of specific ^{2}H substitution, regarding spectral assignments. Subsequently, we and others have explored[2–9] other strategies for assignment purposes, and in particular fully proton coupled spectra have been most informative, yielding information on the number and kind of vicinal ^{1}H–^{13}C interactions, and the characteristic differences in "resonance shapes" for Cα and Cβ resonances in an ortho-disubstituted benzo fragment.[10] The availability of a large number of fluoro-substituted benzenes and naphthalenes[11] has permitted study of the value of fluoro substitution as an assignment aid. We employed this approach in our study of the benzocycloalkenes[3,4] and the results were quite definitive. In this research, we have further utilized this approach, and other aspects of additivity of substituent effects.

Many of our original spectra[1] were obtained at 15.086 MHz in the CW mode, and ^{2}H incorporation, off-resonance noise decoupling (to identify quaternary carbon signals), and chemical shift arguments were employed to assign the spectra. Since that report, we have synthesized and examined the spectra of a large number of naphthalene derivatives, and it was apparent that several of our (and other)[5] assignments required modification. These changes are embodied in this report. While our program was being executed, Ernst[7,8] was also examining selected naphthalene compounds and his report drew attention to some of the previous incorrect assignments alluded to above. While there is some overlap with the published work of Ernst as far as final assignments are concerned, the procedures employed for assignments are in general different, but complementary. In contrast to Ernst's approach,[7,8] we have generally examined at least one specifically ^{2}H-substituted naphthalene, synthesized by standard organic transformations, to provide a completely unambiguous start to the assignment problem. It is gratifying to note that where duplication of effort has occurred with Ernst, agreement in assignment sequence has resulted. (What appear to be systematic differences in the chemical shifts can occur, however.)

As a logical extension of our efforts toward understanding substituent effects in naphthalene by ^{19}F chemical shifts,[11] we have recorded the spectra of a basic set[12,13] of 1- and 2-substituted naphthalenes in chloroform at low dilution (~5%). Ernst has published data for a range of compounds using 10% solutions in acetone,[7,8] and we have completed this solvent series for the 1- and 2-methyl- and -methoxynaphthalenes. Substituent chemical shifts have been calculated and fitted to the dual substituent parameter equation[12,13] to provide substituent parameters. Conclusions based on these ^{13}C results are compared where possible with previous ^{19}F data.[11,12]

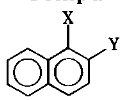
Results and Discussion

A. Assignments. A number of techniques are now available for the assignment of the ^{13}C spectra of aromatic molecules, and details and applications of these strategies have been reported.[1–10] Rather than provide a detailed discussion of the application of these techniques to individual naphthalene compounds, we have indicated in Table I the methods employed for each compound. In almost every case, the different techniques yielded harmonious assignments. Quaternary carbons in these molecules were located by off-resonance noise decoupling, and additionally were usually of relatively low intensity in the PFT spectra. While chemical shifts alone can be unsatisfactory and misleading, they were always considered and can be of much value when the aromatic system is perturbed by substituents capable of substantial resonance interactions, e.g., CN, OCH$_3$, NH$_2$, etc.

The following code has been employed in Table I (in the formula column) to indicate the assignment techniques employed for individual compounds, and the chemical shifts of all compounds examined are in Tables I and II. These assignments, together with those of Ernst,[7,8] should be regarded as established for these compounds: A ≡ consideration of ^{13}C–^{19}F couplings; B ≡ specific ^{2}H incorporation at position 4; C ≡ fully ^{1}H coupled spectrum; D ≡ consideration of specifically fluorinated derivatives; E ≡ specific ^{2}H incorporation at position 5; F ≡ specific ^{2}H incorporation at position 6; G ≡ specific ^{2}H incorporation at position 7.

B. Substituent Effects. The substituent effects exerted in aromatic systems frequently are gauged by NMR chemical shift changes (substituent chemical shifts), and it is now realized that full appreciation of such substituent effects involves examination of aromatic systems other than benzene,

