tion of 2.5 M n-BuLi (10 mL, 25 mmol) was added dropwise. After stirring in the ice bath for 1.5 h, chlorotrimethylsilane (2.5 mL, ca. 20 mmol) was added slowly. The mixture was then stirred for 1 h at 25 °C, diluted with ether, quenched with ice and water, washed with brine, and dried over $MgSO_4$. After evaporation 2.9 g (80% by GC) of crude 17 was obtained. The product was first separated by preparative TLC (silica gel, chloroform/ethyl acetate 9:1 as solvent) and then crystallized from pentane to give 1.9 g (73%): mp 79–81 °C; NMR ($CDCl_3$) δ 0.0 (s, 9 H), 1.30 (s, 9 H), 2.02 (s, 2 H), and 6.98–7.91 (m, 5 H); IR (Nujol) 3255, 1639, 1605, and 1587 cm⁻¹. Anal. Calcd for $C_{15}H_{25}NOSi$: C, 68.38; H, 9.56; N, 5.31. Found: C, 68.17; H, 9.65; N, 5.21.

2'-(β-Hydroxypropyl)-2,2-dimethylpropionanilide (18). A solution of 2,2,2'-trimethylpropionanilide (1.91 g, 10 mmol) in 30 mL of dry THF was lithiated as described for 17 (10 mL, 2.5 M n-BuLi). After stirring in the ice bath for 1.5 h, the solution was cooled to −70 °C and dry acetaldehyde (1.6 mL, ca. 30 mmol) was added slowly. The solution was then stirred for 10 min at −70 °C and 2 h at 0 °C, diluted with ether, quenched with water and ice, washed with brine, and dried over $MgSO_4$. After evaporation 3.8 g of crude 18 was obtained. This product was recrystallized from ethyl acetate/pentane to give 1.67 g (71%): mp 104–105 °C; NMR (Me_2SO) δ 1.08–1.27 (m, 12 H), 2.58–2.70 (m, 2 H), 3.68–4.18 (m, 1 H), 5.58 (d, ex, 1 H), 7.02–7.75 (m, 4 H), and 9.65 (s, ex, 1 H); IR (Nujol) 3360, 3250, and 1656 cm⁻¹. Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.44; H, 9.00; N, 5.94. Found: C, 71.48; H, 8.94; N, 5.92.

2-Carboxy-2,2-dimethylpropionanilide (19). A solution of 2,2,2'-trimethylpropionanilide (1.91 g, 10 mmol) in 30 mL of dry THF was lithiated as described for 17 (10 mL, 2.5 M n-BuLi). In a second flask 30 mL of dry THF was cooled to −70 °C under nitrogen together with 5 g of powdered dry ice. The solution with the lithiated species was now slowly pumped (small steel tube through serum caps, nitrogen pressure) into the flask containing the CO_2. The reaction mixture was then stirred for 10 min at −70 °C, slowly warmed up to 0 °C, diluted with ether, quenched with ice, and extracted several times with 1 N NaOH. The basic solution was acidified with 2 N HCl and extracted with ether and the organic phase was dried over $MgSO_4$. After evaporation 1.7 g (73%) of crude 19 was obtained. This product was recrystallized from ethyl acetate to give 1.5 g (64%): NMR (Me_2SO) δ 1.60 (s, 9 H), 3.62 (s, 2 H), 7.05–7.40 (m, 4 H), 8.98 (s, ex, 1 H), and 12.5 (s, ex, 1 H); IR (Nujol) 3300, 1696, and 1640 cm⁻¹. Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.35; H, 7.28; N, 5.95. Found: C, 66.31; H, 7.38; N, 5.80.

Preparation of Starting Materials. The general procedure involved reaction of the aniline and pivaloyl chloride (1:1) in a two-phase system of methylene chloride–aqueous sodium carbonate for 4–16 h at room temperature: 4a, mp 145 °C (96%); 4b, mp 118–120 °C (97%); 4c, mp 130–131 °C (80%); 4d, mp 124–125 °C (88%); 2,2,2'-trimethylpropionanilide, mp 109–111 °C (85%).

Registry No.—4a, 65854-91-3; 4b, 6625-74-7; 4c, 56619-93-3; 4d, 56619-94-4; 5, 68965-75-3; 6, 68965-76-4; 7, 68965-77-5; 8, 68965-78-6; 9, 68965-79-7; 10, 6141-21-5; 11, 68965-80-0; 12, 68965-81-1; 13, 68965-82-2; 14, 68965-83-3; 15, 68965-84-4; 17, 68975-44-0; 18, 68965-85-5; 19, 68965-86-6; o-fluorobenzonitrile, 394-47-8; dimethyl disulfide, 624-92-0; 2,2,2'-trimethylpropionanilide-, 61495-04-3; chlorotrimethylsilane, 75-77-4; acetaldehyde, 75-07-0; pivaloyl chloride, 3282-30-2; 4-chlorobenzenamine, 106-47-8; benzenamine, 62-53-3; 3-methoxybenzenamine, 536-90-3; 4-methoxybenzenamine, 104-94-9; 2-methylbenzenamine, 95-53-4; methyl iodide, 74-88-4; DMF, 68-12-2; benzaldehyde, 100-52-7.

