October, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (10), 3033—3042 (1979) 3033

The Substituent Effect. 14.[1] The Solvolysis of 6- and 7-Substituted 1-(2-Naphthyl)ethyl Chlorides

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(Received April 13, 1979)

Nine of the title compounds were synthesized, and their solvolysis rates were determined in 80%(v/v) aq acetone at 45 °C. The effects of the *pi*-donor substituents for each substituent position are shown to be excellently described in terms of inductive(I) and *pi*-electronic(*Pi*) effects by means of the LSFE equation ($\log k/k_0=\rho_i\sigma_i+\rho_\pi^+\sigma_\pi^+$), just as with those in the 1-naphthyl systems. When those data are joined with all our substituent effects data for the phenyl, 4-biphenylyl, 2-fluorenyl, and 1-naphthyl systems under identical conditions, it is clear that the overall correspondence between the ρ_i values and Dewar's simple-field-effect function ($1/r$) is satisfactory. On the other hand, the ρ_π^+ values appear to give slightly different responses (separate correlations for the 1- and 2-naphthyl systems) to the SCF-π charge difference values; this may be ascribed to the steric effects on the *Pi* effect in only the 1-naphthyl-solvolysis sets. Furthermore, the position constancy of the I effect ($\rho_{i,6\text{-X-}2}/\rho_{i,7\text{-X-}2}=0.85$) has been observed in the present solvolysis and the available data for dissociation of 2-naphthalenecarboxylic acids involving relatively weak *Pi* effects; the figure is in good agreement with the ratio of $\rho_{i,para}/\rho_{i,meta}=0.85$. Analogous results were also achieved by the same treatment to 2-benzo[*b*]thienyl reactivities. All the results are discussed with respect to the validity of the LSFE equation.

It has been the well-accepted concept that substituent effects on reactivities can be described in a good approximation as an additive function of two basic components, polar (inductive, I) and resonance (*pi*-electronic, *Pi*) effects, each of which is given as a $\rho\sigma$ product.[2–4] Provided that there exists a universal set of inductive and *pi*-electronic substituent constants, the constants should be applicable in principle to any kinds of extended *pi*-system for various reactions. The term of universal substituent constants refers to the unchanged (inherent) electron-donating or -withdrawing capabilities of their own substituents, independent of any different reactivity classes.[2]

We have long focused on such separation and separability problems and have continued our studies of substituent effects on reactivities in certain *pi*-electronic systems. LArSR Eq. 1, originally based upon the phenyl system,[8–10] has been applied to 3′-, 4′-substituted 4-biphenylyl,[5] 7-substituted 2-fluorenyl,[1] and 3-, 4-substituted 1-naphthyl systems:[7]

$$\log k/k_0 = \rho(\sigma^0+r^+\Delta\bar{\sigma}_R^+ + r^-\Delta\bar{\sigma}_R^-) \tag{1}$$

LArSR Eq. 1, however, stands on the reference scale of σ^0 for unexalted phenyl reactivities as a standard, which is separable further into two basic terms, I and *Pi* effects. The σ^0 scale also implies the effect of the substituent position, such as the meta or para position. Therefore, LSFE Eq. 2[6,10–12] is expected to be appropriate to an understanding of the general scheme of the substituent effect in extended *pi*-systems.

$$\log k/k_0 = \rho_i\sigma_i + \rho_\pi^+\sigma_\pi^+ + \rho_\pi^-\sigma_\pi^- \tag{2}$$

The σ_i values are the inductive substituent constants, while the σ_π^+ or σ_π^- values the *pi*-electronic substituent constants for *pi*-donor($-R$) or *pi*-acceptor($+R$) substituents respectively, which, we believe, may be regarded as universal constants independent of any different reactivity classes; the numerical values are defined by $\sigma_i=0.74\sigma'$, $\sigma_\pi^+=0.415\Delta\bar{\sigma}_R^+$, and $\sigma_\pi^-=0.73\ \Delta\bar{\sigma}_R^-$. These scales hold a simple association with σ_p^0 by means of:

$$\sigma_p^0 = \sigma_i + \sigma_\pi^+ + \sigma_\pi^-.^{15)} \tag{3}$$

The substituent-effect parameters obtained by means of the LArSR treatment can, then, be interconverted into those obtained by means of the LSFE treatment:[1]

$$\rho_i = \rho,\ \ \rho_\pi^+ = \rho(1+r^+/0.415),\ \ \rho_\pi^- = \rho(1+r^-/0.73).$$

It must be noted that the different susceptibilities to *Pi* effects for donor and acceptor substituents, even in a given reaction, are essentially expressed as in LSFE Eq. 2. The duality of such ρ_π's is a significant implication of LArSR Eq. 1 and the inevitable conclusion to be induced from it.

On the other hand, DSP Eq. 4 by Taft has been widely applied to many chemical reactivities and physical properties:[2,4,13]

$$\log k/k_0 = \rho_I\sigma_I + \bar{\rho}_R\bar{\sigma}_R \tag{4}$$

We can point out there remain three important differences between our LSFE Eq. 2 and Taft's DSP Eq. 4: that is, (1) the existence of universal *pi*-electronic substituent constants,[6,14] (2) the dual susceptibilities to the *Pi* effects,[6,14,16] and (3) the scaling of the inductive substituent constants.[17] A principal objective of our current studies has been to obtain evidence for the existence of a universal set of *pi*-electronic substituent constants.

A naphthyl system is suitable for studies of substituent effects because of its various substituent positions.[2a] We have already reported the correlations for the solvolysis of the 5-, 6-, and 7-substituted 1-naphthyl systems and for the pK_a of the corresponding 1-naphthalenecarboxylic acids with respect to *pi*-donor substituents, *i.e.*, by means of Eq. 5:[18]

$$\log k/k_0 = \rho_i\sigma_i + \rho_\pi^+\sigma_\pi^+ \tag{5}$$

Here, we have worked with the alternative 2-naphthyl system and have examined the substituent effects at the B-ring positions, namely, the solvolysis of 6- and 7-substituted 1-(2-naphthyl)ethyl chlorides.

