appendix b. effect on chemical shifts of two or three functional groups (Y-CH_2-Z, and Y-CH(W)-Z)

Shoolery's rules (B. P. Dailey and J. W. Shoolery, *J. Am. Chem. Soc.*, 77, 3977 (1955) permit calculation of a shift position of a methylene group attached to two functional groups by the additive effect of the shielding constants in Table 1, below. The sum of the constants is added to δ 0.23, the position for CH_4.

Thus, to calculate the shift for the $-CH_2-$ protons of $C_6H_5CH_2Br$:

C_6H_5	= 1.85	0.23
Br	= 2.33	4.18
	4.18	4.41 = δ value for the $-CH_2-$ group.

Table I. Shielding Constants

Y or *Z*	Shielding Constants	*Y* or *Z*	Shielding Constants
$-CH_3$	0.47	$-C(=O)NR_2$	1.59
$-C=C$	1.32	$-C\equiv N$	1.70
$-C\equiv C$	1.44	$-NR_2$	1.57
$-\phi$	1.85	$-NHC(=O)R$	2.27
$-CF_2$	1.21	$-N_3$	1.97
$-CF_3$	1.14	$-SR$	1.64
$-Cl$	2.53	$-OSO_2R$	3.13
$-Br$	2.33		
$-I$	1.82		
$-OH$	2.56		
$-OR$	2.36		
$-O\phi$	3.23		
$-OC(=O)R$	3.13		
$-C(=O)R$	1.70		
$-C(=O)\phi$	1.84		
$-C(=O)OR$	1.55		

The shielding constants have been used to prepare the chart on page 224. Several values have been added to the original set of constants.

Alternatively, Chart 1 can be used to find the shift position of a methylene group attached to two functional groups from the δ values in the box at the intersection of the horizontal and diagonal groups ("mileage chart"). The upper number in each box is an experimental value; the lower number is calculated from Shoolery's constants.

CHART 1. CHEMICAL SHIFTS FOR METHYLENE GROUPS ATTACHED TO TWO FUNCTIONAL GROUPS (Y−CH_2−Z).

GROUP	$-CH_3$	$-C=C$	$-C\equiv C$	$-\phi$	$-CF_2$	$-CF_3$	$-Cl$	$-Br$	$-I$	$-OH$	$-OR$	$-O\phi$	$-O(C=O)R$	$-(C=O)R$	$-(C=O)\phi$	$-(C=O)OR$	$-C(=O)NR_2$	$-C\equiv N$	$-NR_2$	$-NH(C=O)R$	$-N_3$	$-SR$
		1.90					3.57	3.43	3.20	3.70	3.40		4.25	2.47		2.25	2.23		2.63			2.53
$-CH_3$	1.17	2.02	2.14	2.55	1.91	1.84	3.23	3.03	2.52	3.26	3.06	3.93	3.83	2.40	2.54	2.25	2.29	2.40	2.27	2.97	2.67	2.34
		2.60	3.39	3.30				3.93	3.87		3.95					3.00		3.15	3.30			3.08
$-C=C$		2.87	2.99	3.40	2.76	2.69	4.08	3.88	3.37	4.13	3.91	4.78	4.68	3.25	3.39	3.10	3.14	3.25	3.12	3.82	3.52	3.19
							4.09	3.90					4.71						3.50			
$-C\equiv C$			3.11	3.52	2.88	2.81	4.20	4.00	3.49	4.28	4.03	4.90	4.80	3.37	3.51	3.22	3.26	3.37	3.24	3.97	3.67	3.31
				3.97		3.50	4.50	4.35			4.70	4.91	5.08	3.55		3.40		3.65	3.48			3.68
$-\phi$				3.93	3.29	3.22	4.61	4.41	3.90	4.58	4.44	5.31	5.21	3.78	3.92	3.63	3.66	3.78	3.65	4.34	4.04	3.72
										4.01												
$-CF_2$					2.63	2.58	3.97	3.76	3.26	4.01	3.80	4.67	4.57	3.12	3.28	2.99	3.03	3.12	3.01	3.71	3.41	3.08
									3.56													
$-CF_3$						2.51	3.90	3.70	3.19	3.93	4.73	4.60	4.54	3.07	3.21	2.92	2.96	3.07	2.94	3.64	3.34	3.01
							4.99	5.16	4.99		5.40					4.05	4.17	4.07				
$-Cl$							5.29	5.09	4.58	5.32	5.12	5.99	5.89	4.46	4.60	4.31	4.35	4.46	4.37	5.13	4.73	4.40
								4.94				6.36			4.40	3.70	3.92					
$-Br$								4.89	4.38	5.12	4.92	5.79	5.69	4.26	3.40	4.11	4.15	4.26	4.13	4.83	4.53	4.20
									3.90								3.65	3.65				
$-I$									3.87	4.61	4.41	5.16	5.06	3.75	3.89	3.60	3.64	3.75	3.62	4.32	4.02	3.69
										4.55												
$-OH$										4.35	5.15	6.02	5.92	4.49	4.63	4.34	4.38	4.49	4.35	5.06	4.76	4.43
											5.55					4.13		4.20				
$-OR$											4.95	5.82	5.72	4.29	4.43	4.22	4.18	4.29	4.15	4.94	4.64	4.23
																	4.45					
$-O\phi$											6.69	6.59	5.16	5.30	5.09	4.05	5.16	5.03	5.86	5.56	5.10
														4.42								
$-OC(=O)R$											6.46	5.10	5.20	4.91	4.95	5.10	4.92	5.63	5.37	5.00		
														3.60		3.37			4.10			
$-C(=O)R$												3.63	3.77	3.48	3.52	3.63	3.50	4.20	3.90	3.57		
$-C(=O)\phi$													3.91	3.62	3.66	3.77	3.64	4.34	4.02	3.71		
																3.35			3.17			
$-C(=O)OR$													3.33	3.37	3.48	3.35	4.05	3.75	3.42			
																	3.30					
$-C(=O)NR_2$														3.41	3.52	3.39	4.09	3.79	3.46			
																		3.63	3.50	4.20	3.90	3.57
$-C\equiv N$																			3.10			
$-NR_2$																			3.37	4.07	3.77	3.44
																				4.75	4.45	4.14
$-NHC(=O)R$																						
																					4.15	3.84
$-N_3$																						
																						3.51
$-SR$																						