Table I. Carbon-13 Chemical Shifts[a] of Some Naphthyl Compounds

Registry no.	Compd 	Carbon no. 1	2	3	4	5	6	7	8	9	10	Others	Shift sequence of aromatic carbons
	Y = H X =												
321-38-0	$F^{A,B,C}$	159.5	109.8	126.0	124.2	128.1	127.3	126.6	120.9	124.3	135.7		2, 8, 4, 9, 3, 7, 6, 5, 10, 1
		(253.6)	(19.8)	(8.0)	(4.6)	(3.0)	(~1.0)	(~2.0)	(5.0)	(17.2)	(5.0)		
		157.2	108.27	124.31	122.42	126.22	125.50	124.88	119.29	123.82	133.59		2, 8, 4, 9, 3, 7, 6, 5, 10, 1
90-11-9	$Br^{B,C}$	122.73	129.7	125.75	127.7	128.1	126.4*	126.9*	127.0*	132.0	134.6		
86-53-3	$CN^{B,C,D}$	108.83	131.05	123.53	131.78	127.28	126.12	127.1	123.53	130.75	131.38	116.5	1, 3, 8, 6, 7, 5, 9, 2, 10, 4
		109.94	132.08	124.78	132.39	128.55	127.38	128.39	124.78	132.06	132.70	117.6	1, 3, 8, 6, 7, 5, 9, 2, 4, 10
3163-27-7	$CH_2Br^{B,C,E}$	132.0	127.4	125.0	129.3	128.5	125.8	126.2	123.4	130.8	133.7	31.5	8, 3, 6, 7, 2, 5, 4, 9, 1, 10
4780-79-4	CH_2OH^{E}	136.2	125.0	125.3	128.1	128.5	125.6	126.0	123.5	131.0	133.6	62.8	8, 2, 3, 6, 7, 4, 5, 9, 10, 1
134-32-7	$NH_2{}^{E}$	142.2	109.5	126.3	118.6	128.4	125.7	124.6	120.9	123.6	134.3		2, 4, 8, 9, 7, 6, 3, 5, 10, 1
17085-91-5	$C(CH_3)_3{}^{B,D}$	145.9	123.1	125.0	127.4	129.6	124.5	124.5	126.8	132.0	135.8	31.6, 35.7 (q)	2, 6, 7, 3, 8, 4, 5, 9, 10, 1
6301-54-8	$C(CH_3)_2OH^{B,D}$	143.5	122.6	124.6	128.5	128.9	125.2*	125.0*	127.3	130.9	134.8	31.4, 73.8 (q)	2, 3, 7*, 6*, 8, 4, 5, 9, 10, 1
1855-47-6	$C(=CH_2)CH_3{}^{B}$	144.7	124.5	125.2	127.2	128.3	125.6*	125.8*	125.8*	131.0	133.9	25.1, 116.1, 142.3	2, 3, 6*, 7*, 8*, 4, 5, 9, 10, 1
941-98-0	$COCH_3{}^{B,D}$	134.9	128.8	124.2	132.9	128.3	126.3	127.9	126.0	130.1	133.8	29.6, 201.3	3, 8, 6, 7, 5, 2, 9, 4, 10, 1
86-55-5	$COOH^{B,C,D}$	126.5	129.49	123.45	132.29	127.44	125.04	126.5	124.82	130.35	132.78	168.97	3, 8, 6, 1, 7, 5, 2, 9, 4, 10
	X = H Y =												
323-09-1	$F^{A,C,F,G}$	110.9	161.0	116.2	130.5	128.1	125.2	127.0	127.5	134.7	130.8		1, 3, 6, 7, 8, 5, 4, 10, 9, 2
		(21.0)	(248.8)	(25.9)	(10.1)	(~0)	(2.8)	(1.2)	(5.1)	(9.9)	(~0)		
		109.73	158.98	115.00	128.93	126.55	123.77	125.52	125.52	132.79	129.11		1, 3, 6, 7, 8, 5, 4, 10, 9, 2
580-13-2	$Br^{C,F}$	130.0	119.9	129.4	129.6	127.9	126.3	126.9	127.1	134.3	131.6		2, 6, 7, 8, 5, 3, 4, 1, 10, 9
2876-35-9	$C(CH_3)_3{}^{C,D}$	122.9	148.4	124.7	127.6	128.0	125.2	125.7	127.4	134.0	132.3	31.3 (CH_3), 34.8 (q)	1, 3, 6, 7, 8, 4, 5, 10, 9, 2
18052-85-2	$Si(CH_3)_3{}^{D}$	133.8	137.8	129.8	127.0	128.1	126.2	125.7	128.1	133.1	133.8	−1.1	7, 6, 4, 5, 8, 3, 1, 9, 10, 2
91-59-8	$NH_2{}^{C,F,D}$	107.4	142.65	117.0	127.82	126.39	121.2	125.0	124.5	133.5	126.60		1, 3, 6, 8, 7, 5, 10, 4, 9, 2
135-19-3	$OH^{C,F}$	108.42	151.7	116.54	128.57	126.47	122.40	125.25	125.12	133.21	127.65		1, 3, 6, 8, 7, 5, 10, 4, 9, 2
93-04-9	$OCH_3{}^{D,F}$	105.82	157.7	118.79	129.45	127.73	123.67	126.43	126.82	134.65	129.03	55.27	1, 3, 6, 7, 8, 5, 10, 4, 9, 2
93-08-3	$COCH_3{}^{C,D}$	130.06	134.45	123.79	128.29	127.70	128.34	129.49	132.46	135.48	135.48	26.45, 197.65	3, 7, 5, 4, 6, 8, 1, 9, 2, 10
93-09-4	$COOH^{C,D}$	131.67	128.56	125.76	128.45	128.07	128.56	126.95	129.65	133.00	136.08	169.56	3, 7, 5, 4, 2, 6, 8, 1, 9, 10
613-46-7	$CN^{C,D,F}$	133.79	109.16	126.03	128.97	127.85	128.89	127.50	128.21	131.97	134.34	119.11	2, 3, 7, 5, 8, 6, 4, 9, 1, 10
581-90-8	$CF_3{}^{D}$	126.0	nl	121.7	129.1**	128.1*	128.3*	127.4	129.2**	132.5	134.9		3, 1, 7, 5, 6, 4, 8, 9, 10
		(4.5)		(3.2)	u	u	u	u	u	u	(~0.7)		

[a] Relative to Me_4Si. Asterisked signals indicate possible interchange; nl, not located; u, unresolved or negligible splitting; A, B, C, D, F, G indicate assignment techniques applied. See text.

Table II. Carbon-13 Chemical Shifts of Some Substituted 1- and 2-Fluoronaphthalenes[a]

Registry no.	Compd	Carbon no. 1	2	3	4	5	6	7	8	9	10	Other
59080-27-2	5-F-1-CN-N	110.1	~133.4	125.3	125.7	158.7	111.30	128.6	120.90	~133.4	123.3	117.3
		(3.75)		(2.44)	(6.09)	(253.90)	(19.53)	(8.55)	(4.89)		(17.1)	