Surprisingly few substituent effect data have been published on 2-naphthyl reactivities;[24] available are only data sets as four reactions, in which at least both 6- and 7-substituent effects were studied systematically: (I) the present solvolysis in 80% aq acetone, (II) the detritiation of 2-tritionaphthalenes in CF_3COOH at 70 °C,[19] (III) the dissociation of 2-naphthalenecarboxylic acids in 50% aq EtOH at 25 °C,[2a,20] and (IV) the alkaline hydrolysis of methyl 2-naphthalenecarboxylates in 70% aq dioxane at 25 °C.[21] These 2-naphthyl reactivities belong to the σ^+-type (I and II) as well as the σ-type category (III and IV) and are appropriate for a study of the accurate reaction dependencies of the *I* and *Pi* effects. Further, LSFE Eq. 5 will also be tested for some electrophilic reactivities of the relevant heteroaromatics, such as 2-benzofuryl and 2-benzo[*b*]-thienyl systems.[22,23a]

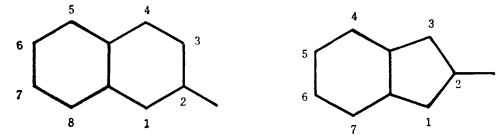

Chart 1.

Accordingly, the present results and discussion bear on the validity and utility of LSFE Eq. 2 in extended *pi*-systems and on the transmission efficiency of the *I* and *Pi* effects.

Experimental[25]

Materials. Commercial 2-acetylnaphthalene was purified through the recrystallization of its picrate (mp 82—83 °C), followed by the fractional distillation of the regenerated ketone using aq NH_3.

6-Substituted 2-Acetylnaphthalenes: 6-Methoxy-,[26] 6-methylthio-,[27] 6-methyl-,[28] and 6-bromo-2-acetylnaphthalenes[29] were prepared by following the literature methods of the Friedel-Crafts acetylation in nitrobenzene and were purified by fractional redistillation or by column chromatography over alumina (eluting with hexane–benzene) or by fractional recrystallization. The 6-bromo-2-acetylnaphthalene was converted to 6-cyano-2-acetylnaphthalene (mp 142—144 °C) by the ordinary method, using CuCN in DMF.[24c,30] The physical constants agreed well with the reported values, as is shown in Table 1.

7-Substituted 2-Acetylnaphthalenes: These compounds were prepared essentially by a combination of such well-known synthetic routes[31] of reactions as the following.

7-Methyl-2-acetylnaphthalene. 3-(*p*-Methylbenzoyl)propanoic acid was prepared by the Friedel-Crafts reaction of succinic anhydride with toluene and $AlCl_3$.[32] The acidification of the aq sodium salt solution gave colorless ppt (mp 129—131 °C; lit, 126—128 °C,[33] 124—126 °C),[34] which was then reduced by a Wolff-Kishner reaction with KOH, 80% aq NH_2NH_2 in diethylene glycol[35] to 4-(*p*-methylphenyl)-butanoic acid (recrystd from hexane, mp 57—58 °C; lit, 59—61 °C,[33] 60—61 °C)[31] and then esterified with 99% EtOH. Ethyl 4-(*p*-methylphenyl)butanoate was distilled at bp 97.5—98 °C/2 mmHg as a GLC pure sample. The ester (80 g) was treated with ethyl formate (64 g) and NaOEt in abs ether[36] to give ethyl 2-formyl-4-(*p*-methylphenyl)butanoate, along with about a half of the starting butanoate ester (43 g). The product was, then, cyclized to ethyl 3,4-dihydro-7-methyl-2-naphthoate, using phosphoric acid and concd H_2SO_4, according to the procedure described by Holmes and Trevoy.[36] The subsequent distillation of the desired ester gave a GLC

TABLE 1. PHYSICAL PROPERTIES AND ANALYTICAL DATA OF 2-ACETYLNAPHTHALENES, 1-(2-NAPHTHYL)ETHANOLS, AND 1-(2-NAPHTHYL)ETHYL CHLORIDES

Group	Subst	Mp or bp (°C or °C/mmHg)	Lit	Carbon Found (Calcd)	Hydrogen Found (Calcd)	Other Found (Calcd)
Ketone	H-2	55—56	56[44b]	84.81(84.68)	5.87(5.92)	
		133—135/5	171—173/17[44b]			
	6-MeO-2	109—110	106.5[26]	78.01(77.98)	5.56(6.04)	
			175—185/0.8[44a]			
	6-MeS-2	124.5—126.5	120[27]	72.19(72.19)	5.64(5.59)	
	6-Me-2	140—144/0.8	*ca.* 154/0.8[28]	84.61(84.75)	6.73(6.57)	
	6-Br-2	104.5—105.5	100.5[29]	58.15(57.86)	3.72(3.64)	(Br)31.84(32.08)
	7-MeO-2	85.0—85.5		77.87(77.98)	5.98(6.04)	
	7-Me-2	95.5—96.0		84.66(84.75)	6.39(6.57)	
	7-Br-2	94.5—95.5		57.81(57.86)	3.36(3.64)	(Br)31.69(32.08)
Alcohol[a]	H-2	75.5—76.0	74[8a]	83.45(83.69)	6.79(7.02)	
	6-Me-2	135—137/1		84.11(83.83)	7.40(7.58)	
	6-Br-2	142—144/0.7		57.49(57.39)	4.30(4.42)	
	6-CN-2	*ca.* 55—57				
	7-MeO-2	86.0—86.5		76.94(77.20)	6.82(6.98)	
	7-Me-2	70.5—71.5		83.64(83.83)	7.37(7.58)	
	7-Br-2	90—91		57.19(57.40)	4.18(4.42)	(Br)31.53(31.82)
Chloride[b]	H-2	68.5—69.0	68[8a]	75.45(75.59)	5.74(5.82)	(Cl)18.48(18.59)
	6-MeS-2	97.5—99.0		65.94(65.95)	5.48(5.53)	(Cl)15.13(14.97)
	6-CN-2	82—83		72.51(72.39)	4.34(4.67)	(Cl)16.17(16.44)
	7-MeO-2	75—76		70.71(70.75)	5.80(5.94)	(Cl)16.01(16.06)
	7-Me-2	66—67		76.28(76.28)	6.16(6.40)	(Cl)17.12(17.32)
	7-Br-2	76—77		53.64(53.47)	3.58(3.74)	(Cl)12.92(13.15)

a) 6-MeS-2, mp 100—102 °C. b) 6-Me-2, bp 115—116 °C/1.2 mmHg. Both 6-MeO-2 and 6-Br-2 derivatives were used immediately after the preparation of the chlorides, without distillation.