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Transmission of Substituent Effects in Heterocyclic Systems by Carbon-13 Nuclear Magnetic Resonance. Benzothiazoles

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The carbon-13 NMR spectra of 57 benzothiazoles including 6-substituted 2-aminobenzothiazoles (1), 6-substituted 2-methylbenzothiazoles (2), 6-substituted benzothiazoles (3), 5-substituted 2-methylbenzothiazoles (4) and 2-substituted benzothiazoles (5) were determined in Me_2SO-d_6. The chemical shift assignments were made based upon the ones previously reported for benzothiazole, 2-aminobenzothiazole, and 2-methylbenzothiazole, chemical shift and signal intensity arguments, and by interpretation of their proton-coupled spectra. The chemical shift data for carbon 2 and carbon 9 for series 1–3 and carbon 2 and carbon 8 for series 4 gave good correlations with simple Hammett constants, and slightly better correlations with a linear combination of σ_m and σ_p, Swain–Lupton, and Taft–DSP treatments. Results from the dual parameter approaches indicate that resonance effects are primarily responsible for the substituent effect on chemical shifts at the carbons in question. The data also indicate that transmission of substituent effects by the sulfur atom is limited and that the primary path of transmission of substituent effects to carbon 2 is through nitrogen. The data from series 3 and 5 suggest that transmission of substituent effects by substituents on carbon 2 to carbon 6 is approximately one-third less effective than transmission by substituents on carbon 6 to carbon 2.

Carbon-13 NMR is recognized as a useful tool to obtain information regarding the electronic environment of carbon atoms of interest. In spite of the fact that quantitative correlations between carbon-13 chemical shifts and calculated electronic densities frequently cannot be obtained, carbon-13 shifts do, however, provide qualitative information about charge densities at carbon atoms of similar hybridization.[1] Carbon-13 NMR spectroscopy has been used extensively for

studying the electronic properties of a wide range of aromatic molecules. Numerous reports of correlations of the carbon-13 chemical shifts by a variety of linear free energy relationships have appeared which relate chemical shifts of aromatic carbons and carbon atoms of π-bonded groups conjugated with substituents on the aromatic ring.[2] Studies of this type have shown correlations between substituents and carbon atoms up to eight covalent bonds away.[3] Good correlations have been noted for carbon-13 shifts and simple Hammett correlations as well as by several two-substituent parameter approaches.[2-4]

Although several studies have been reported which examine the effect of transmission of electronic effects through benzo-fused five-membered heterocycles containing two heteroatoms to an attached side chain, little work has been reported which examines the effect of substituents on reactivity or other properties of specific ring carbon atoms.[5] As a continuation of our NMR studies in heterocyclic systems,[6] and in view of our interest in benzothiazole chemistry,[7] we have examined the effect of substituents on the carbon-13 NMR of series of 5- and 6-substituted benzothiazoles.

Several studies have appeared which examine substituent effects on benzothiazole systems, including a prior ^{1}H NMR study of 2-methylbenzothiazoles,[8] basicities of 2-aminobenzothiazoles,[9] the oxidation of 2-methylmercaptobenzothiazoles,[9a,10] and a nucleophilic displacement reaction of 2-chlorobenzothiazoles.[9a,11] It was concluded from a double parameter approach (vide infra) that the data for the latter three series provided no evidence for transmission of substituent effects through the sulfur atom.[9a] A similar conclusion was drawn in the ^{1}H NMR study. The number of compounds employed in the aforementioned series were limited, 5, 5, 8, and 9, respectively, and from a statistical point of view, for two parameter analysis the results, most particularly for the first two series, are questionable.[12] The relative contributions to transmission of substituent effects by polar and resonance effects through different heteroatoms were not assessed and seem open to question. The series previously studied included both 5- and 6-substituted compounds, and examination of series in which 5 and 6 substituents are treated as a group may not reveal differences in modes of transmission. We decided to examine a more extensive series of both 5- and 6-substituted compounds so that transmission of electronic effects with sets of substituents both meta and para to the sulfur could be evaluated independently. As a means of assessing the transmission of substituent effects in this heterocyclic system and to examine the question of relative transmission via sulfur

and nitrogen, we have studied the effect of substituents at carbon 5 and carbon 6 on the chemical shift of carbon 2. The series of benzothiazoles selected for study include 6-substituted 2-aminobenzothiazoles (1), 6-substituted 2-methylbenzothiazoles (2), 6-substituted benzothiazoles (3), 5-substituted 2-methylbenzothiazoles (4), and 2-substituted benzothiazoles (5). The latter series, 5, was included in the study
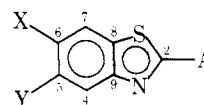
compd no.	A	X	Y
1	NH$_2$	varies	H
2	CH$_3$	varies	H
3	H	varies	H
4	CH$_3$	H	varies
5	varies	H	H

in order to examine transmission of electronic effects in the opposite direction of those operating in 1–4, namely, to observe the effect of substituents on carbon 2 on the chemical shifts of carbons 5 and 6.

Results and Discussion

The carbon-13 NMR chemical shifts for the five series of substituted benzothiazoles (1–5) studied were determined in Me$_2$SO-d_6 solution. The chemical shift data for 1–5 are given in Tables I–V. The values reported are referenced to Me$_4$Si.

The carbon-13 NMR spectra of 1i, 2f, and 5e have been recorded in DMF and their chemical shifts assigned.[13] The assignments reported in the tables were by analogy with the ones reported for 1i, 2f, and 5e,[13] by chemical shift and signal intensity arguments, and by interpretion of their proton-coupled spectra. The signal for carbon 2 is consistently the furthest downfield and was generally readily identified. In most cases the remaining signals could be assigned by comparing calculated shift values based upon substitutent shift increments from the literature.[14] In all series the low intensity signal for carbon 8 appears upfield from the low intensity signal for carbon 9, consistent with the differences in shielding of sulfur and nitrogen atoms. In series 1–3 the signal for carbon 9 varied regularly with the 6 substituent, as expected as a result of their para relationship, over a range of 10–15 ppm, whereas carbon 8 was essentially insensitive to substituent effects. Similarly, in series 4 carbon 8 varied regularly with

