Substituent Effects in 9-Substituted Anthracenes. A Carbon-13 Nuclear Magnetic Resonance Study

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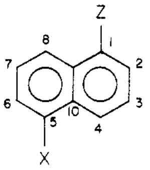
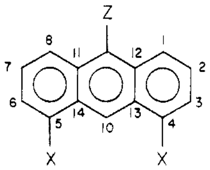
The ^{13}C chemical shifts of 9-substituted anthracenes and of several 9-substituted 4,5-dichloroanthracenes have been measured in deuteriochloroform. From correlations of the shifts of several of the proton-bearing carbons with the Taft dual substituent parameters, the relative distribution of polar and mesomeric effects of the 9-substituents to various ring positions has been deduced. The changes in substituent electronic effects, which result from twisting of axially unsymmetrical substituents and from hydrogen bonding of basic groups with trifluoroacetic acid, are discussed. The transmission of substituent effects appears to follow similar mechanisms in 9-substituted anthracenes and 1-substituted naphthalenes, and there are good linear relationships between many of the ^{13}C shifts of these two systems. Strict additivity of substituent-induced ^{13}C chemical shifts does not hold in 9-substituted 4,5-dichloroanthracenes because the extent to which a substituent exerts its electronic effects at a given position depends on the available charge at that site, and this is a function of the electronic influences of other substituents in the molecule.

The use of ^{13}C chemical shifts in monitoring electronic effects of substituents in aromatic systems has been amply demonstrated in studies of substituted benzenes and naphthalenes.[1] Although it seems likely that substituent effects in 1-substituted naphthalenes 1 and 9-substituted anthracenes 2 are similar, the ^{13}C chemical shifts of very few anthracenes have been reported,[2] and, for most of these, only partial assignment of the resonances was made.



1a, X = H
b, X = Cl



2a, X = H
b, X = Cl

Two recent studies which concern the nature of the polar effect of a substituent on the para position in 9-substituted anthracene have involved the ^{19}F chemical shifts of 9-substituted 10-fluoroanthracenes[3] and the ^{13}C chemical shifts of the para carbon atom in **2a**.[1a]

This paper presents a more complete analysis of substituent effects in 9-substituted anthracenes[4] by using ^{13}C NMR spectroscopy.

Results

The ^{13}C NMR signals of proton-bearing carbon atoms of anthracenes 2 were distinguished from those of substituted and ring-junction carbons by their greater intensities in the proton-decoupled spectrum and by the large one-bond C–H coupling constants associated with these resonances in the proton-coupled spectrum. Assignment of these signals to the proper carbons was made on the basis of the magnitude and multiplicity of the three-bond C–H coupling constants which are largest for β-carbons (C2,7,3,6), smaller for α-carbons (C1,8,4,5), and smallest for the γ-carbon (C10): ^3J(C2–H4, C3–H1, C6–H8, C7–H5) = 8–9 Hz, ^3J(C1–H3, C4–H2, C5–H7, C8–H6) = 5–7 Hz, ^3J(C10–H4,5) = 4–6 Hz. These results, together with the fact that all two-bond C–H coupling constants are negligibly small,[5] led to unambiguous assignments of the CH resonances of all chloroanthracenes **2b** and of the resonances of carbons 1, 8, 4, 5, and 10 of **2a**.

Distinction between the signals of the β-carbons, C2,7 and C3,6, of **2a** was made by assuming that the magnitudes of the substituent-induced shifts of these carbons are similar in the two anthracenes **2a** and **2b**. The resonances of quarternary carbons were assigned by comparing their shifts with those reported for the corresponding 1-substituted naphthalenes **1a**. For several anthracenes, however, assignments of these resonances were based on the changes in shift which occurred when the anthracene was titrated with trifluoroacetic acid in chloroform solution. Hydrogen bonding of trifluoroacetic acid with a lone electron pair of a substituent results in upfield shifts of the resonances of carbons 1, 8, 9, 13, and 14, the largest change being that of C9, downfield shifts of all other resonances, with the largest downfield shift for the resonance of C10, and a larger shift for the resonance of C2,7 than for that of C3,6. Figure 1 illustrates typical titration curves for the case of 9-acetylanthracene.

The chemical shifts and one- and three-bond C–H coupling constants of anthracenes 2, measured as 0.2 M solutions in deuteriochloroform, are summarized in Table I, together with the shifts of the hydrogen-bonded species, as 0.2 M solutions in chloroform containing 7–10 equiv of trifluoroacetic acid. Substituent-induced changes in ^{13}C chemical shifts (SCS)[6] of anthracenes 2 and of the corresponding 1-substituted naphthalenes **1a** (0.5 M solutions in deuteriochloroform) are given in Table II. Although the shifts of most of the naphthalenes have been previously published, they were redetermined in order to have a series of naphthalene substituent shifts corresponding to the

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(1) (a) W. Kitching, M. Bullpitt, D. Gartshore, W. Adcock, and T. C. Khor, *J. Org. Chem.*, **42**, 2411–2418 (1977); (b) L. Ernst, *J. Magn Reson.*, **20**, 544–553 (1975); (c) L. Ernst, *ibid.*, **22**, 279–287 (1976), and references therein; (d) J. Seita, J. Sandstroem, and T. Drakenberg, *Org. Magn. Reson.* 11, 239–244 (1978); (e) N. K. Wilson and J. B. stothers, *J. Magn. Reson.*, **15**, 31–39 (1974); (f) B. Mechin, J. C. Richer, and S. Odiot, *Org. Magn. Reson.*, 14, 79–85 (1980).

(2) (a) W. Adcock, M. Aurangzeb, W. Kitching, N. Smith, and D. Doddrell, *Aust. J. Chem.*, **27**, 1817–1821 (1974); (b) R. S. Ozubko, G. W. Buchanan, and I. C. P. Smith, *Can. J. Chem.*, **52**, 2493–2501 (1974); (c) R. Stoesser, M. Graf, H. Koeppel, and W. Storek, *J. Prakt. Chem.*, 317, 591–600 (1976).

(3) G. L. Anderson, R. C. Parish, and L. M. Stock, *J. Am. Chem. Soc.*, **93**, 6984–6988 (1971).

(4) In this paper the conventional numbering of ring carbons of 10-substituted 1,8-dichloro-anthracenes **2b** has been changed to correspond to that in the monosubstituted anthracenes **2a** for easier comparison of chemical shifts and electronic effects.

(5) F. J. Weigert, and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 2967–2969 (1967).

(6) SCS is the shift of the 9-substituted anthracene relative to the shift of the unsubstituted anthracene.

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Table I. ^{13}C Chemical Shifts[a] and One- and Three-Bond C–H Coupling Constants[b] of 9-Substituted Anthracenes, 2a, and 9-Substituted 4,5-Dichloroanthracenes, 2b, in Deuteriochloroform