pure, colorless liquid (27.6 g); bp 142—144 °C/4 mmHg; NMR (CCl_4) δ=1.33 (3H, t, J=7.1 Hz, $CH_2C\underline{H}_3$), 2.29 (3H, s, $C\underline{H}_3$), 2.4—2.9 (4H, m, $C\underline{H}_2C\underline{H}_2$), 4.20 (2H, q, J=7.1 Hz, $C\underline{H}_2CH_3$), 6.94 (3H, s, Ar), and 7.36 (1H, olefinic); Found: C, 77.78; H, 7.30%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

The ethyl dihydronaphthoate (27 g) was dehydrogenated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 32 g) in xylene (250 ml) under refluxing for 24 h. After a usual work-up, a major fraction of the distillation (bp 133—140 °C/2 mmHg) was collected (solidified on standing) and recrystallized from hexane to give pure ethyl 7-methyl-2-naphthalenecarboxylate (15 g); mp 64.5—65 °C; NMR (CCl_4) δ= 1.42 (3H, t, J=7.1 Hz, $CH_2C\underline{H}_3$), 2.50 (3H, s, $C\underline{H}_3$), 4.37 (2H, q, J=7.1 Hz, $C\underline{H}_2CH_3$), and 7.2—8.4 (6H, m, Ar); Found: C, 78.38; H, 6.65%. Calcd for $C_{14}H_{14}O_2$; C, 78.48; H, 6.59%.

7-Methyl-2-naphthalenecarboxylic acid, obtained from the alkaline hydrolysis, was recrystallized from aq EtOH; mp 208—209 °C (lit, 207—209 °C).[31] 7-Methyl-2-acetylnaphthalene was similarly synthesized (*via* 7-methyl-2-naphthoyl chloride, as has been described elsewhere)[7,8a,18] and purified by recrystallization from hexane; mp 85.0—85.5 °C; NMR (CCl_4) δ= 2.5_5 (3H, s, $C\underline{H}_3$), 2.6_4 (3H, s, $COC\underline{H}_3$), and 7.4—8.4 (6H, m, Ar).

7-Methoxy-2-acetylnaphthalene. 3-(*p*-Methoxybenzoyl)-propanoic acid (mp 148—150 °C; lit, 148—149 °C),[37,38] 4-(*p*-methoxyphenyl)butanoic acid,[38] and ethyl 4-(*p*-methoxyphenyl)butanoate (bp 133.5—134 °C/3 mmHg) were prepared successively by methods similar to those used for the above 7-methyl derivatives. The cyclization of ethyl 4-(*p*-methoxyphenyl)butanoate (74 g) *via* ethyl 2-formyl-4-(*p*-methoxyphenyl)butanoate gave ethyl 3,4-dihydro-7-methoxy-2-naphthalenecarboxylate (17.5 g); bp 169—175 °C/5—6 mmHg; NMR (CCl_4) δ=1.33 (3H, t, J=7.1 Hz, $CH_2C\underline{H}_3$), 2.4—2.9 (4H, m, $C\underline{H}_2C\underline{H}_2$), 3.74 (3H, s, $OC\underline{H}_3$), 4.19 (2H, q, J=7.1 Hz, $C\underline{H}_2CH_3$), 6.6—7.0 (3H, m, Ar), and 7.36 (1H, s, olefinic); Found: C, 72.50; H, 6.70%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

The dehydrogenation of the dihydronaphthalene (28.5 g) with DDQ gave ethyl 7-methoxy-2-naphthalenecarboxylate (21.5 g); bp 188—195 °C/5 mmHg (lit, mp 36—36.5 °C);[39] NMR (CCl_4) δ=1.42 (3H, t, J=7.1 Hz, $CH_2C\underline{H}_3$), 3.88 (3H, s, $OC\underline{H}_3$), 4.37 (2H, q, J=7.1 Hz, $C\underline{H}_2CH_3$), and 7.1—8.4 (6H, m, Ar).

After alkaline hydrolysis, 7-methoxy-2-naphthalenecarboxylic acid was obtained; recrystd from aq EtOH, mp 200.5—201 °C (lit, 194—195 °C,[40] 195.5—196 °C).[39] The naphthalenecarboxylic acid was converted to 7-methoxy-2-acetylnaphthalene, being distilled at 183—189 °C/5 mmHg, and was then recrystallized from hexane–benzene as colorless needles; mp 95.5—96.0 °C; NMR (CCl_4) δ=2.61 (3H, s, $COC\underline{H}_3$), 3.90 (3H, s, $OC\underline{H}_3$), and 7.1—8.2 (6H, m, Ar).

7-Bromo-2-acetylnaphthalene. 3-(*p*-Bromobenzoyl)propanoic acid (mp 148.5—150.5 °C; lit, 148—149 °C),[41] 4-(*p*-bromophenyl)butanoic acid (mp 68.5—69.5 °C; lit, 71—72 °C),[41] and ethyl 4-(*p*-bromophenyl)butanoate (bp 115—117 °C/2 mmHg) were similarly prepared as the corresponding Me and MeO derivatives. The ester condensation and successive cyclization of the ester (89 g) gave ethyl 3,4-dihydro-7-bromo-2-naphthalenecarboxylate, which was distilled at bp 140—153 °C/1 mmHg (35 g) and then recrystallized from hexane to afford the above named substance (mp 67—67.5 °C) as colorless crystals (30 g); NMR (CCl_4) δ=1.33 (3H, t, J=7.1 Hz, $CH_2C\underline{H}_3$), 2.4—2.9 (4H, m, $C\underline{H}_2C\underline{H}_2$), 4.21 (2H, q, J=7.1 Hz, $C\underline{H}_2CH_3$), and 6.9—7.3 (4H, m, Ar and olefinic); Found: C, 55.51; H, 4.42; Br, 28.53%. Calcd for $C_{13}H_{13}O_2Br$: C, 55.54; H, 4.66; Br, 28.42%.