	1-CN-N (calcd)	109.7	131.9	124.5	132.7	127.1	127.2	128.4	124.6	135.9	132.6	
59080-30-7	6-F-1-CN-N	nl	131.9	126.1	132.6	112.0	nl	119.0	127.8	nl	nl	nl
			nr	nr	(4.89)	(20.75)		(25.63)	(8.53)			
	1-CN-N (calcd)		132.5	124.9	133.0	129.0		128.5	125.2			
	1-CN-N (obsd)	109.9	132.1	124.8	132.4	128.6	127.4	128.4	124.8	132.1	132.7	117.6
55831-09-9	1-(7-F-1-N)1-Methylethanol	143.3	123.5	124.0	128.3	131.00	115.4	159.9	111.4	nl	131.9	
						(9.73)	(25.54)	(246.1)	(23.19)		nd	
	1-N-1-Methylethanol (calcd)	143.7	122.3	124.6	128.1	128.4	125.0	124.7	128.4			
	1-N-1-Methylethanol (obsd)	143.5	122.6	124.6	128.5	128.9	125.2	125.0	127.3	130.9	134.8	73.8; 31.4
13916-91-1	6-F-2-NH$_2$-N	107.6	142.1	118.1	127.1	109.6	157.1	115.3	126.5	130.5	126.8	
					(3.66)	(20.14)	(238.0)	(23.8)	(7.32)		(7.32)	
	2-NH$_2$-N (calcd)	107.4	142.7	116.9	127.5	126.6	121.9	124.8	123.9	133.3	125.7	
	2-OCH$_3$-N (obsd)	106.25	158.1	119.1	129.9	128.15	124.0	126.8	127.2	135.3	129.6	
33627-02-0	6-F-2-COCH$_3$N	128.62	132.66	123.69	126.33	109.92	160.48	116.00	130.77	128.14	135.19	26.22; 195.49
						(20.14)	(249.02)	(25.63)	(9.16)		(9.16)	
	2-COCH$_3$-N (calcd)	129.97	134.69	123.97	128.71	128.09	127.3	126.8	129.74	132.6	136.0	
33718-09-1	3-F-2-COCH$_3$-N	131.08	124.5	157.02	111.17	125.47	127.73 (?)	124.67	128.22	128.22	134.73	30.9 (7.32)
		(nr)	(25.63)	(249.02)	(21.97)						(9.15)	193.87 (3.66)
	2-COCH$_3$N (calcd)	130.05	135.3	123.84	129.34	127.85	128.01	126.7	129.57	134.49	135.54	
	2-COCH$_3$N (obsd)	130.06	134.45	123.79	128.29	127.70	128.34	126.65	129.49	132.46	135.48	26.45; 197.65
5043-01-6	6-F-2-COOH-N	130.22	126.44	125.55	126.44	110.14	160.79	116.16	130.96	128.62	135.61	167.46
						(20.14)	(247.19)	(25.63)	(9.16)		(10.99)	
	2-COOH-N (calcd)	131.22	128.45	125.81	128.77	128.26	127.59	126.94	129.88	132.98	136.29	
5043-10-7	7-F-2-COOH-N	129.45	127.92	123.90	127.11	129.23	117.59	159.67	111.32	132.41	131.59	167.49
		(5.49)		(br)		(9.16)	(25.63)	(245.36)	(20.14)	(9.16)		
	2-COOH-N (calcd)	131.78	128.18	125.91	128.41	128.15	128.37	126.47	129.44	133.09	135.95	
5043-22-1	8-F-2-COOH-N	122.93	127.28	125.47	126.84	122.56	127.21	109.33	158.17	122.03	135.24	167.22
		(br)				(br)	(9.15)	(20.15)	(250.85)	(16.48)		
	2-COOH-N (calcd)	131.49	128.18	125.75	128.47	127.89	128.68	126.84	128.81	131.67	135.12	
	2-COOH-N (obsd)	131.67	128.56	125.76	128.45	128.07	128.56	126.95	129.65	133.00	136.08	169.56
62078-75-5	7-F-2-CN-N	131.89	109.56	124.52	127.92	129.37	118.32	159.79	110.46	131.89	130.32	117.67
		(?)				(9.16)	(25.54)	(247.14)	(?)			
	2-CN-N (calcd)	134.22	109.78	126.53	129.22	128.29	129.10	126.59	128.58	132.57	134.67	
	2-CN-N (obsd)	133.79	109.16	126.03	128.97	127.85	128.89	127.50	128.21	131.97	134.34	119.11
62078-76-6	7-F-2-NH$_2$-N	106.7	143.7	116.1	127.9	128.7	111.3	159.8	107.7	134.8	123.55	
		(3.66)				(10.99)	(25.64)	(241.7)	(20.14)	(9.16)	(~0)	
	2-NH$_2$-N (calcd)	107.1	142.5	116.7	127.7	126.1	120.9	124.5	124.7	133.4	126.2	
	2-NH$_2$-N (obsd)	107.4	142.7	117.0	127.8	126.4	121.2	125.0	124.5	133.5	126.6	
575-08-6	6-F-1-COOH-N	127.57	128.73	124.85	131.55	110.59	159.31	116.70	127.96	130.73	134.17	168.49
					(5.49)	(20.14)	(245.36)	(25.63)	(9.15)		(9.15)	
	1-COOH-N (calcd)	128.92	130.76	125.13	133.93	128.76	126.11	127.5	126.93	135.23	134.98	
575-06-4	7-F-1-COOH-N	125.77	130.84	122.99	132.43	130.04	115.62	160.71	109.27	131.75	130.19	168.24
						(9.16)	(25.64)	(243.5)	(23.80)	(11.00)		
	1-COOH-N (calcd)	128.1	131.1	125.00	133.73	128.96	126.4	127.51	127.39	132.43	134.55	
	1-COOH-N (obsd)	126.5	129.49	123.45	132.29	127.44	125.04	126.5	124.82	130.35	132.78	
5471-32-9	2-F-1-COCH$_3$-N	121.64	156.78	114.52	131.71	126.98	124.36	126.98	123.51	129.16	129.38	32.63; 198.53
		(14.65)	(245.36)	(25.63)	(9.15)				(5.49)	(3.67)		
	1-COCH$_3$N (calcd)	139.81	123.6	125.32	130.68	128.33	126.39	127.26	125.9	130.0	133.9	
33718-11-5	8-F-1-COCH$_3$-N	133.96	122.77	124.79	128.08	123.1	125.27	110.36	156.30	118.13	136.03	(9.15); 202.79
							(9.16)	(21.97)	(249.02)			
	1-COCH$_3$N (calcd)	142.57	123.69	125.09	129.76	128.66	126.76	127.89	127.00	~129.6	136.19	
	1-COCH$_3$N (obsd)	134.9	128.4	124.2	132.9	128.3	126.3	127.9	126.00	130.1	133.8	29.6; 201.3
62078-77-7	7-F-2-OCH$_3$-N	104.24	156.94	116.76	128.03	128.64	112.44	159.71	108.89	134.30	124.63	54.59
		(3.66)				(9.16)	(25.64)	(243.53)	(20.14)	(9.16)		
	2-OCH$_3$-N (calcd)	106.62	157.22	118.79	129.38	128.19	123.24	126.53	127.06	135.1	129.12	