compd	Z	shift, δ							
		^{13}C1,8 (^1J, ^3J)	^{13}C2,7 (^1J, ^3J)	^{13}C3,6 (^1J, ^3J)	^{13}C4,5 (^1J, ^3J)	^{13}C9 (^1J, ^3J)	^{13}C10 (^1J, ^3J)	^{13}C11,12	^{13}C13,14
2a	CH_3[c]	124.63 (160.6, 5.5)	124.77 (160.7, 8.9)	125.18 (161.9, 8.8)	129.02 (160.9, 5.8)	130.09	125.30 (159)	131.46	130.09
	Br	127.61 (165.3, 6.4)	127.15 (163.6, 8.6)	125.59 (162.0, 9.0)	128.57 (161.2, 5.8)	122.33	127.08	130.63	132.18
	H	128.13 (161.6, 5.1)	125.32 (160.5, 8.7)	125.32 (160.5, 8.7)	128.13 (161.6, 5.1)	126.20 (158.8, 4.4)	126.20	131.68	131.68
	CN[d]	125.14 (162.8, 5.8)	128.86 (162.9, 9.0)	126.26 (162.5, 8.4)	128.86 (161.5)	105.27	132.62 (160.3, 4.8)	133.15	130.48
	NO_2	121.30 (164.0, 6.1)	128.77 (163.1, 8.5)	126.08 (163.2, 7.8)	128.31 (162.2, 5.6)	144.18	130.28 (161.1, 5.3)	122.57	130.70
	OCH_3[e]	122.27 (163.7, 5.6)	125.14 (162.0, 8.5)	125.43 (161.1, 8.5)	128.43 (161.8, 5.4)	152.29	122.16 (160.5, 5.5)	124.49	132.51
	NH_2	121.05 (154.7, 5.6)	123.74 (161.3, 8.9)	125.16 (160.7, 8.3)	128.93 (161.2, 5.8)	137.90	116.27 (160.7, 5.0)	118.28	132.14
	NH_2[f]	122.14 (155.0, 4.9)	123.12 (160.6, 7.2)	125.31 (160.2, 8.3)	128.68 (160.0, 6.0)	139.92	114.52 (156.4)	117.95	132.59
	CHO[g]	123.49 (163.1, 7.0)	129.09 (160.4, 7.9)	125.62 (160.4, 8.7)	129.23 (160.4, 7.0)	124.58	135.27 (160.4, 4.8)	132.15	131.04
	Cl	124.70 (164.7, 6.5)	126.76 (163.3, 8.4)	125.59 (161.5, 8.9)	128.47 (160.6, 6.1)	128.13	125.97 (159.0, 6.3)	128.85	131.88
	CO_2CH_3[h]	124.99 (161.2, 6.1)	126.99 (161.4, 8.3)	125.43 (161.9, 9.2)	128.60 (161.1, 6.0)	127.68	129.44 (159.6, 4.9)	128.50	130.95
	CO_2H[i]	125.48 (162.6, 5.6)	127.18 (162.3, 8.7)	125.87 (162.3, 9.1)	128.92 (162.1, 5.4)	129.47	129.15 (160.7, 5.5)	128.25	131.47
	$COCH_3$[j]	124.32 (160.2, 5.6)	126.73 (161.7, 8.6)	125.45 (162.0, 7.9)	128.79 (162.5, 5.3)	136.74	128.17 (159.7, 5.4)	126.56	131.08
	(OCH_3)TFA[k]	121.43	126.06	125.68	128.62	149.85	123.68	124.31	132.38
	(CHO)TFA[l]	123.13 (163.1, 7.0)	130.82 (161.7, 8.3)	126.12 (160.4, 8.7)	129.80 (161.7, 6.1)	121.76	139.36 (160.4, 5.2)	133.94	130.89
	(CO_2CH_3)TFA[m]	124.25 (162.6, 6.3)	127.58 (161.2, 7.8)	125.66 (161.2, 8.6)	128.82 (162.3, 5.6)	125.76	130.51 (160.0, 4.8)	128.57	130.91
	$(COCH_3)$TFA[n]	123.55	127.62	125.76	129.08	134.13	129.77	126.78	131.02
	(CN)TFA[o]	124.69 (162.2, 7.0)	129.52 (161.7, 9.2)	126.51 (160.9, 8.3)	129.12 (161.3, 5.2)	103.13 (^3J 7.0)	133.96 (160.4, 4.8)	133.64	130.47
2b	CH_3[p]	123.81 (161.6, 6.6)	125.14 (163.8)	125.49 (166.0, 9.5)	128.94	130.96	119.42 (165.3)	131.68	133.09
	Br	126.99 (168.0, 5.9)	126.97 (164.0)	126.17 (166.2, 8.8)	129.51	123.41	121.43 (166.4)	131.37	132.69
	H	127.21 (162.4, 6.2)	125.57 (163.7)	125.94 (166.6, 9.9)	129.40	127.50 (162.2)	120.90	132.53	132.39
	CN[q]	124.36 (165.4, 6.1)	129.10 (165.7)	126.94 (167.6, 8.5)	129.49	107.23	126.94 (166.4)	134.07	133.44
	NO_2	120.50 (165.1, 6.8)	128.81 (165.7)	126.80 (167.2, 8.5)	128.70	145.55	124.55 (167.0)	123.59	133.11
	OCH_3[r]	121.53 (165.8, 6.9)	125.31 (164.8)	126.19 (164.9, 9.2)	130.08	153.23	116.66 (166.0)	125.99	132.98
	NH_2	120.15	123.66	125.57	129.96	139.28	110.50	119.40	132.79
	NH_2[f]	121.56 (158.9, 7.1)	123.07 (163.8)	126.31 (167.9, 8.9)	130.20	141.60	108.10 (166.7)	119.02	132.71
	Cl	124.03 (167.5, 6.4)	126.74 (165.1)	126.26 (166.2, 8.5)	129.46	129.46	120.47 (166.7)	129.81	132.88
	OCH_3·TFA[s]	120.97 (165.5, 6.9)	125.86 (164.7)	126.29 (165.7, 8.5)	129.95	151.67	117.55 (167.3)	126.36	133.07

[a] Of 0.2 M solutions in parts per million downfield from tetramethylsilane. [b] In hertz. [c] The methyl shift is 13.85 ppm. [d] The shift of CN is 117.19 ppm. [e] The shift of OCH_3 is 63.07 ppm. [f] The solvent is 1:1 deuterioacetone–deuteriochloroform. [g] The carbonyl shift is 170.06 ppm; the one-bond C–H coupling constant is 147.6 Hz. [i] The carboxyl shift is 169.89 ppm. [j] The carbonyl shift is 204.35 ppm; the methyl shift is 33.79 ppm. [k] The shift of OCH_3 is 63.32 ppm. [l] The carbonyl shift is 195.94 ppm; the one-bond C–H coupling constant is 174.4 Hz. [m] The carbonyl shift is 174.72 ppm; the methyl shift is 53.83 ppm. [n] The carbonyl shift is 216.70 ppm; the shift of CH_3 is 33.75 ppm. [o] The CN shift is 116.58 ppm. [p] The methyl shift is 14.65 ppm. [q] The CN shift is 116.33 ppm. [r] The shift of OCH_3 is 63.58 ppm. [s] The shift of OCH_3 is 63.77 ppm.

Table II. Substituent-Induced Chemical Shifts (SCS)[a] of 1-Substituted Naphthalenes, 1,[b] 9-Substituted Anthracenes, 2a and 9-Substituted 4,5-Dichloroanthracenes, 2b, in Deuteriochloroform