The dihydronaphthalene was dehydrogenated with DDQ to give ethyl 7-bromo-2-naphthalenecarboxylate as colorless needles (recrystd from ligroin; mp 92.5—94 °C); NMR (CCl_4) δ=1.4_6 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 4.4_6 (2H, q, J=7 Hz, $C\underline{H}_2CH_3$), and 7.7—8.6 (6H, m, Ar); NMR ($CDCl_3$) δ=1.44 (3H, t, J=7.1 Hz, $CH_2C\underline{H}_3$), 4.45 (2H, q, J=7.1 Hz, $C\underline{H}_2CH_3$), and 7.6—8.5 (6H, m, Ar);[42a] C^{13}-NMR ($CDCl_3$) δ=14.40 ($CH_2\underline{C}H_3$), 61.38 ($\underline{C}H_2CH_3$), 120.80 (C_7), 125.93 (C_3), 128.27 (C_4),†,[42b] 129.00 (C_2), 129.59 (C_5),† 130.22 (C_1) 131.39 (C_8), 131.69 (C_6),† 133.84 and 134.03 (C_9 and C_{10}), and 166.60 ($\underline{C}OOEt$);[42b] Found: C, 55.93; H, 3.73; Br, 28.25%. Calcd for $C_{13}H_{11}O_2Br$: C, 55.94; H, 3.97; Br, 28.63%.

The alkaline hydrolysis of the ester afforded 7-bromo-2-naphthalenecarboxylic acid (mp 241—243 °C; lit, 238—240 °C),[40] which was similarly converted to 7-bromo-2-acetylnaphthalene, having been purified by distillation and then recrystallization from hexane; mp 94.5—95.5 °C; NMR (CCl_4) δ=2.6_5 (3H, s, $COC\underline{H}_3$) and 7.7—8.4 (6H, m, Ar).

1-(6- and 7-Substituted 2-naphthyl)ethanols and Their Chlorides. The alcohols and chlorides were prepared successively from the corresponding ketones with the standard method:[7,8a,18] (i) the reduction of the ketone with $LiAlH_4$ or $NaBH_4$ to give 1-(2-naphthyl)ethanol followed by (ii) the chlorination of the alcohol with dry HCl or $SOCl_2$ to provide 1-(2-naphthyl)ethyl chloride. The NMR data of 1-(7-substituted 2-naphthyl)-ethanols were as follows. 7-Me deriv; NMR (CCl_4) δ=1.47 (3H, d, J=6.3 Hz, $CHOHC\underline{H}_3$), 1.93 (1H, s, $O\underline{H}$), 2.48 (3H, s, $C\underline{H}_3$), 4.89 (1H, q, J=6.3 Hz, $C\underline{H}OHCH_3$), and 7.1—7.7

TABLE 2. SOLVOLYSIS DATA FOR 6- AND 7-SUBSTITUTED 1-(2-NAPHTHYL)ETHYL CHLORIDES IN 80% AQ ACETONE

Subst	Temp/°C	$10^5 k_1/s^{-1}$
H-2	45.0	5.01[b]
	25.0	0.442
6-MeO-2	45.0	835[a]
	25.0	127[a]
	15.0	46.6
	0.0	7.78
	−15.0	1.30
6-MeS-2	45.0	224[a]
	25.0	24.0
	0.0	0.935
6-Me-2	45.0	34.5[c]
	25.0	3.73
6-Br-2	65.0	10.5
	45.0	1.18
	25.0	0.0993[a]
6-CN-2	90.0	3.68
	75.0	0.870
	45.0	0.0325[a]
	25.0	0.00253[a]
7-MeO-2	45.0	5.94[d]
7-Me-2	45.0	9.05[d]
7-Br-2	45.0	0.300[d]

a) Extrapolated from other temperatures by means of the Arrhenius equation. b) Previous value; 5.03 (5.18).[8a] c) Calculated from the LFER of $(\log k/k_0)_{45\,°C} = 0.9436\ (\log k/k_0)_{25\,°C} - 0.036$ (r=0.9996, s=±0.057, n=5). d) For the 7-X-2 series, k_1= $5.17\times 10^{-5}\ s^{-1}$ for the parent H-2 was used for the calculations of the relative rates because of the different batchs and different workers.

(6H, m, Ar). 7-MeO deriv; NMR (CCl_4) $\delta=1.48$ (3H, d, $J=6.4$ Hz, $CHOHC\underline{H}_3$), 1.79 (1H, s, $O\underline{H}$), 3.85 (3H, s, $OC\underline{H}_3$), 4.89 (1H, q, $J=6.4$ Hz, $C\underline{H}OHCH_3$), and 7.0—7.7 (6H, m, Ar). 7-Br deriv; NMR (CCl_4) $\delta=1.49$ (3H, d, $J=6.4$ Hz, $CHOHC\underline{H}_3$), 1.69 (1H, s, $O\underline{H}$), 4.94 (1H, q, $J=6.4$ Hz, $C\underline{H}OHCH_3$), and 7.4—7.9 (6H, m, Ar).

The physical properties and the microanalysis data of the ketones, alcohols, and chlorides are listed in Table 1.

Solvent and Kinetics: The 80% (v/v) aq acetone solvent was prepared by mixing 1 volume of deionized, distilled, and degassed water with 4 volumes of purified acetone at 25 °C, as has been described before.[7,8a,18] Different batches of the aq acetone solvent, which gave slightly different rate constants (Table 2), were employed without calibration for each series of measurements. The solvolysis reaction was followed by the usual titration method (chloride of *ca.* 0.02 M^{-1}, titer of *ca.* 0.02 M^{-1} aq NaOH, indicator of Bromocresol Purple). The bath temperature was controlled to ±0.02 °C. At very low temperatures (−15 °C), the accuracy was estimated to be within 0.1 °C. The kinetic procedures were essentially the same as those reported before.[8a,45a]

All runs followed first-order kinetics, covering over 70—80% of the reaction, except for the 6-CN-2 derivative (50% reaction). The first-order rate constants were calculated by means of the least squares method using the mean infinity reading obtained after over 10 half-lives (corr coeff > 0.9999).[45b] The data points in a run were usually 12 points (2 for infinity reading), but in a few instances 7 points were used, covering up to *ca.* 70% of the reaction. The rate constants from duplicated runs were reproducible within ±2% or better. Very reactive chloride, such as the 6-MeO-2 derivative, was used for the kinetic measurements immediately after the evaporation of the solvent and without purification.

The rate constants, $k_1(s^{-1})$, obtained at various temperatures are given in Table 2.