Table III. ^{13}C Substituent Chemical Shifts (SCS)[a,b] of Substituted Naphthalenes

Registry no.	Substituent	Carbon no. 1	2	3	4	5	6	7	8	9	10
					A. 1-Substituted Naphthalenes						
86-57-7	NO_2	+18.58	−1.95	−1.95	+6.62	+0.58	+1.40	+3.51	−4.90	−8.48	+0.74
	CN	−17.83	+6.66	−0.84	+5.23	+0.58	+1.59	+2.66	−3.12	−1.27	−0.42
	$COCH_3$	+7.39	+2.66	−0.64	+4.92	+0.35	+0.43	+2.04	−2.05	−3.49	+0.35
26458-04-8	CF_3		−1.08	−1.48	+5.04	+1.04	+1.02	+2.02	−3.56	−3.85	+1.05
2216-69-5	OCH_3	+27.54	−22.07	+0.04	−7.70	−0.46	+0.57	−0.68	−5.92	−7.86	+1.02
	NH_2	+14.06	−16.27	+0.39	−9.10	+0.52	−0.13	−1.13	−7.21	−9.94	+0.78
90-12-0	CH_3	+6.34	+0.55	−0.30	−1.37	+0.61	0.00	−0.13	−3.81	−0.88	+0.06
	F	+30.95	−16.42	−0.24	−4.26	−0.38	+0.98	+0.32	−7.37	−8.01	+1.44
	Br	−5.08	+4.04	+0.32	−0.01	+0.38	+0.85	+1.28	−0.61	−1.49	+1.14
	OCH_3[c]	+27.57	−21.85	+0.43	−7.82	−0.43	+0.43	−0.81	−6.09	−8.38	+1.08
	CH_3[c]	+6.15	+0.59	−0.33	−1.40	+0.59	−0.32	−0.32	−3.88	−0.92	+0.16
					B. 2-Substituted Naphthalenes						
581-89-5	NO_2	−3.42	+19.55	−6.70	+1.49	−0.04	+3.80	+1.98	+1.95	−1.66	+2.20
	CN	+6.10	−16.56	+0.35	+1.17	+0.03	+3.08	+1.72	+0.39	−1.37	+1.00
	$COCH_3$	+2.21	+8.67	−1.99	+0.44	−0.16	+2.56	+0.87	+1.64	−1.01	+2.01
581-90-8	CF_3	−1.96		−4.18	+1.14	+0.14	+2.42	+1.52	+1.24	−1.05	+1.35
	OCH_3	−22.14	+31.82	−7.09	+1.49	−0.23	−2.21	+0.55	−1.14	+1.10	−4.52
	NH_2	−19.35	+18.30	−7.61	+1.26	−0.20	−3.38	+0.52	−2.12	+1.43	−5.53
91-57-6	CH_3	−1.08	+9.62	+2.30	−0.66	−0.30	−0.88	+0.03	−0.30	+0.19	−1.79
	F	−17.04	+34.84	−9.58	+2.39	−0.05	−0.75	+1.01	−0.57	+0.70	−3.93
	Br	+1.66	−6.18	+3.41	+2.01	−0.07	+0.42	+1.04	−1.04	+1.01	−1.66
	OCH_3[c]	−22.12	+29.93	−7.23	+1.35	−0.27	−2.43	+0.43	−1.13	+1.30	−4.53
	CH_3[c]	−1.13	+9.38	+2.11	−0.61	−0.21	−0.91	−0.05	−0.21	+0.27	−1.73

[a] Defined as the difference (ppm) between the ^{13}C chemical shift of the substituted compound and that of the appropriate carbon in the parent hydrocarbon. Positive values indicate decreased shielding. [b] Unless otherwise specified, all compounds were run in deuteriochloroform (0.5–1.0 M). Naphthalene ($DCCl_3$, relative to Me_4Si): 127.96 (C1); 125.88 (C2); 133.55 (C9). [c] Solvent, deuterioacetone (0.5 M). Naphthalene [$(CD_3)_2CO$; relative to Me_4Si]: 128.66 (C1); 126.67 (C2); 134.38 (C9).

e.g., naphthalenes or anthracene. With the definite assignments for a number of key naphthyl compounds now available, we are in a position to report analysis of spectra recorded at low concentrations, so that meaningful appraisal of intramolecular effects on ^{13}C shifts in this system can be made. These results are discussed below.

The ^{13}C substituent chemical shift (SCS) data for 1- and 2-substituted naphthalenes ($DCCl_3$ solvent) together with the results for the methyl- and methoxy-substituted naphthalenes (acetone-d_6 solvent) are listed in Table III. A wide variety of substituents exhibiting a range of electronic characteristics was chosen in order to provide a meaningful correlative analysis by the Taft dual substituent parameter (DSP)[12,13] equation

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

where p^i = substituent effect property; σ_I and σ_R are the substituent polar and resonance effect parameters, respectively; ρ_I and ρ_R represent the susceptibilities of the property to each of the substituent properties; the ratio or blend $\rho_R/\rho_I \equiv \lambda$.

Table IV gives the results of the best fits of the SCS data ($DCCl_3$ and acetone-d_6) to eq 1. The SCS for CH_3 and OCH_3 in acetone-d_6 (Table III) were combined with the recently published data of Ernst[7,8] to provide an adequate basis set of substituents (NO_2, CN, CHO, $COCH_3$, F, Cl, Br, I, CH_3, and OCH_3)[12,13] for the correlative analysis for this solvent. However, because acetone is a fairly basic solvent, the data for substituents (NH_2, OH, and COOH) whose electronic properties are markedly perturbed by hydrogen-bonding interactions were excluded. The discriminatory precision of fit achieved with the $\sigma_R{}^\circ$ parameters over that obtained with the σ_R (BA) parameters is not highly significant and in two dispositions (Table IV, 4α and 8β, acetone-d_6) the latter scale provided the best fit. An important feature of the analyses in the two vastly different solvent systems is that the DSP parameters are mutually consistent regarding the overall precision and pattern of fits. Thus intermolecular interactions (solute–solute and solute–solvent) are not grossly distorting the picture as far as intramolecular effects in the various dispositions are concerned.