Table I. Carbon-13 Chemical Shift Assignments (ppm) for 6-Substituted 2-Aminobenzothiazoles (1) [a]

compd no.	X	2	4	5	6	7	8	9	X shift
1a	NH$_2$	162.1	117.9	112.9	143.0	105.3	131.8	143.6	
1b	OH	163.5	117.9	113.4	151.8	106.8	131.6	145.4	
1c	NHAc	165.3	117.4	117.2	132.8	111.5	130.8	148.4	167.5, 20.8
1d	OCH$_3$	164.4	117.9	112.7	154.0	105.4	131.7	146.5	55.5
1e	OC$_2$H$_5$	164.3	117.8	113.2	153.2	106.1	131.6	146.5	63.5, 14.8
1f	CH$_3$	165.4	117.1	126.2	129.6	120.5	129.6	150.3	21.0
1g	C$_2$H$_5$	165.3	117.2	125.0	136.2	119.3	130.7	150.5	27.9, 16.0
1h[b]	F	166.0	117.8	112.4	156.9	107.5	131.6	149.1	
1i	H	166.0	117.4	125.0	121.0	121.0	130.6	152.4	
1j	Br	166.7	118.8	127.9	111.8	122.8	132.8	151.6	
1k	Cl	166.7	118.3	125.2	124.3	120.2	132.3	151.4	
1l	COOH	169.1	116.8	127.0	122.8*	122.3*	130.7	156.1	166.8
1m	CO$_2$Et	169.2	116.8	126.6	122.0*	121.8*	130.8	156.4	165.1, 60.9, 14.2
1n	CN	169.7	117.6	129.3	101.9	124.9	131.5	156.1	119.3
1o	NO$_2$	171.3	117.3	121.7	140.4	116.6	131.3	158.1	

[a] Asterisks denote assignments which may be reversed. [b] $^1J_6$(CF) = 233.4, $^2J_5$(CF) = 23.4, $^2J_7$(CF) = 27.7, $^3J_4$(CF) = 8.8, $^3J_8$(CF) = 10.7; coupling constants are in hertz, and subscript corresponds to carbon number.

Table II. Carbon-13 Chemical Shift Assignments (ppm) for 6-Substituted 2-Methylbenzothiazoles (2)

compd no.	X	2	4	5	6	7	8	9	CH₃	X shift
2a	NH₂	159.5	121.7	114.1	146.2	103.9	136.4	144.3	19.4	
2b	OH	162.3	122.1	115.0	154.8	106.4	136.3	146.2	19.5	
2c	OCH₃	163.5	122.0	114.6	156.5	104.5	136.2	147.0	19.5	55.5
2d	NHAc	164.8	121.5	118.1	136.1	111.0	135.5	148.6	19.6	168.0, 24.0
2e	CH₃	165.0	121.1	126.9	133.9	121.5	135.0	150.8	.6	20.9
2f	H	166.3	121.5	125.6	124.3	121.5	134.9	152.6	19.7	
2gᵃ	F	166.5	122.7	113.9	159.0	108.0	136.1	149.4	19.7	
2h	Br	167.6	123.0	128.7	117.0	124.1	136.9	151.6	19.7	
2i	Cl	167.6	122.6	126.0	128.9	121.2	136.4	151.4	19.7	
2j	COOH	170.5	121.4	126.7	126.8	123.6	135.1	155.4	20.0	166.6
2k	COOEt	170.8	121.4	126.3	125.8	123.4	135.1	155.5	19.9	164.9, 60.7, 14.1
2l	NO₂	173.6	121.7	120.7	143.6	118.3	135.4	156.2	20.0	

ᵃ $^1J_6(CF) = 242.2$, $^2J_5(CF) = 24.4$, $^2J_7(CF) = 27.3$, $^3J_4(CF) = 19.8$, $^3J_8(CF) = 12.9$; coupling constants are in hertz, and subscript corresponds to carbon number.

Table III. Carbon-13 Chemical Shift Assignments (ppm) for 6-Substituted Benzothiazoles (3) ᵃ

compd no.	X	2	4	5	6	7	8	9	X shift
3a	NH₂	148.7	122.8	114.7	146.9	103.6	134.9	144.5	
3b	OH	151.6	123.1	115.6	155.3	106.5	134.6	146.3	
3c	OCH₃	152.8	123.1	115.3	157.1	104.5	134.7	147.2	55.6
3d	NHAc	154.0	122.6	118.5	136.8	111.3	133.9	148.7	168.1, 24.0
3e	CH₃	154.2	122.2	127.3	134.8	121.5	133.3	150.8	20.9
3fᵇ	F	155.7	123.9	114.4	158.5	108.3	134.6	151.4	
3g	H	155.5	122.1*	125.1*	125.8*	122.7*	133.2	152.6	
3h	Br	156.6	124.1	128.9	117.9	124.6	135.3	151.6	
3i	Cl	156.7	123.8	126.3	129.8	121.7	134.9	151.5	
3j	COOH	159.3	122.6	126.7	127.6	124.3	133.5	155.3	166.5
3k	CO₂Et	159.6	122.7	126.3	126.5	124.1	133.6	155.4	164.9, 60.8, 14.1
3l	NO₂	162.3	123.1	120.8	144.3	119.2	134.1	156.1	

ᵃ Asterisks denote assignments which may be reversed. ᵇ $^1J_6(CF) = 272.5$, $^2J_5(CF) = 19.8$, $^2J_7(CF) = 27.3$, $^3J_4(CF) = 19.8$, $^3J_8(CF) = 11.7$; coupling constants are in hertz, and subscript corresponds to carbon number.