Results and Discussion

The logarithmic relative rates of 6- and 7-substituted 1-(2-naphthyl)ethyl chlorides with respect to the parent unsubstituted 2-naphthyl derivative in 80% aq acetone at 45 °C and 25 °C are summarized in Table 3, along with some activation parameters. The reaction conditions are our standard ones in our studies of a series of solvolysis reactions. The log k/k_0 values in Table 3 can, then, be directly compared with the other corresponding solvolysis sets in the phenyl,[8a] 4-biphenylyl,[5] 2-fluorenyl,[1] and 1-naphthyl systems.[7,18]

TABLE 3. LOG k/k_0 VALUES FOR THE SOLVOLYSIS OF SUBSTITUTED 1-(2-NAPHTHYL)ETHYL CHLORIDES IN 80% AQ ACETONE

Subst	(log k/k_0) at 25 °C	(log k/k_0) at 45 °C	ΔH^* kcal/mol	$-\Delta S^*$ eu
H-2	0.000	0.000	22.3	8.3
6-MeO-2	2.46[a]	2.22[a]	17.1	14.4
6-MeS-2	1.735	1.65[a]	20.4	6.5
6-Me-2	0.926	0.84[c]	20.4	10.5
6-Br-2	−0.65[a]	−0.628	22.7	9.8
6-CN-2	−2.24[a]	−2.19[a]	23.4	14.6
7-MeO-2		0.060[d]		
7-Me-2		0.234[d]		
7-Br-2		−1.236[d]		

a), c), and d) are the same as in the footnotes in Table 2.

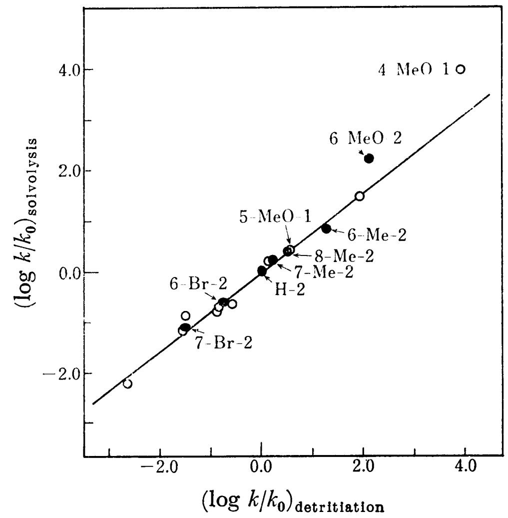

Fig. 1. A rate plot between the present solvolysis (45 °C) and the detritiation (70 °C) in the 2-naphthyl (closed circle) and in the 1-naphthyl (open circle) systems.

In the present 2-naphthyl series, the log k/k_0 varies widely not only with the substituent change, but also with the position change, just as in the 1-naphthyl series. Figure 1 shows a plot of the logarithmic relative rates for the present solvolysis, I (at 45 °C), against those for II (at 70 °C).[19a] Although common substituents are so limited, all the points except for the 6-MeO-2 derivative in the 2-naphthyl system (closed circle) fall on or near the line for the 1-naphthyl system (open circle).[18] The detritiation data for the 6-Cl-2 and 7-Cl-2 derivatives were employed in this figure instead of those for the Br derivatives.

The MeO group may be modified in CH_3COOH by hydrogen-bonding interaction, which appears to reduce mainly its ability to make a *pi*-electron donation.[18,46] The modification seems to be consistent with the fact that deviations are serious only in a strongly conjugative position, in which the *pi*-electronic contribution is important, but not appreciable in weakly conjugative (5-MeO-1) and essentially nonconjugative positions. The single correlation line for 1- and 2-naphthyl derivatives, except for such a single MeO group, reflects a similar blend of the *I*/*Pi* effects in the two naphthyl series between I and II.

On the contrary, Fig. 2 illustrates a plot of I (at 45 °C) against III (at 25 °C).[2a,20] Note that the plot does not show an overall linearity in the 2-naphthyl system from the MeO to the CN substituents (closed circle); the same is true in the 1-naphthyl system (open circle). This is similar to the plot of the σ^+ reactivity data against the σ values in the phenyl system: that is, (i) all the substituents at the conjugate position (7-MeO-2, 7-Br-2, 7-Me-2), the *pi*-acceptor ($+R$) substituents at the conjugate position (6-CN-2), and the unsubstituted one make a straight line, and (ii) the *pi*-donor ($-R$) substituents at the conjugate position (6-MeO-2, 6-Me-2, 6-Br-2) substantially deviate upward from the correlation line, the deviations depending upon the

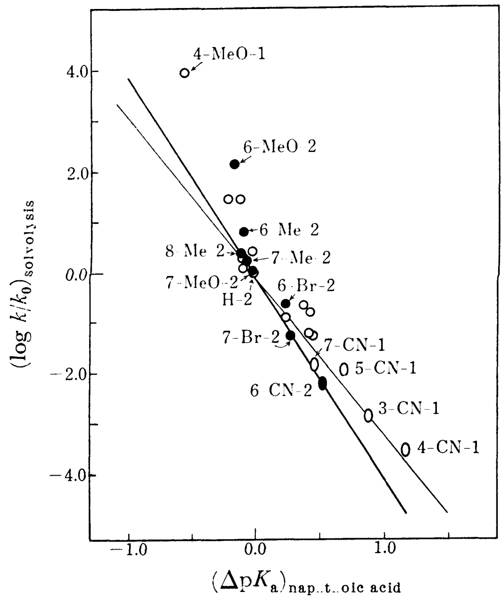

Fig. 2. A plot of the log k/k_0 in the present solvolysis (45 °C) *vs.* ΔpK_a in the corresponding naphthoic acids; closed circle for 2-naphthyl and open circle for 1-naphthyl systems.

order of the *pi*-donor ability: MeO>Me≥Br. Analogous phenomena have been observed in the 2-fluorenyl[1] and 4-biphenylyl systems.[5] As far as electrophilic reactivities are concerned, it can be generally deduced from extended *pi*-electron systems that the blend of the *I-Pi* effects of the donor substituents at the conjugate positions varies with the reactions of different electron demands, whereas the blend for acceptor substituents, even at conjugate positions, does not. All these facts are in line with the general features of the substituent effects observed in the Hammett-type treatment of general benzene reactivities.