It should be noted that the results for the proximate carbon sites (C1, C2, and C9 in 1-substituted naphthalenes; C1, C2, and C3 in 2-substituted naphthalenes) are not given because of the extremely poor precision of fits. This was expected as it is well known that carbon sites close to the point of substitution are markedly affected by steric, neighboring group, magnetic anisotropy, and bond order effects as well as electronic phenomena.[14] The ^{13}C nucleus can be a reliable monitor of total charge density at remote carbon centers only since here the above mentioned proximity factors are considered negligible. This proposition is exemplified by a number of successful empirical and theoretical correlations which have clearly established that para ^{13}C SCS of monosubstituted benzenes accurately reflect the charge density at that position.[15]

Bearing in mind that a ^{13}C NMR study of monosubstituted naphthalenes provides information for three more nonproximate sites than a corresponding substituent effect study which employs a side chain probe or detector (^{19}F NMR and chemical reactivity studies), a cursory examination of the results set out in Table VI indicates that the overall analysis provides some distinct similarities with the DSP results for the ^{19}F SCS data[11,12] when compared with the analysis of reactivity data at the corresponding dispositions. Although some discussion of the ^{19}F NMR situation has been presented,[11,12] it is instructive to note the salient features. The overall precision of fits achieved by the DSP equation is significantly worse than those reported for reactivity data.[12] Further, the shielding data display different λ blending factors, i.e., SCS

Table IV. Best Fit Parameters of Dual Substituent Parameter Equation for Substituent ^{13}C NMR Shielding Effects in Naphthalene

Carbon no.[a] (disposition)	Type	Solvent	ρ_I	ρ_R	λ	SD[b]	f[c]	n[d]
	A. 1-Substituted Naphthalenes							
3 (4β)	σ_R°	$DCCl_3$	−1.80	−1.63	0.91	0.44	0.49	9
4 (4α)	σ_R°	$DCCl_3$	5.92	19.98	3.38	0.66	0.12	9
5 (5α)	σ_R°	$DCCl_3$	0.82	0.59	0.72	0.46	0.80	9
6 (5β)	σ_R°	$DCCl_3$	2.23	0.41	0.18	0.17	0.18	9
7 (8β)	σ_R°	$DCCl_3$	4.10	3.89	0.95	0.27	0.15	9
10	σ_R°	$DCCl_3$	1.36	−1.66	−1.22	0.40	0.46	9
3 (4β)	σ_R°	Acetone	−0.70	−2.25	3.22	0.52	0.69	10
4 (4α)	σ_R°	Acetone	6.87	18.90	2.75	0.88	0.18	10
4 (4α)	σ_R(BA)	Acetone	7.11	15.66	2.20	0.45	0.10	10
5 (5α)	σ_R°	Acetone	1.56	1.27	0.81	0.34	0.46	10
6 (5β)	σ_R°	Acetone	2.68	0.57	0.21	0.18	0.16	10
7 (8β)	σ_R°	Acetone	4.98	4.26	0.85	0.38	0.18	10
7 (8β)	σ_R(BA)	Acetone	4.90	3.30	0.67	0.25	0.12	10
10	σ_R°	Acetone	1.36	−1.95	−1.54	0.40	0.45	10
	B. 2-Substituted Naphthalenes							
4 (3α)	σ_R°	$DCCl_3$	2.95	−2.00	−0.68	0.31	0.21	9
5 (6α)	σ_R°	$DCCl_3$	−0.04	0.36	−9.70	0.13	0.78	9
6 (6β)	σ_R°	$DCCl_3$	4.01	7.74	1.93	0.14	0.06	9
7 (7β)	σ_R°	$DCCl_3$	2.85	0.37	0.13	0.19	0.16	9
8 (7α)	σ_R°	$DCCl_3$	1.28	4.32	3.39	0.52	0.40	9
9	σ_R°	$DCCl_3$	−1.30	−3.80	2.91	0.34	0.30	9
10	σ_R°	$DCCl_3$	0.41	11.23	27.11	0.38	0.12	9
4 (3α)	σ_R°	Acetone	3.72	−1.43	−0.39	0.39	0.23	10
5 (6α)	σ_R°	Acetone	0.27	0.45	1.65	0.12	0.66	10
6 (6β)	σ_R°	Acetone	4.50	7.63	1.70	0.15	0.07	10
7 (7β)	σ_R°	Acetone	3.21	1.04	0.32	0.12	0.09	10
8 (7α)	σ_R°	Acetone	1.34	4.62	3.45	0.55	0.44	10
9	σ_R°	Acetone	−0.73	−4.08	5.61	0.47	0.44	10
10	σ_R°	Acetone	0.63	10.03	15.88	0.32	0.13	10

[a] The Greek letter indicates the position of the detector, the numeral that of the substituent. This nomenclature has been used for specifying the various dispositions of substituted fluoronaphthalenes. [b] The standard deviation of the fit. [c] 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 $f \leqslant 0.1$. [d] The number of substituents in the data set.

consist of distinctly different blends of polar and mesomeric effects as compared to reactivity substituent effects. However, while the positional dependencies of ρ_I values differ markedly, the positional dependencies of ρ_R values appear to display essentially similar patterns for the appropriate comparisons between these two kinds of measurements. This is particularly the case for the formally conjugated dispositions.