Table IV. Carbon-13 Chemical Shift Assignments (ppm) for 5-Substituted 2-Methylbenzothiazoles (4)

compd no.	Y	2	4	5	6	7	8	9	CH₃	Y shift
4a	NH₂	165.8	105.4	147.3	113.7	121.2	121.8	154.3	19.7	
4b	OH	167.1	107.1	155.9	114.3	121.7	125.0	154.1	19.8	
4c	OCH₃	167.5	105.0	158.1	113.8	121.8	126.6	154.0	19.8	55.4
4d	NHAc	168.0	111.7	137.5	116.8	121.3	129.0	153.2	19.8	167.2, 24.0
4e	CH₃	166.3	121.6	135.1	125.8	121.0	131.9	153.0	19.7	20.9
4f	H	166.3	121.5	125.6	124.3	121.5	134.9	152.6	19.7	
4g	Cl	169.0	121.1	130.4	124.4	122.9	133.6	153.5	19.8	
4h	I	168.1	130.0	90.6	132.6	123.5	134.7	154.1	19.9	
4i	COOH	168.3	122.5	128.6	124.7	121.8	139.6	152.4	19.9	166.7
4j	CN	169.9	125.8	108.4	126.9	123.3	140.3	152.2	19.9	118.6
4k	NO₂	171.1	116.3	145.7	118.6	122.7	141.9	152.1	19.9	

Table V. Carbon-13 Chemical Shift Assignments (ppm) for 2-Substituted Benzothiazoles (5) ᵃ

compd no.	A	2	4	5	6	7	8	9	A shift
5a	NH₂	166.0	117.4	125.0	121.0	121.0	130.6	152.4	
5b	OCH₃	172.4	120.3*	125.9	123.4	121.7*	131.1	148.6	58.7
5c	CH₃	166.3	121.5*	125.6	124.3	121.5*	134.9	152.6	19.6
5d	SCH₃	167.4	120.7*	126.0	123.9	121.4*	134.2	152.5	15.5
5e	H	155.5	122.1**	125.8*	125.1*	122.7**	133.2	152.6	
5f	Cl	152.4	122.0**	126.7*	125.8*	122.1**	135.4	150.1	
5g	COOH	159.6	122.7	127.0*	127.3*	124.5	136.1	152.6	161.2
5h	COOC₂H₅	157.7	122.5	126.9*	127.4*	124.5	135.7	152.3	159.7, 62.5, 14.0
5i	COCH₃	165.9	122.7	126.9*	127.5*	124.7	136.2	152.6	192.3, 26.0
5j	NO₂	165.5	123.3	128.1*	129.0*	125.4	136.3	148.2	

ᵃ Asterisks denote assignments which may be reversed.

substituent, whereas carbon 9 was essentially insensitive to substituent variations. The assignment of the signal for carbon 6 in 1–3 and carbon 5 in 4 is based upon its intensity and by using shift parameters. The assignments for carbon 4 in 1–3 and carbon 7 in 4 were confirmed by examining their proton-coupled spectra. The signal for these carbons is always a sharp doublet as a result of the absence of coupling to the proton three bonds away (meta-type coupling). The two signals remaining to be assigned arise from carbons 5 and 7 in series 1–3 and carbons 4 and 6 in series 4. These signals are recognizable by difference, and their shifts are predicted by employing substituent shift parameters. These signals were differentiated by examination of the proton-coupled spectra. In the coupled spectra of series 1–3 the signal for carbon 7 is a sharp pair of doublets, whereas the signal for carbon 5 is a broader pair of doublets which is consistent with additional coupling expected to arise from the proton attached to carbon 4. In series 4 carbons 4 and 6 were similarly identified. Assignment of the proton-bearing carbons of the benzene ring in series 5 was much more difficult and arbitrary. As noted in Table V a number of the assignments may be reversed. The signals for carbons 5 and 6 could be assigned only based upon their correlation with Hammett parameters for the substituents in the 2 position.

Treatment of the carbon-13 data for carbons 2 and 9 for 1–3 using only the simple Hammett approach employing σ_p and $\sigma_p{}^+$ gave reasonable correlations (Table VI).[15] Throughout the sets carbon 2 was better correlated by σ_p, whereas better results were obtained for carbon 9 by using $\sigma_p{}^+$. Interestingly, carbon 2 in series 1, the 2-amino series, was approximately one-third less sensitive to substituent effects than in series 2 and 3 ($\rho_1 = 6.2$; $\rho_2 = 9.7$; $\rho_3 = 9.2$). This diminution of substituent effects might be attributed to a cross-conjugation interaction arising from a competition between electron donation of the 2-amino group and the effect of substituents on carbon 6. On the other hand, substituent effects on carbon 9 are essentially the same for the three series ($\rho_1 = 7.0$; $\rho_2 = 6.0$; $\rho_3 = 5.8$). Correlation of series 4 shows a similar result in that carbon 2 data correlate well with σ_m and carbon 8 data correlate with $\sigma_p{}^+$.

Adequate correlations were obtained using the simple

Hammett approach and the σ_p, σ_m relationship for series 2 and 4, suggesting that transmission of electronic effects through sulfur is limited. More detailed information on the transmission of electronic effects was sought by analyzing the data using two parameter approaches. Some years ago the pK's of six 5- or 6-substituted indole-3-carboxylic acids were treated with the one-term Hammett equation, and it was concluded that no transmission occurred through the nitrogen atom.[16] In contrast, the report[16] cited a study of substituted indole-2-carboxylic acid systems which showed good correlations with a linear combination of σ_m and σ_p values for substituents in the 6 position by the expression log $K/K_0 = \rho_{CH}\sigma_p + \rho_{NH}\sigma_m$, where ρ_{CH}/ρ_{NH} was close to unity. These later results are indicative of equally effective transmission of electronic effects by carbon and nitrogen.