The next feature of this figure is the separate slopes for the 2-naphthyl (a solid line) and 1-naphthyl (a fine line) systems; each line is drawn through the substituents for which no additional resonance exaltation effect can be expected. The slope for the 2-naphthyl system is 25% larger than that for the 1-naphthyl system. Any one of the three reactions (I, II, and III) has a higher sensitivity to the substituent changes in the 2-naphthyl than in the 1-naphthyl system. This probably arises from the different steric effects with the peri-hydrogen on the reaction center. Special care should be taken in the discussion of the apparent substituent constants in the 2-naphthyl system compared with the 1-naphthyl system, for example, the use of the ρ in the phenyl system. Since the ρ value for the solvolysis of 1-(3,4-X-1-naphthyl)ethyl chlorides (by LArSR or LSFE for 4-X-1) was found to be −5.1,[7] compatible with the ρ of −5.0 for the phenyl system,[8a] the separate lines in Fig. 2 imply the possibility that the treatment of the substituent effects for the dissociation of both 1- and 2-naphthalenecarboxylic acids with a single, common ρ[20] is not appropriate.

At the intermediate in the present solvolysis, where a positive charge is developed, the 6-X-2 naphthyl system can be stabilized by an extended quinoid structure throughout the A and B rings. The higher stability of 2,6-naphthoquinone than, for example, 1,7-naphthoquinone or 1,5-naphthoquinone[47] may tell us qualitatively of the larger contribution of such a 2,6-naphthoquinonoid structure. Our attempt to correlate the 6-X-2 reactivities with simple σ^+ parameters[48] appears to have been practically successful. It provides $\rho^+ = -3.05$, with a correlation coefficient of 0.9990 ($s = \pm 0.080$, $n = 6$), suggesting quite a large *pi*-electronic exaltation effect in this series. The LArSR approach gives a more precise description (Fig. 3) by the use of:

$$\log k/k_0 = -3.275(\sigma_p^0 + 0.872\Delta\bar{\sigma}_R^+) - 0.053$$

with a corr coeff of 0.9997 and a standard deviation of ± 0.044 ($n = 6$).[49] On the basis of the ρ and r^+ values thus obtained, the LSFE ρ_i and ρ_π^+ values are estimated to be as listed in Table 4; the ρ_π^+/ρ_i ratio is *ca.* 3.1.

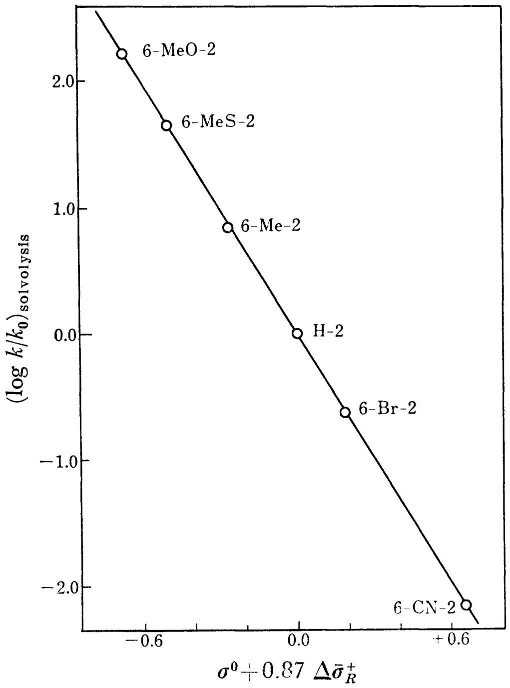

Fig. 3. The LArSR plot for the solvolysis of 6-substituted 1-(2-naphthyl)ethyl chlorides at 45 °C.

In the 7-X-2 naphthyl reactivities, there is no single σ-type parameter to describe the substituent effects. We arrived at the view that the effects for 7-X-2 of I may correlate well with the quantity of $(\sigma_p^0 + \sigma_m)/2$ rather than with that of σ_p^0 or σ_m.[50] This indicates that the ρ_π^+/ρ_i ratio is close to 0.7 (rather than to 1.0 or 0.4).

For the present aim to ascertain the general features of the position dependency of the *I* and *Pi* components of substituents in extended *pi*-systems, it should be appropriate to use the LSFE approach, using their universal substituent constants. It would seem that a large number of data including both $-R$ and $+R$ substituents would give the most reliable statistical parameters of ρ_i, ρ_π^+, and ρ_π^- in LSFE Eq. 2 when three independent variables are used (σ_i, σ_π^+, and σ_π^-).[6,16,54] In the present cases, we have treated only *pi*-donor substituents and then utilized the simplified LSFE Eq. 5 for each substituent position in the naphthalene ring.

TABLE 4. CORRELATIONAL PARAMETERS FOR THE SOLVOLYSIS OF 1-(2-NAPHTHYL)ETHYL CHLORIDES AT 45 °C[a)]
$\log k/k_0=\rho_i\sigma_i+\rho_\pi^+\sigma_\pi^+ +(\rho_\pi^-\sigma_\pi^-)$

Series	Method[b)]	ρ_i	ρ_π^+	ρ_π^-	$\pm s$[c)]	R[d)]	n(Subst)[e)]
6-X-2	LArSR Eq. 1	−3.28	−10.2	(−3.3)	0.044	0.9998	6(MeO,MeS, Me, Br, H, CN)
	LSFE Eq. 5	−3.45	−10.4		0.069	0.9991	5(MeO, MeS, Me, Br, H)
	LSFE Eq. 5[f)]	−3.49	−10.3		0.092	0.9991	4(MeO, Me, Br, H)
7-X-2	LSFE Eq. 5	−3.89	−2.96		0.121	0.9946	4(MeO, Me, Br, H)

a) See also Table 5. b) See Text. c) Standard deviation. d) Correlation coefficient. e) Substituents involved in calculation. f) Without SMe.

The regression parameters derived are given in Table 4. The substituent constants employed here are the same as those in previous reports.[18)] The reliability of such statistically derived ρ_i and ρ_π^+ parameters depends greatly upon the variation in the electronic natures of the substituents as well as on those numbers.[2a,51,52)] The present series involve four common, typical substituents—MeO, Me, Br, H. Such a variety should provide meaningful results for the present purpose.