		shift							
compd	Z	C1,(8)[c]	C2,(7)[c]	C3,(6)[c]	C4,(5)[c]	C9(1)[c]	C10(4)[c]	C11,12(9)[c]	C13,14(10)[c]
1a	CH_3	−3.83	−0.15	−0.33	0.61	6.32	−1.53	−0.87	0.10
2a		−3.50	−0.55	−0.14	0.89	3.89	−0.90	−1.59	−0.22
2b		−3.40	−0.43	−0.45	−0.46	3.46	−1.48	−0.85	0.70
1a	Br	−0.78	1.50	0.86	0.39	−5.07	0.00	−1.48	1.11
2a		−0.52	1.83	0.27	0.44	−3.87	0.88	−1.05	0.50
2b		−0.22	1.40	0.23	0.11	−4.09	0.53	−1.16	0.30
1a	CN	−2.73	2.80	1.71	0.72	−17.61	5.34	−1.13	−0.54
1b		−2.78	2.74	1.72	−1.47	−17.39	5.32		
2a		−2.99	3.54	0.94	0.73	−20.93	6.42	1.47	−1.20
2b		−2.85	3.53	1.00	0.09	−20.27	6.04	1.54	1.05
1a	NO_2	−4.82	3.62	1.52	0.72	18.69	6.78	−8.41	0.83
2a		−6.83	3.45	0.76	0.18	17.98	4.08	−9.11	−0.98
2b		−6.71	3.24	0.86	−0.70	18.05	3.65	−8.94	0.72
1a	OCH_3	−5.91	−0.66	0.56	−0.45	27.58	−7.67	−7.86	1.00
2a		−5.86	−0.18	0.11	0.30	26.09	−4.04	−7.19	0.83
2b		−5.68	−0.26	0.25	0.68	25.73	−4.24	−6.54	0.59
1a	NH_2	−7.14	−1.03	−0.03	0.62	14.17	−8.99	−9.85	0.88
2a		−7.08	−1.58	−0.16	0.80	11.70	−9.93	−13.40	0.46
2b		−7.06	−1.91	−0.37	0.56	11.78	−10.40	−13.13	0.40
2a	NH_2[d]	−5.99	−2.20	−0.01	0.55	13.72	−11.68	−13.73	0.91
2b		−5.65	−2.50	0.37	0.80	14.10	−12.80	−13.51	0.32
1a	Cl	−3.46	1.22	0.86	0.31	4.08	−0.77	−2.66	1.07
2a		−3.43	1.44	0.27	0.34	1.93	−0.23	−2.83	0.20
2b		−3.18	1.17	0.32	0.06	1.96	−0.43	−2.72	0.49
1a	(OCH_3)TFA	−6.13	−0.36	0.71	−0.29	27.25	−6.83	−7.68	1.16
2a		−6.70	0.74	0.36	0.49	23.65	−2.52	−7.37	0.70
2b		−6.24	0.29	−0.35	0.55	24.17	−3.35	−6.17	0.68
1a	CHO	−3.01	3.25	1.15	0.58	3.57	7.28	−2.94	0.23
2a		−4.64	3.77	0.30	1.10	−1.62	9.07	0.47	−0.64
1a	CO_2CH_3	−2.08	1.87	0.34	0.59	−0.83	5.51	−2.20	0.31
2a		−3.14	1.67	0.11	0.47	1.48	3.24	−3.18	−0.73
1a	CO_2H[d]	−1.67	2.06	0.70	1.05	−0.41	5.80	−1.63	0.90
2a		−2.65	1.86	0.55	0.79	3.27	2.95	−3.43	−0.21
1a	$COCH_3$	−1.83	2.23	0.64	0.54	7.61	5.12	−3.34	0.51
2a		−3.81	1.41	0.13	0.66	10.54	1.97	−5.12	−0.60
1a	$(COCH_3)$TFA	−2.44	3.15	1.17	0.96	5.93	7.46		0.64
2a		−4.58	2.30	0.44	0.95	7.93	3.57	−4.90	−0.66
1a	(CHO)TFA	−3.30	4.25	1.72	1.10	2.17	10.13	−2.72	0.37
2a		−5.00	5.50	0.80	1.67	−4.44	13.16	2.26	−0.79
1a	(CO_2CH_3)TFA	−2.82	2.41	0.75	1.01	3.11	6.65	−7.30	0.57
2a		−3.88	2.26	0.34	0.69	−0.44	4.31	−3.11	−0.77
1a	(CN)TFA	−3.25	3.32	2.08	1.03	−19.67	6.66	−1.07	−0.46
2a		−3.44	4.20	1.19	0.99	−23.07	7.76	1.96	−1.21

[a] In parts per million; SCS is the ^{13}C shift of the Z-substituted compound minus the ^{13}C shift for the compound with Z = H. [b] Assignments of the shifts of naphthalene itself (0.2 M in deuteriochloroform): C1,4,5,8, 127.87 ppm; C2,3,6,7, 125.79 ppm; C9,10, 133.50 ppm. [c] Numbers in parentheses refer to the corresponding numbering in naphthalenes. [d] In 1:1 deuterioacetone–deuteriochloroform.

same solvent and concentration.

Discussion

The chemical shifts of carbons 2, 7, and 10 of monosubstituted anthracenes **2a** having small or axially symmetrical substituents correlate with those of carbons 4 and 7, respectively, of the corresponding 1-substituted naphthalenes **1a** (correlation coefficients of 0.998 and 0.999; see Table III). Therefore, to these carbons, which are formally conjugated with the substituent, are transmitted the electronic effects of the substituent group by similar mechanisms in the two systems. The shifts of anthracenes **2** range over 20 (C10) and 6 (C2,7) ppm and give excellent correlations (correlation coefficient of 0.995 or better) with the Taft dual substituent parameters (DSP)[7] according to eq 1, where ρ_I and σ_R are the polar and resonance (benzoic

$$\delta(^{13}C_i(Z = Z)) = \rho_I\sigma_I + \rho_R\sigma_R + \delta(^{13}C_i(Z = H)) \quad (1)$$

acid type) parameters,[8] respectively, for substituents Z, while the coefficients ρ_I and ρ_R reflect the sensitivity of the ^{13}C chemical shifts to these substituent effects. The constants ρ_I and ρ_R for anthracenes **2** are given in Table IV, together with relevant correlation data. The chemical shifts of anthracenes **2a** with large, nonlinear substituents such as NO_2, OCH_3, $COCH_3$ deviated from the correlation lines of eq 1 and were omitted from the regression analyses. Such deviations are clearly associated with the spatial interaction of the 9-substituent with the two peri hydrogens, H1 and H8, which causes twisting of the substituent

Table III. Correlation of ^{13}C Chemical Shifts of 9-Substituted Anthracenes 2a and 1-Substituted Naphthalenes 1a: $\delta(^{13}C_i(2a)) = \rho\delta(^{13}C_j(1a)) + b$

$C_i(2a)/C_j(1a)$[b]	ρ	b[a]	r[c]	rms[d]
C10/C4	1.127	−17.40	0.998	0.31
C2,7/C7	1.330	−42.17	0.999	0.10
C4,5/C5	1.014	−1.49	0.946	0.11
C1,8/C8	1.001	0.18	0.996	0.20

[a] In parts per million. [b] Number of points in the correlation was seven in every case. [c] Correlation coefficient. [d] Root-mean-square error in parts per million.

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(7) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709–724, 3146–3156 (1963).

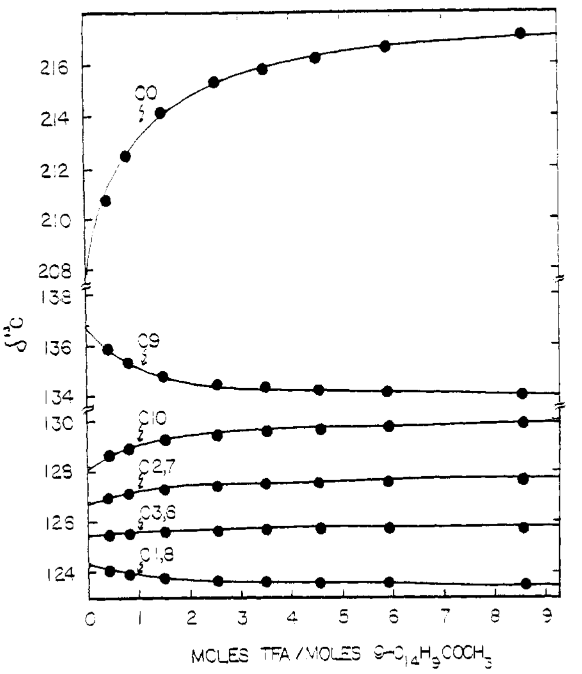

Figure 1. ^{13}C chemical shifts of 9-acetylanthracene as function of the molar ratio of trifluoroacetic acid to anthracene. Not all of the titration curves are shown.

Table IV. Correlation of ^{13}C Chemical Shifts of 9-Substituted Anthracenes, 2a, and 9-Substituted 4,5-Dichloroanthracenes, 2b, with the DSP Equation (Eq 1)

compd	C_i	ρ_I	ρ_R	r[a]	n[b]	rms[c]
2a	C10	6.673	13.853	0.997	6	0.40
2b	C10	6.461	14.517	0.999	10	0.30
2a	C2,7	5.267	2.856	0.995	6	0.17
2b	C2,7	4.764	3.309	0.995	10	0.19
2a	C3,6	1.162[d]		0.935	11	0.12
2b	C3,6	1.000[d]		0.909	10	0.18

[a] Correlation coefficient. [b] Number of points in the correlation. [c] Root-mean square error in parts per million. [d] ρ_m for correlation of the shifts with σ_m.