The use of this linear combination (see Table VII) of σ_m and σ_p resulted in improvement of the correlation for the data of both carbon 2 and carbons 8 and 9 in series 1–4. Consistent with the single parameter results for 1–4, better correlations for carbon 2 data were obtained with σ constants, whereas carbon 8 and 9 data were better correlated with σ^+ constants. Contribution to the correlation by σ_p was evaluated by employing the Swain–Lupton technique for assessment of the contribution of coefficients to multiple regression expressions.[17] Series 1–3 reveal about an 85% dependency upon σ_p for correlation of carbon 2 data, whereas carbon 2 data for series 4 have only about a 15% dependency on σ_p. Thus, the data from series 1–4 consistently indicate that nitrogen is transmitting electronic effects 5–6 times more effectively than sulfur. Carbon 9 in series 1–3 and carbon 8 in series 4, para to the substituent, experience the greater shifts as a function of substituent, and all are correlated by the two parameter approach with a comparable dependency upon $\sigma_p{}^+$ of about 70%. This result provides an internal test which shows that the transmission of substituent effects predominately via nitrogen in 1–3 is not merely a result of the para relationship of the substituent and nitrogen.

Analysis of the data by the Swain–Lupton[17] approach leads to conclusions which are consistent with the linear combination of σ_m and σ_p approach. Good correlations are obtained by the Swain–Lupton approach; however, they are generally

Table VI. Correlations of C-13 Chemical Shifts of Substituted Benzothiazoles with Hammett Constants [a,b]

compd no.	σ	C atom obsd	ρ	i	r	SD	n
1	σ_p	2	6.194	166.0	0.987	0.412	14[c]
1	$\sigma_p{}^+$	2	3.989	166.9	0.969	0.639	14[c]
1	σ_p	9	10.353	150.3	0.951	1.39	14[c]
1	$\sigma_p{}^+$	9	6.959	152.0	0.970	1.04	14[c]
2	σ_p	2	9.681	166.0	0.995	0.393	11[c]
2	$\sigma_p{}^+$	2	6.212	167.5	0.982	0.759	11[c]
2	σ_p	9	8.901	150.4	0.940	1.34	11[c]
2	$\sigma_p{}^+$	9	5.960	151.7	0.968	0.979	11[c]
3	σ_p	2	9.228	155.1	0.994	0.390	11[c]
3	$\sigma_p{}^+$	2	5.934	156.5	0.984	0.690	11[c]
3	σ_p	9	8.674	150.6	0.948	1.205	11[c]
3	$\sigma_p{}^+$	9	5.835	151.9	0.981	0.719	11[c]
4	σ_m	2	5.923	166.5	0.974	0.305	11
4	$\sigma_m{}^+$	2	5.916	166.6	0.967	0.384	9[d]
4	σ_p	8	14.173	131.9	0.967	1.713	10
4	$\sigma_p{}^+$	8	9.673	134.2	0.992	0.845	10
5	σ_m	5	3.357	125.6	0.981	0.136	10
5	$\sigma_m{}^+$	5	3.392	125.7	0.973	0.179	10
5	σ_p	6	5.496	124.7	0.986	0.370	10
5	$\sigma_p{}^+$	6	3.529	125.7	0.986	0.369	10

[a] σ and σ^+ values were from ref 15. [b] ρ = slope, i = calculated intercept, r = correlation coefficient, SD = standard deviation, and n = number of points. [c] C-13 shifts for the NHAc-substituted compound were not used in the correlations due to the absence of a substituent constant. [d] C-13 shifts for the OH- and NHAc-substituted compounds were not used in the correlations due to the absence of substituent constants.

Table VII. Two Parameter Correlations with σ_m and σ_p of C-13 Chemical Shifts of Substituted Benzothiazoles [a,b]

compd no.	σ	C atom obsd	ρ_m	ρ_p	i	SE	c	n	% ρ_p
1	σ^+	2	1.377 ± 1.485	3.603 ± 0.674	166.5	0.706	0.969	12[c]	83 ± 15
1	σ	2	−1.850 ± 0.975	7.233 ± 0.605	166.3	0.388	0.991	14[d]	86 ± 7
1	σ^+	9	−4.393 ± 2.159	8.620 ± 0.970	151.8	1.126	0.976	12[c]	79 ± 8
1	σ	9	−11.61 ± 1.490	16.873 ± 0.926	152.4	0.593	0.993	14[d]	69 ± 3
2	σ^+	2	2.132 ± 1.886	5.586 ± 0.803	166.9	0.802	0.984	10[e]	84 ± 12
2	σ	2	−2.666 ± 1.025	11.20 ± 0.658	166.5	0.333	0.997	10[e]	86 ± 5
2	σ^+	9	−5.681 ± 1.721	7.990 ± 0.733	153.2	0.732	0.985	10[e]	74 ± 6
2	σ	9	−11.730 ± 0.892	15.32 ± 0.544	152.7	0.316	0.997	11	67 ± 2
3	σ^+	2	1.932 ± 1.697	5.381 ± 0.723	156.0	0.721	0.986	10[e]	85 ± 11
3	σ	2	−2.580 ± 1.043	10.71 ± 0.670	155.6	0.339	0.997	10[e]	86 ± 5
3	σ^+	9	−4.083 ± 1.279	7.240 ± 0.545	153.0	0.544	0.991	10[e]	78 ± 5
3	σ	9	−9.728 ± 1.630	13.998 ± 0.994	152.5	0.577	0.990	11[e]	69 ± 4
4	σ^+	2	7.023 ± 0.994	−0.550 ± 0.431	166.3	0.396	0.981	9[e]	14 ± 9
4	σ	2	7.158 ± 1.208	−0.789 ± 0.773	166.4	0.349	0.985	9[e]	14 ± 12
4	σ^+	8	−4.148 ± 1.940	11.181 ± 0.841	135.2	0.773	0.995	9	85 ± 6
4	σ	8	−14.665 ± 2.116	22.386 ± 1.286	134.7	0.693	0.996	9	71 ± 3
5	σ^+	5	2.743 ± 0.401	0.293 ± 0.154	125.8	0.165	0.987	10	21 ± 9
5	σ	5	2.376 ± 0.351	0.643 ± 0.214	125.8	0.102	0.995	10	30 ± 8
5	σ^+	6	1.846 ± 0.753	2.921 ± 0.289	125.3	0.309	0.994	10	80 ± 7
5	σ	6	−1.721 ± 1.293	6.472 ± 0.788	125.0	0.275	0.991	10	86 ± 9