We believe that the most important aspect of the correlative analysis of the ^{13}C NMR shielding data concerns the several significant differences, when compared with the corresponding ^{19}F NMR DSP results. Firstly, it can be seen from Table IV that the susceptibility coefficients (ρ_I and ρ_R) at C5 (5α) and C5 (6α) in 1- and 2-substituted naphthalenes, respectively, indicate very feeble polar and resonance effects at these positions. However, because the precision of fits for these dispositions is extremely poor, this feature is best exemplified by examining the ^{13}C SCS for these two dispositions listed in Table III. It can be seen for a series of substituents covering a wide range of electronic effects that the SCS at these positions (5α and 6α) are confined to a very narrow range and generally show no obvious correlation with the electronic properties of the substituent.[16] The 5α disposition, which is formally a conjugated position, is slightly but more irregularly affected than the unconjugated 6α orientation, but this probably has its origin in structural factors of the kind previously alluded to for the corresponding ^{19}F SCS, rather than specific electronic effects.[11,17] Hence it is very reasonable that, as a good first approximation, polar and resonance effects can be considered negligible at the 5α and 6α dispositions in monosubstituted naphthalenes as determined by the ^{13}C probe. However, the situation is significantly different when monitored by ^{19}F chemical shifts.[11,18] Now substantial residual polar effects at both dispositions are observed and, although mesomerism is indicated to be virtually zero in the 5α disposition, significant secondary mesomeric effects are observed for the unconjugated 6α orientation.[18,19] Two important conclusions follow. Firstly, the nature of polar substituent effects as determined by the two probes is completely different. Recent studies[4,20,21] of geometrically well-defined model systems indicate quite unambiguously that electrostatic field induced π polarization is the dominant, if not exclusive, long-range mechanism transmitting the influence of the primary inductive substituent effect as indicated by aryl ^{13}C chemical shifts. More recently, this has been further confirmed by Reynolds and Hamer,[22] who have shown that the pattern of ρ_I values from a DSP analysis of the ^{13}C SCS for 4-substituted biphenyls is very similar to the SCS for 4-ammoniobiphenyl (relative to 4-methylbiphenyl)[23] and to the chemical shift and π electron density patterns in phenylalkane derivatives. Further confirmation is achieved from the current study by noting (Chart I) the similar pattern displayed by the ρ_I values (Table IV, $DCCl_3$) for the two monosubstituted naphthalenes and the ^{13}C chemical shifts for 1- and 2-ammonionaphthalenes relative to the chemical shifts for 1- and 2-methylnaphthalene (Table V, CF_3CO_2H as solvent), respectively. The significantly larger ρ_I values in acetone compared to $DCCl_3$ (Table III) suggests that field-induced π polarization is increased when substituent polarity is enhanced

Table VA. Carbon-13 Chemical Shifts[a] of Amino- and Methyl-Substituted Naphthalenes in CF_3CO_2H[b]

Compd	Carbon no. 1	2	3	4	5	6	7	8	9	10	Other
1-Naphthylamine	124.22	121.30	124.96	131.4	129.38	127.97	128.71	118.99	126.17	134.77	
2-Naphthylamine	122.01	125.60	119.04	131.24	128.17	128.17	127.85	128.17	133.68	133.27	
1-Methylnaphthalene	134.95	126.56	125.94	126.82	128.70	125.94	125.94	124.32	133.09	134.10	19.38
2-Methylnaphthalene	127.01	136.47	128.54	127.57	127.92	125.29	126.20	127.92	134.26	132.28	21.72
Naphthalene	128.07	126.12	126.12	128.07	128.07	126.12	126.12	128.07	133.68	133.68	

[a] Relative to Me_4Si. [b] CF_3 (quartet): 96.55, 108.94, 121.33, 133.68; COOH (quartet): 159, 160.89, 162.81, 164.69.

Table VB. Carbon-13 Chemical Shifts[a] of Some Fluoro-Substituted Naphthylamines in CF_3CO_2H

Registry no.	Compd	Carbon no. 1	2	3	4	5	6	7	8	9	10
438-32-4	4-F-1-NH_2		120.19 (8.71)	109.02 (23.25)	160.19 (253.57)	121.77 (5.09)	128.48 (~2)	129.79	119.42 (2.47)	127.77 (5.83)	125.13 (17.39)
62078-78-8	6-F-1-NH_2	124.79	121.29	126.33	130.53	112.80 (19.59)	161.52 (246.77)	118.84 (26.13)	122.59 (7.99)	123.40	136.05 (8.69)
	6-F-2-NH_2	121.67	125.09 (2.93)	120.07	129.67	110.81 (21.97)	160.94 (244.66)	117.87 (24.90)	129.67	129.67	133.62 (9.52)
	7-F-2-NH_2	121.79	127.41	119.12	131.12	131.34 (10.2)	118.69 (18.93)	162.30 (246.06)	111.61 (21.85)	134.66 (10.2)	131.12

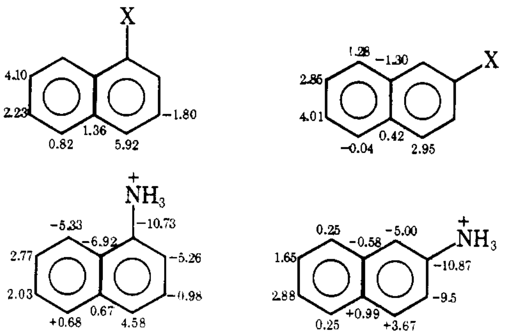
[a] Relative to Me_4Si.

Table VC. Calculated Chemical Shifts[a,b] for 1- and 2-Naphthylamine in CF_3CO_2H

Compd	Carbon no. 1	2	3	4	5	6	7	8	9	10
4-F-1-NH_2		120.43	125.44	129.24	129.14	128.16	128.81	119.80	126.33	133.14
6-F-1-NH_2	124.84	122.04	125.23	131.10	129.84	126.67	128.42	120.29	127.33	135.35
6-F-2-NH_2	121.72	125.84	119.84	130.24	127.85	126.10	127.45	127.28	133.60	132.90
7-F-2-NH_2	122.36	126.40	119.87	131.17	128.95	128.27	127.46	128.65	133.96	133.05

[a] Relative to Me_4Si. [b] Calculated by utilizing the ^{13}C SCS for fluorine (Table III).