In the case of the 6-X-2 naphthyl series, the parameters from LSFE Eq. 5 (without the CN group) agreed quite well with those from the LArSR treatment, including the CN group. The identity of the correlation parameters with and without the CN, associated with high correlation coefficients, suggests that the ρ_π^- value must be rather close to the ρ_i value. In a previous paper,[1)] it has been demonstrated that the reactivities in the 6-X-2 naphthyl derivatives can generally be expressed by the LArSR approach, involving both *pi*-donor and *pi*-acceptor substituents (CN or NO_2). This means that $\rho_\pi^-\simeq\rho_i$ holds generally, as a good approximation, in spite of varying contributions by *Pi* effects of *pi*-donor groups.

To minimize the probability of an accidental correlation due to experimental error, *etc.*, we used here the correlation values of ρ_i and ρ_π^+, including the CN group, for wider coverage. The $-\rho_i$ value for 7-X-2 naphthyl has been shown to be larger than that for the 6-X-2 series. The $\rho_{i,6\text{-X-2}}/\rho_{i,7\text{-X-2}}$ ratio is calculated to be 0.85 by the use of −3.3/−3.9; this value is in good agreement with the $\rho_{i,para}/\rho_{i,meta}$ value of 0.85, but it seems to be slightly larger than the relevant values of $\rho_{i,6\text{-X-1}}/\rho_{i,7\text{-X-1}}$ or $\rho_{i,6\text{-X-1}}/\rho_{i,5\text{-X-1}}$ of *ca.* 0.75 in the 1-naphthyl series (see also Table 5).[18)] It is apparent that the *I* effect of substituents from the 7-position is more effectively transmitted than that from the 6-position in the 2-naphthyl system. This can reasonably be related to the shorter distance or less intervening sp^2-carbons in the 7-X-2 system than in the 6-X-2 system. On the other hand, the resulting $-\rho_\pi^+$ for the 6-X-2 is larger by a factor of 3 than that for the 7-X-2 system; this is in qualitative accord with the prediction from MO calculations.[2a,3,19b,20,23)]

In Table 5 are collected the full sets of ρ_i and ρ_π^+ values derived from our solvolysis rates. Figure 4 gives the overall correspondence of the empirical ρ_i sets to Dewar's $1/r$ function, which has been shown to be appropriate for 1-naphthyl reactivities.[18)] The figure seems to justify again the soundness of the simple function, covering a wide enough range, from the phenyl to the 2-fluorenyl system. Although the deviation of the 7-X-2 naphthyl appears to be slightly large, no other complicated functions, such as $(\cos\theta)/r^2$ (Table 5), can provide any appreciable improvement in the correlation. Therefore, it is apparent that the angle factors are unimportant. Herein, the *r* refers to Dewar's simplest distance between the naphthyl carbons to which substituents and reaction site are attached,[3a)] and θ is the angle between the above distance vector and a C–X dipole vector. It is characteristic that, instead of the 4-biphenylyl sets which had previously

TABLE 5. COMPARISONS BETWEEN EMPIRICAL AND THEORETICAL PARAMETERS FOR THE SOLVOLYSIS OF 1-ARYLETHYL CHLORIDES IN 80% AQ ACETONE AT 45 °C

Aryl system	Method[11t)]	ρ_i	ρ_π^+	Ratio of $1/r$[d)]	Ratio of $\cos\theta/r^2$ [d)]	MO index SCF-π Δq[e)]
4-X-1 Phenyl	LArSR[8)]	−4.95[a)]	−18.7[a)]	1.00	1.00	0.200
3-X-1 Phenyl	LArSR[8)]	−5.79[b)]	−2.48[b)]	1.15	0.96	0.042
7-X-2 Fluorenyl	LArSR[1)]	−2.28[a,c)]	−6.79[a,c)]	0.40	0.25	
4′-X-4 Biphenylyl	LArSR[5)]	−1.56[a)]	−4.71[a)]	0.40	0.25	
3′-X-4 Biphenylyl	LArSR[5)]	(−1.83)[b)]		0.44	0.18	
3-X-1 Naphthyl	LSFE[18)]	−6.96	−2.56	1.15	0.96	0.019
4-X-1 Naphthyl	LSFE[18)]	−5.09	−17.6	1.00	1.00	0.225
5-X-1 Naphthyl	LSFE[18)]	−3.82	−4.40	0.76	0.65	0.084
6-X-1 Naphthyl	LSFE[18)]	−2.90	−2.43	0.67	0.67	0.043
7-X-1 Naphthyl	LSFE[18)]	−3.66	−7.74	0.76	0.50	0.107
6-X-2 Naphthyl	LArSR[f)]	−3.28	−10.2	0.56	0.42	0.116
7-X-2 Naphthyl	LSFE[f)]	−3.89	−2.96	0.58	0.38	0.045

a) Calcd with $\rho_i=\rho$, $\rho_\pi^+=\rho(1+r^+/0.415)$.[1)] b) Calcd with $\rho_{i,meta}=1.17\rho_{i,para}$.[15)] c) The temperature factor of 0.957 was used from 25 °C to 45 °C.[5)] d) See Text. e) Ref. 23b. f) Present study.

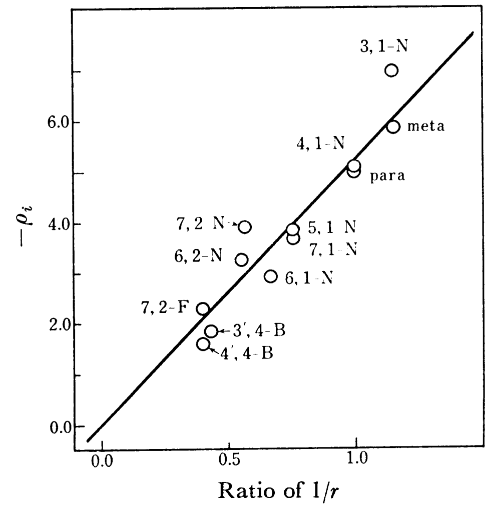

Fig. 4. A plot of the ρ_i values *vs.* a ratio of Dewar's $1/r$; N(Naphthyl), F(Fluorenyl), and B(Biphenylyl).

been applied to Dewar's FM equation,[3a] the planar 2-fluorenyl set fits the line much more closely (Fig. 4). This observation is not inconsistent with our earlier conclusion of the $1/R^2$ dependence of the I effect in the 4-biphenylyl relative to the phenyl system.[5] Even bearing the crudeness of the approximation in mind, the inductive effect in various extended *pi*-systems for the present solvolysis series may be explicable in terms of Dewar's $1/r$ parameter (to a practical approximation) if the *peri*-hydrogen steric effect does not exert any observable effects on the ρ_i values. This conclusion will be further evaluated on the basis of available solvolysis data for heteroaromatics (see below).