[a] σ and σ^+ values were taken from ref 15. [b] Data treatment uses the same method employed by Swain and Lupton. ρ_m = regression coefficient for σ_m, ρ_p = regression coefficient for σ_p, i = calculated intercept, SE = standard error of estimate, c = multiple correlation coefficient, n = number of points, and % ρ_p = percent contribution to correlation from σ_p. [c] C-13 shifts for OH-, NHAc-, and OEt-substituted compounds were not used in the data treatment due to the absence of substituent constants. [d] C-13 shifts for NHAc-substituted compounds were not used in the data treatment due to the absence of substituent constants. [e] C-13 shifts for OH- and NHAc-substituted compounds were not used in the data treatment due to the absence of substituent constants.

Table VIII. Swain–Lupton Treatment of C-13 Chemical Shifts of Substituted Benzothiazoles [a]

compd no.	C atom obsd	f	r	i	SE	c	n	% R
1	2	3.075 ± 0.316	6.749 ± 0.384	166.3	0.388	0.990	15	65 ± 3
1	9	2.420 ± 0.557	13.878 ± 0.678	152.4	0.685	0.990	15	83 ± 3
2	2	4.706 ± 0.426	10.44 ± 0.495	166.4	0.455	0.994	12	67 ± 2
2	9	1.507 ± 0.509	12.28 ± 0.592	152.6	0.544	0.992	12	88 ± 4
3	2	4.486 ± 0.410	9.945 ± 0.477	155.5	0.438	0.994	12	67 ± 2
3	9	1.496 ± 0.480	11.952 ± 0.558	152.5	0.512	0.992	12	88 ± 3
4	2	3.718 ± 0.321	1.336 ± 0.378	166.4	0.332	0.983	11	24 ± 5
4	8	3.649 ± 0.987	18.71 ± 1.164	134.5	1.02	0.990	11	82 ± 4
5	5	1.794 ± 0.109	1.279 ± 0.132	125.8	0.102	0.995	10	37 ± 3
5	6	2.599 ± 0.4025	6.010 ± 0.485	125.0	0.376	0.990	10	66 ± 4

[a] F and R values were taken from ref 17. Data analysis was by the method of Swain–Lupton. f and r are regression coefficients for F and R, respectively, i = calculated intercept, SE = standard error of estimate, c = multiple correlation coefficient. n = number of points, and % R = percent contribution from the resonance parameter to the correlation.

no better than those obtained by simple combination of σ_m and σ_p (Table VIII). In series 1–3 data for carbon 2 show a high dependency upon resonance effects, approximately 65%, whereas in series 4 the dependency on resonance is approximately 25%. Analogously, the benzene ring carbons 9 and 8, para to the substituent, in 1–3 and 4, respectively, showed the same dependency (85%) on the resonance parameter.

An alternate method of analysis which has found utility in treatment of carbon-13 chemical shift data[2a,b] is the dual substituent parameter (DSP) approach developed by Taft.[18] The results of using the DSP approach are found in Table IX. There are four different types of σ_R values, and analysis of the correlations shows that in general $\sigma_{R(BA)}$ values give somewhat better correlations; however, the correlations are only slightly better than those obtained with $\sigma_R°$. Evaluation of the contribution by the σ_R term shows that data for carbon 2 in series 1–3 reveals a 62% dependency, whereas in series 4 the dependency on σ_R is about 23%. The carbons in the benzene ring para to the substituent, carbons 9 and 8 in 1–3 and 4, respectively, showed 75–80% dependency upon the σ_R term.

The DSP results are in good agreement with those obtained from the Swain–Lupton treatment. They both support the

argument that resonance is the predominate influence in accounting for the chemical shifts of both carbon 9 (and 8) and carbon 2 in the benzothiazoles studied.

As was mentioned previously, assignment of the chemical shifts for the proton-bearing carbons of interest, 5 and 6, in series 5 was made by correlation with substituent constants. These assignments are based upon the assumption that substituents on carbon 2 will affect carbons 5 and 6 in a comparable manner to the effect that substituents on carbon 5 or 6 have on carbon 2. Reasonable correlations were obtained using all four of the data treatment methods (Tables VI–IX). Because the assignments were made on the basis of Hammett correlations, discussion of transmission of substituent effects in series 5 leads to the possibility of becoming involved in circular logic. However, reversal of the assignments would result in marked deviations; consequently, we believe it is unlikely that the assignments for carbons 5 and 6 are in error. The range in chemical shift of carbon 6 for 5, as the 2 substituent was varied from strong electron donor to strong electron withdrawer, is 8 ppm, whereas the same range for carbon 2 in series 3 is about 14 ppm. This result indicates that transmission of electronic effects in the two directions is not