Table V. Effective Values[a] of σ_I and σ_R Twisted and Hydrogen-Bonded Substituents in 9-Substituted Anthracenes 2

substituent, Z	δ_I[b]	δ_R[b]	δ_m
OCH_3	0.19 (0.27)	−0.42 (−0.61)	
NO_2	0.69 (0.65)	−0.07 (0.15)	
CHO	0.51 (0.31)	0.37 (0.26)	
CO_2CH_3	0.28 (0.30)	0.06 (0.14)	
CO_2H	0.34 (0.34)	0.01 (0.14)	
$COCH_3$	0.28 (0.28)	−0.03 (0.16)	
NH_2	0.12[c] (0.08)[d]	−0.82[c] (−0.91)[d]	
$(OCH_3)TFA$[e]	0.35[f] (0.51)	−0.38[f] (−0.42)[g]	0.35 (0.12)[g]
(CN)TFA[e]	0.69 (0.74)	0.19 (0.13)[g]	1.07 (0.68)[g]
(CHO)TFA[e]	0.74 (0.53)	0.56 (0.37)[g]	0.73 (0.38)[g]
$(CO_2CH_3)TFA$[e]	0.38 (0.35)	0.10 (0.06)[g]	0.34
$(COCH_3)TFA$[e]	0.42 (0.46)	0.02 (−0.03)[g]	0.42 (0.31)[g]

[a] Calculated from the chemical shifts of C2,7 and C10 of 2a by using eq 1. [b] Values in parentheses are literature values.[8] [c] The value in deuteriochloroform. [d] The value in 1:1 (v/v) deuteriochloroform-deuterioacetone. [e] The substituent is hydrogen bonded with trifluoroacetic acid. [f] Incompletely hydrogen bonded. Decomposition after several hours. [g] The value in deuteriochloroform without trifluoroacetic acid.

group and less efficient aryl–Z orbital overlap. For these twisted substituents, and for substituents hydrogen-bonded with trifluoroacetic acid, "effective" values of the σ_I and σ_R parameters were calculated from the experimental shifts of C2,7 and C10 of the monosubstituted anthracene **2a** by using eq 1 (see Table V), and these were employed in the DSP correlations of the chloroanthracenes **2b**, since substituent steric effects are expected to be the same in the two anthracenes. The excellent fit (see Table IV) of the shifts of carbons 2, 7, and 10 of *all* 9-substituted chloroanthracenes **2b** to the correlation lines of eq 1, with standard as well as derived values of the substituent constants, demonstrated for the case of C10 in Figure 2, is proof that the DSP treatment is valid for the limited set of shifts of anthracenes **2a** as well as for the more extensive series of shifts of the chloroanthracenes **2b**.

Rotation of the 9-substituents does not alter their polar effects at distant carbons as indicated by the values of σ_I of Table V which do not differ markedly from those obtained from studies of substituted benzenes.[8] However, for substituents in the twisted conformation, smaller resonance effects are reflected in reduced absolute values of σ_R, as for methoxy, carboxyl, and methyl carboxylate, for which large torsional angles have been reported for the crystalline 9-substituted anthracenes.[9] For the 9-nitro and 9-acetyl groups with torsional angles of 65–111°[10,11a] and 80°[10] for the anthracene in solution, the values of σ_R are

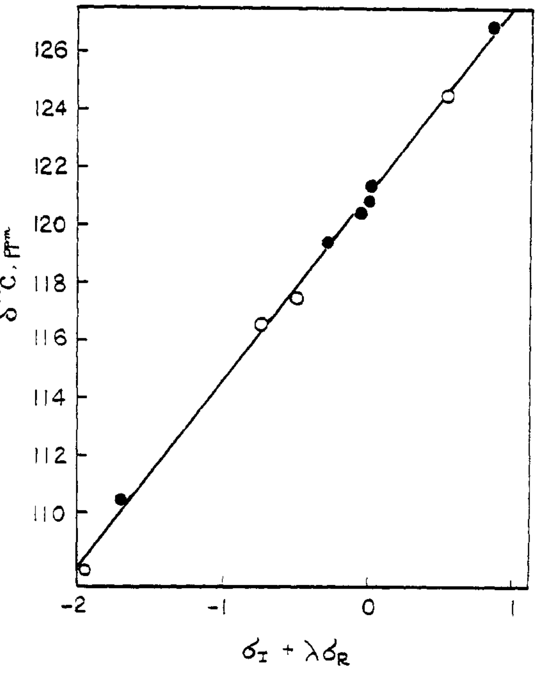

Figure 2. Correlation of the ^{13}C chemical shifts of carbon 10 of anthracenes **2b** with $\sigma_I + \lambda\sigma_R$, where $\lambda = \rho_R/\rho_I$, using effective (○) and normal (●) values of σ_I and σ_R (see Table V and ref 8).

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(8) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, 1–80 (1973).

(9) J. C. J. Bart and G. M. J. Schmidt, *Isr. J. Chem.*, **9**, 429–448 (1971).

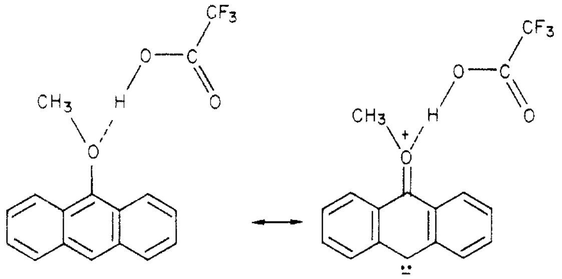
(10) R. J. W. LeFevre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc. B*, 775–778 (1968).

(11) J. Trotter, *Acta Crystallogr.*, **12**, 237–242, 922–928 (1959).

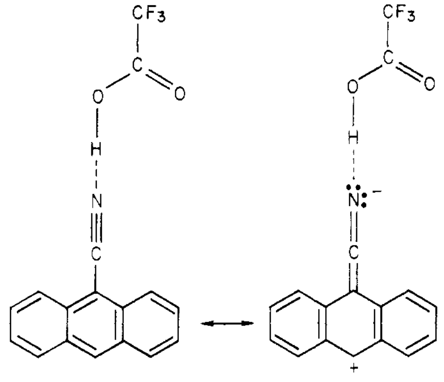
also expected to be small positive numbers or zero. The small *negative* values, −0.07 and −0.03, respectively, derived for these substituents from eq 1 (see Table V), could be the result of experimental errors or of a small amount of mesomeric electron donation by these normally electron-attracting groups,[12] arising from electron repulsion between lone electron pairs of the substituent oxygens above the aromatic plane and the negative charge density of the very proximate[13] p orbital of carbon 9.

In contrast, the values of both σ_I and σ_R, derived for the formyl group in 9-anthraldehyde, are exalted, indicating larger-than-normal electron-withdrawing mesomeric and polar effects of this substituent in the anthracene system. In crystalline 9-anthraldehyde, spatial interactions between the substituent and the peri hydrogens cause compression of the OCH valency angle to less than the normal 120°, which permits the formyl group to remain nearly coplanar with the aromatic rings (torsional angle of 27°).[11b] Such angular distortions increase the s character of the formyl carbon atom, and this could result in the greater electron-attracting potential of the substituent in anthracene.[14]

Hydrogen bonding of trifluoroacetic acid with the 9-substituents of anthracenes **2** produces downfield shifts of the resonances of carbons 2, 7, and 10, and this corresponds to the more positive values of both σ_I and σ_R listed in Table V. The larger values of σ_I, derived here for hydrogen-bonded substituents, are in excellent agreement with those obtained from ^{19}F chemical shifts of meta-substituted fluorobenzenes, likewise hydrogen-bonded with trifluoroacetic acid.[15] These changes in substituent inductive effects may be attributed to the greater polarity of the C–Z bond in the hydrogen-bonded complex. The less negative value of σ_R for hydrogen-bonded +M groups such as methoxy reflects the decrease in contributions to the resonance hybrid of dipolar structures such as **3b** which are destabilized by hydrogen bond formation. On the other hand, the mesomeric effects and values of σ_R of electron attracting groups such as cyano increase with hydrogen bonding because charged forms such as **4b** can be stabilized by trifluoroacetic acid more effectively than **4a** in a stronger association with the negatively charged substituent atom.



3a 3b



4a 4b

The largest downfield shifts are those associated with hydrogen bonding of the formyl substituent, as, for example, the hydrogen-bonding shift of carbon 10, which is 4 ppm in 9-anthraldehyde compared to 1–2 ppm in all other 9-substituted anthracenes. These results imply a much greater degree of proton transfer in the hydrogen-bonded complex of the formyl group than in that of the other substituents.

Deshielding of carbons 2, 7, and 10 is also observed for hydrogen bonding of basic 9-substituents by acids weaker than trifluoroacetic acid. Thus, changing the solvent from 1:1 acetone–chloroform to chloroform shifts the resonances of C10 and C2,7 of 9-aminoanthracene downfield by 1.75 and 0.62 ppm, respectively, which corresponds to a change in the value of σ_I of the amino substituent from 0.08 to 0.12 and of σ_R from −0.91 to −0.82.