Chart I



by a more polar solvent.[24]

Thus, since the $\rho_I\sigma_I$ terms for ^{13}C NMR shielding effects are dominated by field-induced π polarization, and since this effect is negligible at the 5α and 6α disposition, it follows that the observed ^{19}F NMR polar substituent effects at these dispositions must have their origin in the through-space component (direct field effect) of the electrostatic-field vector acting on the potential π component of the C–F bond.[25,26] Assuming a common effective dielectric constant and by utilizing readily determined angle/distance relationships,[27] the polar effect values in the 5α and 6α orientations can be used to estimate direct electric-field contributions to the ^{19}F SCS at the various dispositions in substituted fluoronaphthalenes[11,25] as well as in para-substituted fluorobenzenes[28] and 10-substituted 9-fluoroanthracenes.[29] Calculated contributions for fluorine as the substituent are given in Table VI. This substituent was chosen because of its steric size (similar to hydrogen) and hence its ^{19}F SCS at the 5α disposition (−2.15 ppm, DMF)[11] should be uncomplicated by potential structural factors and therefore be only a manifestation of substituent polarity. The results listed in Table VI indicate that although direct field effects are clearly dominant in fluorobenzenes,[30] this is not the case in many of the dispositions of substituted fluoronaphthalenes and fluoroanthracenes where field-induced π polarization is apparently important. This may be the reason for the observed variable ρ values when the FMMF treatment is applied to the ^{19}F SCS of aryl fluorides[31] as the method treats only direct field effects. Reynolds and Hamer[22] have recently drawn attention to this limitation of the FMMF method in connection with Schulman and co-workers'[32] erroneous conclusions concerning the relative importance of polar field effects on aryl ^{13}C chemical shifts.

These workers[22] have also presented estimates of direct field contributions to the ^{19}F SCS for para-substituted fluorobenzenes and 10-substituted 9-fluoroanthracenes, 45 and 25%, respectively, using the NO_2 group as an example, which are significantly different from the percentage dissections listed in Table VI. Their estimates are based on the Buckingham equation[33] for linear electric field effects in which the coefficient (A) was evaluated from the ^{19}F chemical shifts of 4-substituted β,β-difluorostyrenes.[34] However, we believe that our determinations probably are more realistic for aryl fluorides since a recent study[35] of a new model system suggests that the response of ^{19}F chemical shifts to an applied electric field is markedly determined by the electronic structure of the chemical bonds in the immediate vicinity of the fluorine atom. A full discussion on the nature of ^{19}F NMR polar substituent effects must await the completion of a study of new model

Table VI. Estimates of Direct Field Effects to ^{19}F SCS of Aryl Fluorides for Fluorine as Substituent in DMF

Aromatic system	Disposition[a]	Cos θ/r^2 [b]	Total polar field effect, ppm[c]	Direct field contribution, ppm[d]	% direct field contribution
Benzene	Para	1	−4.68	−3.61 (−3.31)	77 (71)
Anthracene	9,10	1	−8.33	−3.61 (−3.31)	43 (40)
Naphthalene	4α	1	−6.81	−3.61 (−3.31)	53 (49)
Naphthalene	5α	0.65	−2.15	−2.15	100
Naphthalene	6α	0.37	−1.34	−1.34	100
Naphthalene	7α	0.22	−1.81	−0.79 (−0.73)	44 (40)
Naphthalene	6β	0.42	−3.65	−1.52 (−1.39)	42 (38)
Naphthalene	7β	0.41	−2.34	−1.48 (−1.36)	63 (58)
Naphthalene	8β	0.65	−4.49	−2.35 (−2.15)	52 (48)

[a] The Greek letter indicates the position of the detector, the numeral that of the substituent. [b] Relative values. θ is the angle between a line of length r drawn between the midpoints of the CF bonds. [c] Dissected by DSP equation ($\rho_I\rho_I$). Values for ρ_I were taken from the literature (ref 11 and 28) while σ_I for fluorine was taken as 0.50 (ref 13). The sign convention commonly employed for ^{19}F chemical shifts is generally opposite to that for ^{13}C chemical shifts. [d] Estimated from the direct field effect at the 6α disposition and the appropriate relative angle/distance relationships. The values in parentheses are similar estimates derived from the 5α orientation.

systems[36] which should help to illuminate the overall situation.

The second significant conclusion that can be made from a comparison of the ^{13}C and ^{19}F SCS in the 6α disposition is that the latter parameter is much more sensitive to mesomeric-field effects.[25,31,37] This is exemplified further by the fact that in the 7β disposition the electronic effect of the *amino* substituent leads to a slight *downfield* shift (0.15 ppm, acetone-d_6)[7b] as monitored by ^{13}C NMR while the corresponding shift by ^{19}F NMR is significantly *upfield* (1.03 ppm, DMF).[38]

Secondly, it can be seen from Table IV that all the formally conjugated positions (C4 in 1-X-naphthalenes; C6, C8, and C10 in 2-X-naphthalenes) are reasonably well correlated by eq 1 except for the 5α and 7α dispositions. Although the poor correlation for the 5α disposition was expected on the basis of the ^{19}F NMR DSP results,[11] the result for the 7α orientation was surprising given that the corresponding ^{19}F SCS are well fitted by the DSP equation.[11] We are unable to offer an explanation for this apparent anomaly. However, we should point out that serious discrepancies between ^{13}C and ^{19}F SCS have recently been noted within a series of benzocycloalkenes.[3,30c] Here bond-order effects within the carbocyclic ring appear to be implicated. Interestingly, Ernst[8] has demonstrated an approximate linear correspondence between ^{13}C SCS at the 7 position of 1-X-naphthalenes and electron densities calculated by INDO MO theory. Nevertheless, the correlation for this disposition was poor, and substantially worse than those for other formally conjugated positions.