Table IX. Dual Substituent Parameter Treatment for C-13 Chemical Shifts for Substituted Benzothiazoles[a]

compd no.	C atom obsd	σ_I, σ_R°							$\sigma_I, \sigma_{R(BA)}$						
		ρ_I	ρ_R	i	SE	c	n	$\%\rho_R$	ρ_I	ρ_R	i	SE	c	n	$\%\rho_R$
1	2	5.29 ± 0.673	8.578 ± 0.666	166.2	0.464	0.988	10[b]	62 ± 3	5.195 ± 0.780	6.118 ± 0.553	166.3	0.536	0.985	10[b]	61 ± 4
1	9	5.072 ± 1.048	16.766 ± 1.037	152.2	0.723	0.990	10[c]	77 ± 4	4.831 ± 0.942	12.0756 ± 0.667	152.4	0.648	0.992	10[c]	77 ± 4
2	2	8.874 ± 1.087	13.49 ± 1.091	166.3	0.721	0.986	10[c]	61 ± 3	8.427 ± 0.741	9.616 ± 0.521	166.4	0.489	0.994	10[c]	62 ± 2
2	9	3.847 ± 1.200	15.058 ± 1.205	152.3	0.796	0.981	10[c]	80 ± 5	3.341 ± 0.666	10.767 ± 0.469	152.4	0.440	0.994	10[c]	82 ± 3
3	2	8.456 ± 1.179	12.854 ± 1.185	155.4	0.782	0.982	10[c]	61 ± 4	8.017 ± 0.724	9.219 ± 0.509	155.5	0.477	0.993	10[c]	62 ± 2
3	9	4.794 ± 1.635	13.756 ± 1.642	152.0	1.08	0.962	10[c]	74 ± 7	4.316 ± 1.22	9.902 ± 0.857	152.2	0.803	0.979	10[c]	77 ± 5
4	2	6.26 ± 0.651	2.034 ± 0.694	166.5	0.405	0.980	9[c]	23 ± 6	6.234 ± 0.615	1.436 ± 0.453	166.5	0.386	0.982	9[c]	23 ± 6
4	8	6.922 ± 2.344	23.706 ± 2.501	134.4	1.458	0.980	9[c]	76 ± 6	7.167 ± 1.025	16.657 ± 0.755	134.4	0.643	0.996	9[c]	75 ± 3
5	5	3.006 ± 0.237	1.991 ± 0.206	125.8	0.139	0.991	9[d]	46 ± 3	3.010 ± 0.183	1.424 ± 0.112	125.8	0.108	0.995	9[d]	46 ± 2
5	6	4.635 ± 0.921	7.835 ± 0.802	125.0	0.540	0.981	9[d]	69 ± 5	4.632 ± 0.521	5.647 ± 0.321	125.1	0.306	0.994	9[d]	69 ± 3

compd no.	C atom obsd	σ_I, σ_R^-							σ_I, σ_R^+						
		ρ_I	ρ_R	i	SE	c	n	$\%\rho_R$	ρ_I	ρ_R	i	SE	c	n	$\%\rho_R$
1	2	4.545 ± 0.962	5.896 ± 0.650	165.7	0.646	0.997	10[b]	66 ± 5	4.885 ± 1.216	3.495 ± 0.505	166.5	0.824	0.963	10[b]	60 ± 7
1	9	3.704 ± 2.078	11.322 ± 1.404	151.2	1.394	0.962	10[c]	82 ± 9	4.187 ± 1.932	6.941 ± 0.903	152.8	1.310	0.967	10[c]	78 ± 8
2	2	7.711 ± 2.094	8.910 ± 1.454	165.5	1.364	0.957	9[c]	62 ± 7	7.601 ± 1.357	5.378 ± 0.540	166.8	0.884	0.979	10[c]	64 ± 5
2	9	2.558 ± 2.407	9.795 ± 1.671	151.4	1.567	0.933	9[c]	84 ± 12	2.396 ± 1.306	6.054 ± 0.519	152.9	0.850	0.978	10[c]	86 ± 6
3	2	7.366 ± 2.166	8.440 ± 1.503	154.6	1.410	0.949	9[c]	62 ± 8	7.208 ± 1.203	5.184 ± 0.478	155.9	0.784	0.982	10[c]	64 ± 4
3	9	3.692 ± 2.832	8.642 ± 1.965	151.2	1.844	0.897	9[c]	76 ± 14	3.359 ± 1.009	5.721 ± 0.401	152.7	0.657	0.986	10	81 ± 5
4	2	5.790 ± 0.705	1.680 ± 0.541	166.4	0.397	0.984	8[c]	26 ± 7	6.311 ± 0.673	0.734 ± 0.273	166.5	0.424	0.978	9[c]	22 ± 7
4	8	3.038 ± 4.336	17.348 ± 3.324	133.6	2.443	0.950	8[c]	87 ± 16	7.554 ± 1.377	9.064 ± 0.558	134.6	0.869	0.993	8[e]	75 ± 4
5	5	2.676 ± 0.353	1.377 ± 0.209	125.7	0.197	0.982	9[d]	50 ± 5	3.020 ± 0.252	0.800 ± 0.090	125.9	0.148	0.992	8[f]	43 ± 4
5	6	3.370 ± 1.462	5.375 ± 0.864	124.5	0.814	0.958	9[d]	75 ± 9	4.662 ± 0.640	3.169 ± 0.228	125.3	0.377	0.992	8[f]	66 ± 3

[a] DSP approach and σ_I and σ_R values from Taft et al.[18] For data analysis, the method of Swain–Lupton was employed. ρ_I and ρ_R = regression coefficients for σ_I and σ_R, i = calculated intercept, SE = standard error of estimate, c = multiple correlation coefficient, n = data points used, and $\%\,\rho_R$ = contribution of σ_R to correlation. [b] C-13 data for OH-, NHAc-, OC_2H_5-, C_2H_5-, and COOH-substituted compounds were not used in the data treatment due to the absence of substituent constants. [c] C-13 shifts for OH- and COOH-substituted compounds were not used in the data treatment due to the absence of substituent constants. [d] C-13 shifts for COOH-substituted compounds were not used in the data treatment. [e] C-13 shifts for OH-, NHAc-, and COOH-substituted compounds were not used in the data treatment due to the absence of substituent constants. [f] C-13 shifts for SCH_3- and COOH-substituted compounds were not used in the data treatment due to the absence of substituent constants.

equal. The reason for diminution of transmission of substituent effects from carbon 2 to 6 compared to carbon 6 to 2 is not clear. However, the fact that carbon 2 is a carbonyl-like carbon (electron deficient carbon), in contrast to carbon 6, and is therefore capable of making greater demands upon the substituent may explain this difference. It is interesting that, in spite of the magnitude difference noted, the mode of transmission in the two series **3** and **5** seems to be comparable as indicated by equally good correlation coefficients and similar % σ_p, % R, and % $\sigma_{R(BA)}$ dependency.