From the relative magnitudes of the sensitivity parameters ρ_R of eq 1 (Table IV) it is apparent that resonance effects of the substituents Z in anthracenes **2** are transmitted more effectively to the meso carbon, C10, than to C2,7 (ρ_R(C10) ≈ 14, ρ_R(C2,7) ≈ 3), as predicted by molecular orbital calculations. The polar effects of the substituents are also somewhat stronger at C10 than at C2,7 because the value of ρ_I(C10), about 7, is larger than that of ρ_I(C2,7), about 5. This could be the result of a substituent electric field effect, transmitted more effectively through the cavity of the central benzene ring to carbon 10 than along the path of higher dielectric constant of the intervening aromatic system to carbons 2 and 7. The substituent polar effect could also involve the usual σ-inductive effect of successive polarizations of intervening bonds, as well as a π-inductive contribution which is greater at C10 because it is mesomerically transmitted, with ρ_R(C10) > ρ_R(C2,7). The weight of the π-inductive contribution in the overall substituent polar effect, estimated from the values of ρ_R and ρ_I, is at most 15% for **2a** and **2b**.

The chemical shifts of carbons 3 and 6 of anthracenes **2** vary less than 1.5 ppm but correlate reasonably well with σ_m (correlation coefficient 0.91–0.94, Table IV) and with the shifts of C6 of 1-substituted naphthalenes (for **2a** and **1a**). Substituent resonance effects are clearly not involved at these "meta-like" positions because the chemical shifts of *all* the anthracenes fit the correlation line, even the shifts of those with twisted substituents. As expected, hydrogen bonding of the substituents with trifluoroacetic acid causes small but consistent downfield shifts of the C3,6 resonances and more positive values of σ_m (see Table V).

The substituent-induced changes in chemical shift of the other "meta-oriented" carbons, C13,14 of monosubstituted

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(12) Mesomeric electron donation by the nitro substituent has been proposed to account for the similarity in ^{15}N chemical shifts of the terminal nitrogens of phenyl- and 4-nitrophenyldiazonium ions. R. O. Duthaler, H. G. Foerster, and J. D. Roberts, *J. Am. Chem. Soc.*, **100**, 4974–4979 (1978).

(13) The distance between the oxygen and carbon 9 in 9-nitroanthracene, calculated for a torsional angle of 90°, is 2.13 Å, and this corresponds to a minimum distance of separation of the p orbitals of oxygen and C9 of about 0.4 Å.

(14) CNDO molecular orbital calculations predict a decrease in σ electron density at the para carbon atom of benzaldehyde in going from a normal geometry to one corresponding to the geometry of 9-anthraldehyde. These calculations also predict an increase in π electron density at that carbon resulting from this structural change. However, the failure of the CNDO method to correctly assess π charge density at para carbons in substituted benzenes has been noted by R. T. C. Brownlee and R. W. Taft, *J. Am. Chem. Soc.*, **92**, 7007–7019 (1970).

(15) P. R. Wells, S. Ehrenson, and R. W. Taft, *Prog. Phys. Org. Chem.*, 6, 147 (1966).

Table VI. Effect of Chloro Substitution on the ^{13}C Chemical Shifts[a] of 9-Substituted Anthracenes: $\Delta\delta(^{13}C_i(2b, Z = Z)) - \delta(^{13}C_i(2a, Z = Z))$

	Δδ							
substituent	$^{13}C1,8$	$^{13}C2,7$	$^{13}C3,6$	$^{13}C4,5$	$^{13}C9$	$^{13}C10$	$^{13}C11,12$	$^{13}C13,14$
H	−0.92	0.25	0.62	1.27	1.30	−5.30	0.85	0.71
CH_3[b]	−0.82	0.37	0.31	−0.08	0.87	−5.88	1.59	1.63
Br	−0.62	−0.18	0.58	0.94	1.08	−5.65	0.74	0.51
Cl	−0.67	−0.02	0.67	0.99	1.33	−5.50	0.94	1.00
OCH_3[c]	−0.74	0.17	0.76	1.65	0.94	−5.50	1.50	0.47
NH_2	−0.90	−0.08	0.41	1.03	1.38	−5.77	1.12	0.65
NH_2[d]	−0.58	−0.05	1.00	1.52	1.68	−6.42	1.07	0.12
NO_2	−0.80	−0.04	0.72	0.39	1.37	−5.73	1.02	2.41
CN[e]	−0.78	0.24	0.68	0.63	1.96	−5.68	0.92	2.96
(OCH_3)TFA[f]	−0.46	−0.20	0.61	1.33	1.82	−6.13	2.05	0.69

[a] In parts per million. Positive values are downfield shifts. [b] The change in the shift of CH_3 is 0.80 ppm. [c] The change in the shift of OCH_3 is 0.51 ppm. [d] In 1:1 deuterioacetone–deuteriochloroform. [e] The change in the shift of CN is −0.86 ppm. [f] Hydrogen bonded with trifluoroacetic acid. The change in the shift of (OCH_3)TFA is 0.45 ppm.

anthracenes **2a** are in the direction of the substituent-induced changes in σ electron density at these carbons associated with the alternating inductive effect of CNDO molecular orbital theory.[16] Thus substituents such as CHO, $COCH_3$, NO_2, CN, and CO_2R produce upfield shifts and OCH_3, NH_2, and the halogens downfield shifts of these resonances (see Table II).

Substitution at carbon 9 causes the resonances of C1,8 of anthracenes **2** to shift upfield because of the substituent steric (γ) effect[17] (Table II). The shielding effect of the large 9-bromo substituent, −0.52 ppm for **2a**, is, however, much smaller than expected from the large upfield shifts, between −3 and −7 ppm, produced by all other substituents. Clearly, more than just simple steric and inductive effects are involved. The substituent-induced shifts (SCS) of carbons 1,8 of the monosubstituted anthracenes with small or axially symmetrical substituents and those of C8 of the corresponding 1-substituted naphthalenes **1a** are the same within 0.3 ppm (see Table II). Therefore, the origin and magnitudes of the various factors contributing to the substituent proximity effect at adjacent peri carbons are identical in the two systems. The trend of the C1,8 resonances of the anthracenes to be shifted downfield with increasing halogen size, −3.18 (Cl) and −0.22 ppm (Br) in **2b**, parallels that of the C8 resonance in 1-halonaphthalenes,[1b] −7.73 (F), −3.88 (Cl), −1.20 (Br), and +3.84 ppm (I), and that of the ^{15}N shifts of 8-halo-1-naphthylamines,[18] 314.2, 313.3, and 311.8 ppm upfield from $H^{15}NO_3$ for Cl, Br, and I, respectively. These trends cannot be attributed to changes in the magnetic anisotropy of the carbon–halogen bonds because the proton shifts, H1,8 in anthracenes **2b** and NH_2 in the halonaphthylamines, are affected in the opposite sense, both moving progressively upfield for Cl, Br, and I as substituents.