Conclusions

Three main conclusions follow from this study. Firstly, it is abundantly clear that shielding data involve similar factors of a different order of complexity, and factors different from, those encountered in the study of substituent effects on conventional chemical properties. Hence attempts to interpret these single state properties in terms of chemical reactivity parameters may fail depending on the substrate and disposition in question. However, it is apparent that shielding parameters from the 6β and 7β orientations of 2-substituted naphthalenes are well correlated by eq 1 and, thus, where structural and stereochemical factors may be a problem with the less rigid benzene system,[11] these two naphthalene dispositions may be usefully employed for estimating σ_I and $\sigma_R{}^\circ$ for certain substituents.[11] We are currently investigating this proposition with respect to a reevaluation of the electronic characteristics of various groups.[39]

Secondly, ^{19}F NMR polar and mesomeric effects are somewhat more complicated than the corresponding effects determining ^{13}C SCS due to significant contributions by direct field and mesomeric-field effects. Previously, Adcock and Dewar[25] had noted from SCF MO calculations for benzaldehyde and the naphthaldehydes that the negative charge in the formally meta positions varied considerably. The negative charge in the 4 position of β-naphthaldehyde was considerably greater than that at the 3 position in α-naphthaldehyde and the meta position in benzaldehyde. This was the basis for the suggestion that direct mesomeric effects were responsible for the unusual ^{19}F SCS in the 4β position of naphthalene. However, the ρ_I values (Chart I) and the chemical shifts for $^+NH_3$ (relative to CH_3) (Chart I) indicate unambiguously that the origin of this phenomenon is field induced π polarization and not mesomerism.

Hence, it now appears that the anomalously small ^{19}F SCS previously observed for +F+M substituents (NO_2, CN, COOH, CF_3) in the 4β disposition is a situation where direct field and field-induced π polarization effects are opposed, leading to a small net polar field response. These results for the 4β disposition are not in accord with expectations based on the polarity parameter (σ_I), and the possibility therefore arises that DSP analyses for such dispositions may break down due to a failure to distinguish between primary inductive and mesomeric phenomena, which distinction is the basis of the DSP approach. The surprisingly poor correlation for the 7α ^{13}C data may be due, at least in part, to considerations of this type. In this connection, Ernst[8] has noted for the nonproximate conjugative positions in benzene and naphthalene that, although ^{13}C SCS correlate reasonably well with formal charge densities computed by INDO MO theory, the slopes ($\Delta\delta/\Delta\rho$) for the various dispositions differ widely (187–324 ppm/e). (Slopes are in the sequence 6β > 4α ~ para > 7α ~ 8β > C_{10}.) This sequence was noted previously[40,31] for the FMMF treatment of ^{19}F SCS of aryl fluorides giving rise to variable ρ values, attributed by us (vide supra) to nonincorporation of field-induced π polarization in the FMMF treatment. There seems every reason to believe that the INDO MO method also suffers from this defect, and while good correlations may result for dispositions where resonance effects (ρ_R) dominate, poor correlations (7α!) may result where there is not a fortuitous reflection of field-induced π polarization in the calculated formal charge.

Thirdly, the established importance of field-induced π polarization and direct mesomeric effects as the dominant mechanisms determining ^{13}C SCS in aromatic systems suggests that a simple two-parameter treatment of the kind recently proposed by Sardella[41] will be of limited generality.

The apparent success of the Sardella formulation[41] for strongly polar substituents rests on a somewhat fortuitous correspondence between atom–atom polarizabilities and field-induced π polarization effects in some dispositions. However, it should be noted that there are many dispositions in 1- and 2-substituted naphthalenes where such a correspondence does not hold.

Finally, in view of recent semantic confusion surrounding π-inductive effects, we feel compelled to clarify our past and present usage of the term "π-inductive effect". This term may be traced to Jaffé[42] and Dewar[43] and was envisaged as an inductomesomeric (or inductoelectromeric) phenomenon, and in semiempirical treatments[40,31,37] was incorporated into the mesomeric constant for a substituent as the transmission factors to various ring sites would be identical.[37] We have employed the term in this fashion and hence interposition of a methylene group between an electronegative atom or group and the aryl ring essentially ensures a feeble π-inductive effect. The classic field effect[44] of a substituent is conceptually clear and not in dispute, but we have consistently regarded field-induced π polarization as distinct from the π-inductive effect as the transmission factors for the former can be quite different from these for the latter and not readily determined by any a priori treatment. Recently, some authors[20,22,30b,45] have grouped inductomesomeric and field-induced π polarization under the general term "π-inductive effect" on the basis that both mechanisms involve no charge transfer between the aryl ring and the substituent. We believe that this approach complicates unnecessarily any attempt at a semiempirical treatment of substituent effects.

Experimental Section

Spectra. Spectra were recorded in the pulse Fourier transform mode at 22.625 or 67.89 MHz on Bruker spectrometers. Some spectra were also recorded at 15.086 MHz in the CW mode. The solutions were ca. 10–15 mol % in the compounds for assignment purposes and somewhat less (5%) for the careful evaluation of substituent effects. This level of concentration has been considered by others[24,46,47] to be of satisfactory dilution for meaningful appraisal of intramolecular effects. For acquisition of ^1H coupled spectra, solutions were somewhat more concentrated, but checks indicated that for $CDCl_3$ solvent, differential concentration effects on chemical shifts were not a complication. For comparisons at different field strengths, the standard compounds (e.g., naphthalene, and the fluoronaphthalenes) were examined under the appropriate conditions, as some systematic differences in chemical shifts did occur for the different situations.

Compounds. The (nondeuterated) monosubstituted naphthalenes were generally commercially available. The substituted fluoronaphthalenes represent part of the collection of one of us (W.A.), while the specifically deuterated naphthalenes were synthesized by standard organic transformations. The coincidence of their spectra (and other physical properties), other than for the effects of ^2H substitution, with those of authentic ^1H specimens confirms their constitution. "Scrambling" of deuterium in the synthesis was not anticipated, and did not occur as judged by the ^{13}C spectra.

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