Hammett Linear Free Energy Substituent Constants

Table 3.26. Substituent Constants[a]

Substituent	Structure	σ_m	σ_p	σ^+	σ^-	σ_I	σ_R
Acetamido	CH_3CONH	0.21	0.00	−0.60	0.46	0.28	−0.35
Acetoxy	CH_3CO_2	0.37	0.45	0.19		0.38	−0.23
Acetyl	CH_3CO	0.38	0.50		0.84	0.30	0.20
Amino	NH_2	−0.16	−0.66	−1.30	−0.15	0.17	−0.80
Bromo	Br	0.37	0.23	0.15	0.25	0.47	−0.25
t-Butyl	$(CH_3)_3C$	−0.10	−0.20	−0.26	−0.13	−0.01	−0.18
Carboxy	HO_2C	0.37	0.45	0.42	0.77	0.30	0.11
Chloro	Cl	0.37	0.23	0.11	0.19	0.47	−0.25
Cyano	$N{\equiv}C$	0.56	0.66	0.66	1.00	0.57	0.08
Diazonium	$N^+{\equiv}N$	1.76	1.91		3.43		
Dimethylamino	$(CH_3)_2N$	−0.16	−0.83	−1.70	−0.12	0.13	−0.88
Ethoxy	C_2H_5O	0.10	−0.24	−0.81	−0.28	0.28	−0.57
Ethenyl	$CH_2{=}CH$	−0.06	0.04	−0.16		0.11	−0.15
Ethyl	C_2H_5	−0.07	−0.15	−0.30	−0.19	−0.01	−0.14
Ethynyl	$HC{\equiv}C$	0.21	0.23	0.18	0.53	0.29	−0.04
Fluoro	F	0.34	0.06	−0.07	−0.03	0.54	−0.48
Hydrogen	H	0.0	0.0	0.0	0.0	0.0	0.0
Hydroxy	HO	0.12	−0.37	−0.92	−0.37	0.24	−0.62
Methanesulfonyl	CH_3SO_2	0.60	0.72		1.13	0.59	0.11
Methoxy	CH_3O	0.12	−0.27	−0.78	−0.26	0.30	−0.58
Methoxycarbonyl	CH_3OCO	0.37	0.45	0.49	0.74	0.32	0.11
Methyl	CH_3	−0.07	−0.17	−0.31	−0.17	−0.01	−0.16
Methylthio	CH_3S	0.15	0.00	−0.60	0.06	0.30	
Nitro	NO_2	0.71	0.78	0.79	1.27	0.67	0.10
Phenyl	C_6H_5	0.06	0.01	−0.18	0.02	0.12	−0.11
Trifluoromethyl	CF_3	0.43	0.54	0.61	0.65	0.40	0.11
Trimethylammonio	$(CH_3)_3N^+$	0.88	0.82	0.41	0.77	1.07	−0.11
Trimethylsilyl	$(CH_3)_3Si$	−0.04	−0.07	0.02		−0.11	0.12

a. Values of σ_m, σ_p, σ^+, and σ^- are from C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, **91**, 165 (1991); Values of σ_I and σ_R are from M. Charton, *Prog. Phys. Org. Chem.*, **13**, 119 (1981).

$\sigma < 0$ is ERG

$\sigma > 0$ is EWG