All 9-substituents in monosubstituted anthracenes **2a** produce downfield shifts of the C4,5 resonances, and this implies net electron withdrawal from these carbons which are formally conjugated with the substituents.[19] The smallness of the shift changes (less than 2 ppm) and the fact that they can be similar for substituents with as widely different mesomeric and inductive properties as methyl (0.92 ppm), amino (0.82 ppm), and cyano (0.74 ppm) suggest that opposing influences are involved. The substituent-induced shifts of carbons 4 and 5 of monosubstituted anthracenes **2a** having small or linear substituents and of carbon 5 of 1-substituted naphthalenes **1a** are identical within 0.3 ppm (see Table II). In the case of large, unsymmetrical groups which can have different torsional angles in **1a** and **2a**, differences in these shift changes for anthracenes and naphthalenes correlate roughly with differences in the effective values of σ_R calculated for the substituents in the two aromatic systems, as shown in Figure 3. The slope of the correlation line, 1.7, is the value of ρ_R for the transmission of substituent mesomeric effects to carbons 4 and 5 in 9-substituted anthracenes, and this is close to 2.9, the value for ρ_R(C2,7) for the transmission of mesomeric effects to carbons 2 and 7. Thus resonance effects in 9-substituted anthracenes **2a** are transmitted about equally well to all the conjugated positions of the adjacent aromatic rings.[20]

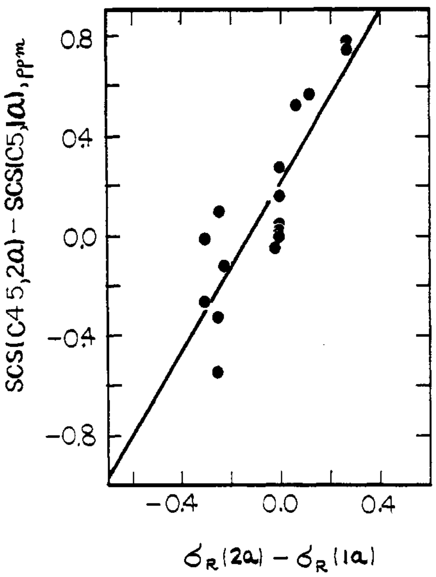

Figure 3. Correlation of the difference in substituent-induced shifts of C4,5 of anthracenes **2a** and of C5 of naphthalenes **1a** with the difference in the corresponding effective values of σ_R of the substituents in **2a** and **1a**.

The effect on the ^{13}C chemical shifts of anthracene **2a**

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[16] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970.

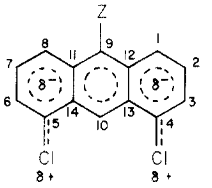
[17] V. Cheney and D. M. Grant, *J. Am. Chem. Soc.*, 89, 5319–5327 (1967).

[18] I. I. Schuster and J. D. Roberts, *J. Org. Chem.*, 45, 284–287 (1980).

[19] The deshielding effect of 9-substituents on the resonances of carbons 4 and 5 has a counterpart in the deshielding of the ^{19}F resonance by the 1-substituents in 5-fluoro-1-substituted naphthalenes. W. Adcock, J. Alste, S. Q. Rizvi, and M. Aurangzeb, *J. Am. Chem. Soc.*, 98, 1701–1711 (1976).

[20] Dipole moment measurements indicate a greater degree of mesomeric interaction between the nitro and amino substituents in 7-nitro-1-naphthylamine than in 5-nitro-1-naphthylamine. J. H. Richards and S. Walker, *Tetrahedron*, 20, 841–853 (1964). Mesomeric effects of the 5-substituents on the solvolysis rates of 5-substituted 1-chloromethylnaphthalenes appear to be absent. K. C. Schreiber and R. G. Byers, *J. Am. Chem. Soc.*, 84, 859–862 (1962).

of substituting chlorine for hydrogen at carbons 4 and 5, **2a** → **2b**, is summarized in Table VI. Chlorosubstitution of anthracene itself, **2a** → **2b** (Z = H), causes the resonances of the para carbons (C1,8) to move upfield by 0.92 ppm because of increased negative charge at these positions arising from aryl–chloro resonance, **5**, and those of the ortho and meta carbons (C3,6 and C2,7) to move downfield, 0.62 and 0.25 ppm, respectively, as a consequence of the strong electron-attracting inductive effect of the chlorine atom (σ_I = 0.46). The weak electron-donating mesomeric effects of chlorine in **2b** on conjugated positions of the adjacent ring are obscured by other, more dominating influences of the chloro substituent so that chlorosubstitution of anthracene at C4,5 produces a 1.30-ppm *downfield* shift of the C9 resonance. The mechanism of this deshielding by chlorine may be the same as that which produces downfield shifts of the C4,5 resonances by substitution at C9 in **2a**, since these effects are transmitted along the same molecular pathways, C9–C11(12)–C14-(13)–C5(4).



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Question of the Additivity of Substituent-Induced Shifts. The steric effects of two chlorine atoms are not additive because the upfield shift of the C10 resonance for **2a** → **2b** (Z = H), −5.30 ppm, is not twice that of the substituent-induced shift of carbon 8 for **1a** → **1b** (Z = H), −3.46 ppm. Indeed, none of the ^{13}C chemical shifts of the anthracenes **2b** exhibit strictly additive behavior as seen from the "chlorosubstitution shifts" of Table VI which vary for each carbon atom according to the nature of Z.

The chloro substituents of **2b** influence the extent to which both polar and mesomeric effects of Z are transmitted to carbons 2, 7, 10, 3, and 6 as seen from the values of ρ_I, ρ_R, and ρ_m for **2a** and **2b** in Table IV. Compared to those for **2a**, the resonance effects of the 9-substituents at these carbons are somewhat more important, and the polar effects less so, in the 9-substituted dichloroanthracenes **2b**. The quantities ($\Delta\rho_I\sigma_I + \Delta\rho_R\sigma_R$) and $\Delta\rho_m\sigma_m$ are the deviations from additivity of the substituent-induced shifts of carbons 2, 7, and 10 and of C3,6, respectively, in anthracenes **2b**, and these are clearly a function of the electronic effects of the individual substituents.

Opposing trends of Z- and chloro-induced shifts, observed for the resonances of carbons 13 and 14, follow the linear relationship of Figure 4. The extent to which electron density is withdrawn from carbons 13 and 14 by the *o*-chlorine atoms of **2b** is reflected in the magnitude of the downfield "chlorosubstitution shifts" of C13,14 [$\Delta\delta$(^{13}C13,14) for **2a** (Z = Z) → **2b** (Z = Z); see Table VI], and is dependent on the amount of charge available at these carbons as a result of the polar effects of the meta-oriented 9-substituents, Z. Thus, the downfield shifts of the C13,14 resonances, which are observed when chlorine is substituted for hydrogen at carbons 4 and 5, are quite small in anthracenes with electron-attracting 9-substituents which themselves remove electron density from carbons 13 and 14, and they become progressively larger in anthracenes with increasingly electron-donating groups (more negative values of the SCS of carbons 13 and 14 of **2a**; see Figure 4).

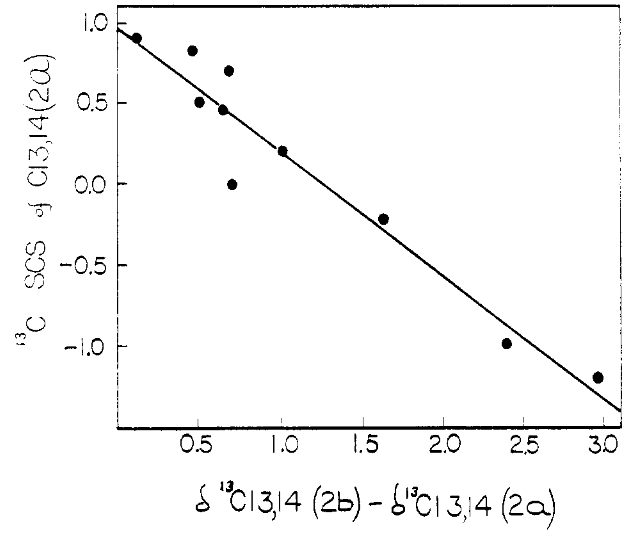

Figure 4. Correlation of the substituent-induced shifts of C13,14 of anthracenes **2a** with the chlorosubstitution shifts of C13,14, δ[^{13}C13,14 (**2b**, Z = Z)] − δ[^{13}C13,14 (**2a**, Z = Z)].

Table VII. Residual Shifts[a] and Chloro Substitution Shifts[b] of Carbons 4,5 of 9-Substituted Anthracenes

substituent, Z	chlorosubstitution shift	residual shift	σ_R
CH_3	−0.08	1.08	−0.11
NO_2	0.39	0.30	−0.07
CN	0.63	0.51	0.13
Br	0.94	0.76	−0.19
Cl	0.99	0.73	−0.23
NH_2	1.03	2.20	−0.82
H	1.27	0.00	0.00
(OCH_3)TFA	1.33	1.14	−0.38
NH_2[c]	1.52	2.10	−0.91
OCH_3	1.65	1.02	−0.42

[a] Residual shift = (SCS of C4,5 of 2a) − 1.7σ_R ppm. Positive values are downfield shifts. [b] See Table VI. [c] The values for the anthracene in 1:1 deuterioacetone–deuteriochloroform.