Experimental Section

Carbon NMR spectra were obtained employing a JEOL FX-60Q Fourier transform NMR spectrometer operating at a frequency of 15.04 MHz. Data were accumulated on a Texas Instruments 980B computer using 8192 data points over a 4K Hz spectral width to yield a data point resolution of 0.99 Hz. For noise-decoupled spectra, samples were irradiated using a pulse width corresponding to 45° and a 5-s pulse repetition time was used. For the proton-coupled spectra, a gated pulse sequence was used to obtain NOE intensification of the signals. The NMR samples were prepared by weight as 0.5 molar solutions using commercial NMR grade dimethyl-d_6 sulfoxide. The signals were referenced to Me$_4$Si by giving the most intense solvent signal the value of 39.6 ppm.

The linear free energy statistical treatment of the data was carried out as previously described.[19]

The benzothiazoles employed, with one exception, were known compounds and either were commercial samples or were prepared by conventional procedures. The compounds were either distilled or recrystallized to give physical constants in accord with literature values. The synthesis of one compound not previously reported, 6-fluorobenzothiazole (**3f**), is outlined below.

2-Amino-5-fluorobenzenethiol[20] (4.25 g, 0.03 mol), 8 g of formic acid (90%), and a trace of zinc dust were refluxed for 3 h and then poured into water, and the solid was collected by filtration. The solid was washed with water and extracted with ether. The ether extract was dried (Na$_2$SO$_4$) and the ether evaporated. The residual solid was recrystallized from low boiling petroleum ether to yield 1.5 g, mp 55–56 °C, of **3f**. Anal. Calcd for C$_7$H$_4$FNS: C, 54.88; H, 2.63; N, 9.15. Found: C, 54.61; H, 2.73; N, 9.02.

2-Amino-6-cyanobenzothiazole (1n). This compound has been reported earlier,[21] prepared by another route, but we found a different value for its melting point. A solution of *p*-aminobenzonitrile (9 g, 0.08 mol) in 50 mL of 95% acetic acid was added to a solution of 30 g of KSCN in 100 mL of 95% acetic acid solution. The mixture was cooled to 0 °C, and a solution of 7.5 mL of Br$_2$ in 30 mL of acetic acid was added slowly with vigorous stirring so that the temperature remained between 0 and 10 °C. After addition was complete, the stirring was continued for 1 h at 5 ° and then the mixture was poured into 1 L of water. The solid was collected and recrystallized from ethanol to yield 3.5 g of 4-cyano-2-thiocyanatoaniline of mp 184 °C. Anal. Calcd for C$_8$H$_5$N$_3$S: C, 54.84; H, 2.88; N, 23.98. Found: C, 54.78; H, 2.91; N, 23.99.

The above product (1.2 g, 0.006 mol), 5 mL of concentrated HCl, and 10 mL of water were refluxed for 2 h. The solution was cooled, and the product was filtered, washed with water, and crystallized from 50% ethanol to yield 1 g, mp 217–218 °C (lit.[21] mp 196 °C). Anal. Calcd for C$_8$H$_5$N$_3$S: C, 54.84; H, 2.88. Found: C, 54.88; H, 2.88.

Registry No.—**1a**, 5407-51-2; **1b**, 26278-79-5; **1c**, 22307-44-4; **1d**, 1747-60-0; **1e**, 94-45-1; **1f**, 12536-91-6; **1g**, 21224-16-8; **1h**, 348-40-3; **1i**, 136-95-8; **1j**, 15864-32-1; **1k**, 95-24-9; **1l**, 93-85-6; **1m**, 50850-93-6; **1n**, 19759-66-1; **1o**, 6285-57-0; **2a**, 2941-62-0; **2b**, 68867-14-1; **2c**, 2941-72-2; **2d**, 68867-15-2; **2e**, 2941-71-1; **2f**, 120-75-2; **2g**, 399-75-7; **2h**, 5304-21-2; **2i**, 4146-24-1; **2j**, 24851-69-2; **2k**, 68867-16-3; **2l**, 2941-63-1; **3a**, 533-30-2; **3b**, 13599-84-3; **3c**, 2942-13-4; **3d**, 36894-61-8; **3e**, 2942-15-6; **3f**, 1644-85-5; **3g**, 95-16-9; **3h**, 53218-26-1; **3i**, 2786-51-8; **3j**, 68867-17-4; **3k**, 19989-64-1; **3l**, 2942-06-5; **4a**, 13382-43-9; **4b**, 68867-18-5; **4c**, 2941-69-7; **4d**, 68867-19-6; **4e**, 2941-71-1; **4g**, 1006-99-1; **4h**, 68867-20-9; **4i**, 6941-28-2; **4j**, 42474-60-2; **4k**, 2941-66-4; **5b**, 63321-86-8; **5d**, 615-22-5; **5f**, 615-20-3; **5g**, 3622-04-6; **5h**, 32137-76-1; **5i**, 1629-78-3; **5j**, 23505-64-8; 2-amino-5-fluorobenzenethiol, 33264-82-3; *p*-aminobenzonitrile, 873-74-5; 4-cyano-2-thiocyanatoaniline, 68867-21-0.

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