The largest deviations from additivity involve the shifts of the substituted carbons themselves, C9 and C4,5. The 1.27-ppm downfield shift of the resonances of carbons 4 and 5 for **2a** → **2b** (Z = H) is a composite of an upfied shift, due to the C–Cl bond magnetic anisotropy, and a larger downfield shift resulting from removal of charge density from carbons 4 and 5 by substitution of the more electronegative chlorine atoms for hydrogen. The magnitude of this downfield component varies according to the amount of charge available at carbons 4 and 5, and this is a function of the electronic effects of the 9-substituents, Z, which involve both σ- and π-electron densities.

σ-Electron substituent effects at carbons 4 and 5 are roughly proportional to the "residual shifts" of Table VII, which are the substituent-induced shifts of carbons 4 and 5 of **2a** from which the resonance contribution, 1.7σ_R, has been subtracted. As seen in Table VII, the larger chlorosubstitution shifts of C4,5, which are associated with greater withdrawal of electron density from these carbons by the chlorine atoms of **2b**, involve those 9-substituents which, through resonance, can furnish sufficient π electron charge to the chloro-substituted carbons (large negative values of σ_R) to counterbalance the removal of σ-electron density by their polar effects (positive values of residual shifts). Thus hydrogen bonding of a 9-substituent is associated with smaller chlorosubstitution shifts of the resonances of C4,5 and with less polarized C–Cl bonds in **2b**, because it results in more positive values of σ_I and σ_R and

Table VIII. Proton Chemical Shifts[a,b] of 9-Substituted 4,5-Dichloroanthracenes **2b**

substituent	shift, δ			
	H1,8	H2,7	H3,6	H10
CH_3	8.157	7.393	7.590	9.176
Br	8.384	7.467	7.616	9.246
H	7.900	7.378	7.597	9.208
CN	8.278	7.606	7.687	9.393
NO_2	7.798	7.560	7.704	9.472
OCH_3	8.671	7.411	7.618	9.075
NH_2	7.853	7.308	7.587	8.664
Cl	8.418	7.510	7.661	9.256

[a] In ppm downfield from tetramethylsilane. Solutions are 0.08 molar in deuteriochloroform. [b] The H-H coupling constants are *J*(H1-H2,H7-H8) = 8.8 Hz, *J*(H2-H3,H6-H7) = 7.2 Hz, *J*(H1-H3, H6-H8) ≈ *J*(H1,8-H10) = 1.0 Hz.

Table IX. Correlation of ^{13}C and ^1H Chemical Shifts of 9-Substituted 4,5-Dichloroanthracenes **2b**: $\delta(^{13}C_i) = \rho\delta(^1H_i) + b$

C_i/H_i	ρ	b^a	n^b	r^c	rms[d]
C10/H10	17.847	−44.28	7[e]	0.990	0.60
C2,7/H2,7	18.194	−9.21	8	0.974	0.39
C3,6/H3,6	10.586	45.37	8	0.932	0.18

[a] In parts per million. [b] Number of points in the correlation. [c] Correlation coefficient. [d] Root-mean-square error (ppm) in the ^{13}C shift. [e] The shifts for Z = CN were omitted in the regression analysis.

decreased σ- and π-electron densities at carbons 4 and 5.

For similar reasons, substituting cyano for hydrogen at C1 of naphthalene produces a 0.72-ppm downfield shift of the C5 resonance in **1a** but a 1.47-ppm upfield shift in 5-chloronaphthalene, **1b** (Z = H) → **1b** (Z = CN).

Concerted substituent effects of the type described are probably also involved in the nonadditive behavior of the substituent-induced shifts of carbon 9 in **2b**. However, these are not readily delineated because additional factors such as changes in bond order and in magnetic anisotropies of the C-Z bonds may be involved.

Proton Chemical Shifts of Anthracenes 2b. The proton chemical shifts of the 9-substituted dichloroanthracenes **2b** are listed in Table VIII. There is a fair linear correlation between the ^{13}C chemical shifts of the proton-bearing carbons, C3, 6,2,7,10 of **2b**, and the shifts of the corresponding protons (see Table IX for correlation data). The shift of H10 of dichlorocyanoanthracene **2b** (Z = CN) deviated from the correlation line of the other substituents by being too far upfield by about 0.2 ppm. Such shielding can be attributed to the large magnetic anisotropy effect of the CN bond which can be significant even at a para position.[21]

If both proton and ^{13}C chemical shifts are dominated by changes in π charge density at carbon, slopes of 16–20 are expected for the correlations of Table IX, because a unit change in π charge density for an sp^2 carbon atom induces ^{13}C and ^1H shifts of 160–200 and 10 ppm, respectively. The observed values, 11–18 ppm, are in approximate agreement with this prediction.

As expected, the shifts of the peri carbons and protons, C1,8 and H1,8, do not correlate because they are influenced in different ways by steric, magnetic, and electric effects of the substituents Z.

Experimental Section

Monosubstituted anthracenes **2a** and naphthalenes **1a** with the following substituents were commercial materials which were used without further purification: **1a** and **2a**, Z = H, Br, Cl, CH_3, $COCH_3$, CHO, CN, CO_2H; **1a**, Z = NH_2, NO_2. 9-Nitro-,[23] 9-amino-,[24] and 9-methoxyanthracenes[25] were prepared according to published procedures. 1-Methoxynaphthalene was obtained from 1-naphthol by using a standard method for the preparation of anisole from phenol.[26] The fraction boiling at 128–153 °C (10 torr) was used in the NMR analysis. 1,8-Dichloroanthracene (**2b**, Z = H) was prepared from 1,8-dichloro-9,10-anthraquinone by using Fieser's procedure[27] for the reduction of anthraquinone to anthracene. After recrystallization from chloroform–ethanol, the product melted at 158–159 °C (lit.[28] mp 158 °C). 5-Chloro-1-naphthonitrile (**1b**, Z = CN) was obtained by a published procedure.[29] It was purified by eluting the crude material through a column of alumina with chloroform and then recrystallizing it from ethanol. The melting point was 149–151 °C (lit.[29] mp 145 °C).

Methyl Esters of 1-Naphthoic and 9-Anthracenecarboxylic Acids (1a and 2a, Z = CO_2CH_3). A 0.02-mol sample of the acid was dissolved in a solution of sodium methoxide in methanol prepared by dissolving 0.7 g of sodium metal in 150 mL of methanol. The solution was heated to refluxing and about 4 mL (0.04 mol) of dimethyl sulfate was added dropwise over 1 h. After this addition the reaction mixture was refluxed for another 2 h, cooled, and poured into ice–water. The methyl ester of 9-anthracenecarboxylic acid, which precipitated, was filtered, washed with water, and then recrystallized from methanol. The melting point was 108.5–110.0 °C (lit.[30] mp 112.7–113.2 °C). The methyl ester of 1-naphthoic acid was extracted from the aqueous solution with several portions of ether. The extracts were washed once with 10% sodium carbonate solution and then with saturated sodium chloride solution until the washings were neutral and were then dried over magnesium sulfate. After removal of most of the ether at atmospheric pressure, the liquid was distilled under reduced pressure and the fraction boiling at 156–165 °C (20 torr) collected.

4,5-Dichloro-9-nitroanthracene (2b, Z = NO_2). A 5.48-g sample of 1,8-dichloroanthracene (0.022 mol) was suspended in 50 mL of glacial acetic acid containing 2 mL of acetic anhydride and 0.25 mL of concentrated sulfuric acid. To this mixture at room temperature was slowly added 1.6 mL of concentrated nitric acid (70%) with stirring over 1 h, without external heating. Stirring was continued for another hour, and then a solution of 10 mL of concentrated hydrochloric acid in 10 mL of glacial acetic acid was added. After the mixture was stirred at room temperature for an additional 2 h, the pale yellow solid which had formed was filtered (sintered glass) and washed twice with 5 mL of acetic acid and then with water until the washings were neutral. The solid was titurated with 25 mL of warm (60–70 °C) 10% sodium hydroxide solution and the thick slurry suction filtered. The tituration and filtration were repeated four more times with 10 mL of sodium hydroxide solution each time. Finally, the product was washed thoroughly with warm water until the washings were neutral, air-dried, and recrystallized from glacial acetic acid to give the bright yellow nitroanthracene melting at 199.5–202.5 °C (lit.[31] mp 203 °C).

4,5-Dichloro-9-aminoanthracene (2b, Z = NH_2). To 1.31 g (0.0045 mol) of 4,5-dichloro-9-nitroanthracene dissolved in 20 mL of boiling acetic acid was slowly added with vigorous stirring

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a warm solution of 10 g of stannous chloride in 10 mL of concentrated hydrochloric acid. The mixture was heated at the boiling point for 10 min and then cooled. The pale yellow solid was filtered (sintered glass) and washed with cold glacial acetic acid and then with dilute hydrochloric acid. It was next suspended in about 100 mL of cold 5% ammonium hydroxide solution and vigorously stirred for 20 min in order to liberate the free base. The mixture was filtered and the solid taken up in about 50 mL of ethanol. The white tin salts which did not dissolve were filtered off. Careful addition of water to the alcohol solution reprecipitated the orange dichloroaminoanthracene which was filtered, dried in a vacuum desiccator, and then stored under nitrogen. It melted at 195–199 °C with decomposition.

4,5-Dichloro-9-bromoanthracene (2b, Z = Br). A solution of 1.3 mL (0.025 mol) iodine monochloride in 5 mL of carbon tetrachloride was slowly added to a refluxing mixture of 2.5 g (0.01 mol) 1,8-dichloroanthracene in 25 mL of carbon tetrachloride. After the addition, refluxing was continued until no more hydrogen chloride was evolved (about 5 h). The reaction mixture was cooled, diluted with 50 mL of carbon tetrachloride, shaken with an aqueous solution of sodium thiosulfate to remove the molecular iodine which had formed, and dried over magnesium sulfate after separation of the aqueous layer. On evaporation of the solvent, a yellow solid was isolated which melted at 155–192 °C. This was recrystallized several times from very small amounts of chloroform to give a sample melting at 191–196 °C (lit. mp 193 °C[32], 191 °C[33]).

4,5-Dichloro-9-cyanoanthracene (2b, Z = CN). A mixture of 3 g (0.012 mol) of 4,5-dichloro-9-bromoanthracene, 0.08 g of cuprous cyanide, and 0.07 g of copper sulfate in 20 mL of freshly distilled quinoline was heated at 200 °C for 2 h. When the reaction mixture was cooled, a solid precipitated which was filtered, washed with ethanol, and then dissolved in a small amount of chloroform. The chloroform solution was eluted through a column of alumina with more chloroform. The solvent was evaporated, and the residue was recrystallized several times from ethyl acetate–ethanol to give the bright yellow fluffy dichlorocyanoanthracene melting at 245–247 °C.

4,5-Dichloro-9-methoxyanthracene (2b, Z = OCH_3). A warm solution of 52 g of stannous chloride in 52 mL of concentrated hydrochloric acid was added to a suspension of 26.6 g (0.096 mol) of 1,8-dichloro-9,10-anthraquinone in 200 mL of glacial acetic acid. The mixture was refluxed for 3 h and then cooled slightly. Water was added to induce precipitation of the product, and the mixture was allowed to stand overnight at room temperature for further crystallization. The product, which was a mixture of isomeric dichloroanthrones, was filtered and air-dried.

To 13.6 g of the dichloroanthrone mixture (0.051 mol) in 130 mL of methanol was added a solution of 4.12 g of sodium hydroxide dissolved in a minimum amount of water. The mixture was refluxed, and 10 mL of dimethyl sulfate was added in small portions over 2 h. After being refluxed for another hour, the reaction mixture was poured into ice-water, and the resulting precipitate was filtered and dried. It was eluted through a column of alumina with chloroform and then recrystallized from aqueous ethanol to give material melting at 132–136 °C.

4,5-Dichloro-9-methylanthracene (2b, Z = CH_3). A solution of 3.58 g (0.014 mol) of isomeric dichloroanthrones (see above) in 20 mL of dry tetrahydrofuran was added dropwise to the Grignard reagent prepared from 0.34 g (0.014 mol) of magnesium and 1 mL of methyl iodide in 10 mL of dry tetrahydrofuran. The reaction mixture was heated on a steam bath for 2 h to complete the reaction, cooled, and poured into a mixture of 50 mL of 2 M sulfuric acid and 20 g of ice. The aqueous mixture was extracted several times with ether, and the extracts were washed with dilute sodium bicarbonate and sodium chloride solutions before being dried over magnesium sulfate. Evaporation of the solvent gave a residue which was eluted through a column of alumina with chloroform. Recrystallization of the crude material from ethanol gave a bright yellow solid melting at 154–156 °C.

All melting points were taken with a Fisher-Johns melting point apparatus and are uncorrected. The structures of the chloro compounds were confirmed by their infrared, proton NMR, and high-resolution mass spectra and by comparison of their melting points with literature values. The chloroanthracenes **2b** (Z = NH_2, CN, CH_3, and OCH_3) are new compounds. Because the last two of these had been derived from a mixture of isomeric materials, their structures were further confirmed by combustion analyses. Anal. Calcd for $C_{15}H_{10}Cl_2O$ (**2b**, Z = OCH_3): C, 65.01; H, 3.64; Cl, 25.58. Found: C, 64.24; H, 3.48; Cl, 25.47. Calcd for $C_{15}H_{10}Cl_2$ (**2b**, Z = CH_3): C, 68.99; H, 3.86; Cl, 27.15. Found: C, 69.02; H, 4.00; Cl, 26.98.

NMR Spectra. The ^{13}C NMR spectra of the anthracenes and naphthalenes as 0.2 and 0.5 M solutions, respectively, in deuteriochloroform containing 5% cyclohexane as an internal reference were obtained by using a Varian CFT-20 NMR spectrometer operating at 20.00 MHz and a Bruker WH-200 NMR spectrometer at 50.32 MHz. The shifts were measured at ambient temperatures except when heating was necessary to prevent precipitation of the solute. The shifts were determined relative to the ^{13}C resonance of internal cyclohexane and were converted to the Me_4Si scale by using $\delta(^{13}C(Me_4Si)) = \delta(^{13}C(C_6H_{12})) + 26.92$ ppm.

Proton spectra of 0.08 M solutions of the chloroanthracenes **2b** in deuteriochloroform containing 5% cyclohexane were obtained at ambient temperatures by using the Bruker WH-200 instrument operating at 200.00 MHz. The shifts, measured relative to internal cyclohexane, were converted to the Me_4Si scale by using $\delta(^1H(Me_4Si)) = \delta(^1H(C_6H_{12})) + 1.43$ ppm.

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Registry No. **1a** (Z = CH_3), 90-12-0; **1a** (Z = Br), 90-11-9; **1a** (Z = CN), 86-53-3; **1a** (Z = NO_2), 86-57-7; **1a** (Z = OCH_3), 2216-69-5; **1a** (Z = NH_2), 134-32-7; **1a** (Z = Cl), 90-13-1; **1a** (Z = CHO), 66-77-3; **1a** (Z = CO_2CH_3), 2459-24-7; **1a** (Z = CO_2H), 86-55-5; **1a** (Z = $COCH_3$), 941-98-0; **1b** (Z = CN), 73399-85-6; **2a** (Z = CH_3), 779-02-2; **2a** (Z = Br), 1564-64-3; **2a** (Z = CN), 1210-12-4; **2a** (Z = NO_2), 602-60-8; **2a** (Z = OCH_3), 2395-96-2; **2a** (Z = NH_2), 779-03-3; **2a** (Z = Cl), 716-53-0; **2a** (Z = CHO), 642-31-9; **2a** (Z = CO_2CH_3), 1504-39-8; **2a** (Z = CO_2H), 723-62-6; **2a** (Z = $COCH_3$), 784-04-3; **2b** (Z = CH_3), 17122-95-1; **2b** (Z = Br), 14935-25-2; **2b** (Z = CN), 79619-26-4; **2b** (Z = NO_2), 79619-27-5; **2b** (Z = OCH_3), 57502-71-3; **2b** (Z = NH_2), 79619-28-6; **2b** (Z = Cl), 74018-43-2; 1,8-dichloroanthracene, 14381-66-9; 1,8-dichloro-9,10-anthraquinone, 82-43-9.

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