In the solvolysis of 6-substituted bicyclo[4.4.0]dec-2-yl tosylates, which constitute a good model of the 6-X-2 naphthyl sigma skeleton, Tanida *et al.* suggested the importance of the field effect based upon the rate ratio of $k_{ax}/k_{eq}=0.7$—0.9.[55]

Previously, we noted a good relationship between the ρ_π^+ values and Forsyth's theoretical Δq_{ij} values (the regional charge difference at a substituent position).[53] Resently, Forsyth, Spear, and Olah have reported extensive sets of Δq; the change in charge density for the process of Ar→ArCH$_2^+$ was calculated by the use of a PPP SCF-π method.[23b,58] Figure 5 illustrates the correspondence between the empirical ρ_π^+ and the charge difference (Δq), giving two lines covering the 1- and 2-naphthyl and phenyl sets. The higher-slope line involves 4-X-1 phenyl and 6-X-2 naphthyl groups, while the lower line involves 4-X-1 naphthyl and 7-X-1 naphthyl groups; the four ρ_π^+ values of these groups are more reliable than the other groups in Fig. 5 because of their wider coverage of the reactivity change. The MO calculations do not involve any accounts of the steric effects. The separate response (Fig. 5) is explicable; that is, the 1-naphthyl ρ_π^+ sets, appreciably 4-X-1 and 7-X-1, are influenced more efficiently by steric effects caused by *peri*-hydrogen and give lower ρ_π^+ values than would be expected with other steric-free sets.

As a conclusion, the good coincidence between the empirical and theoretical coefficients with respect to the I and Pi effects, covering a wide range of *pi*-systems, provides evidence justifying the validity of the description of the substituent effects in terms of the I and Pi effects by means of the LSFE equation.

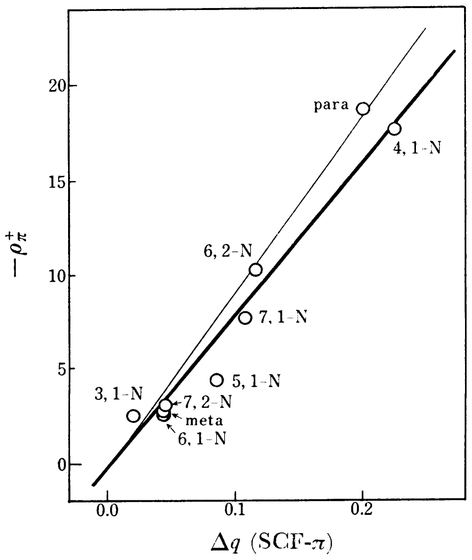

Fig. 5. A plot of the ρ_π^+ values *vs.* Δq of Forsyth's charge difference values by PPP SCF-π method.[23b]

The LSFE approach has been further tested for other reactions[59] or other extended *pi*-systems: the III, IV, and the (V) solvolysis of 1-(2-benzofuryl)ethyl *p*-nitrobenzoates,[22] the (VI) solvolysis of 1-(2-benzo[*b*]-thienyl)ethyl *p*-nitrobenzoates,[23] the (VII) acetolysis of 2-(1-azulenyl)ethyl tosylates,[56a] and the (VIII) dissociation of 1-azulenecarboxylic acids.[56b] The correlation results are summarized in Table 6, in which almost all the series provide very satisfactory correlations ($R>0.995$).[61] Since common substituents are involved in most cases, the correlation parameters (ρ_i, ρ_π^+) can be estimated with a similar reliability without paying attention to improper substituent constants in certain groups.

In the case of the III and IV reactions, the $\rho_{i,7\text{-X-2}}$ is apparently larger than the $\rho_{i,6\text{-X-2}}$ and the $\rho_{i,6\text{-X-2}}/\rho_{i,7\text{-X-2}}$ ratio is calculated to be 0.85 for III and 0.87 for IV. The features are in line with that for the I solvolysis. The identical ρ_i ratio of 0.85, in spite of the obviously different amount of the Pi effect, means that the I effect in the 2-napthyl system also remains the position constant. At present, the meaning of the difference between the factor of the present 0.85 in the 2-naphthyl and the previous 0.75 in the 1-naphthyl[18] is not clear. The other sets of solvolysis data, such as for the 5-X-2 and 8-X-2 naphthyl systems, will clarify the significance of such a figure for the entire B-ring positions.

With this purpose in mind, the 2-benzofuryl and 2-benzothienyl reactivities have been chosen. These heteroaromatic systems are similar to the 2-naphthyl system; an oxygen or sulfur atom substituted for the CH=CH group. The empirical $-\rho_i$ values for 5- and 6-substituent positions in the two heteroaromatics are nearly equal: 4.1 ± 0.1 for V and 4.1 ± 0.2 for VI.

TABLE 6. CORRELATIONAL PARAMETERS FOR REACTIVITIES IN 2-NAPHTHYL AND RELEVANT SYSTEMS

Reaction type[a]	Condition	Subst position	Method[b]	ρ_i	ρ_π^+	R	Subst and note
III: 2-Naph–COOH, pK_a[2a,20]	50E, 25 °C	6-X-2	A	0.74	0.97	0.995	NMe$_2$,MeO,Me,Br,Cl, F,H,CN,NO$_2$[c]
		7-X-2	A	0.87	0.57	0.993	NMe$_2$,NH$_2$,MeO,Me,Br, Cl,F,H,CN,NO$_2$[d]
IV: 2-Naph–COOMe+OH[21]	70D, 25 °C	6-X-2	C	1.72	2.43	0.995	MeO,Me,F,Cl,H,CN,NO$_2$[e]
		7-X-2	A	(1.97)	(3.56)	(0.996)	F,Cl,H,CN,NO$_2$[f]
V: 2-Benzofuryl–$\underset{\text{OPNB}}{\underset{\vert}{\text{CH}}}$–Me, Solv[22]	80E, 75 °C	5-X-2	B	−4.21	−4.79	0.998	MeO,Me,Cl,H[g]
		6-X-2	B	−4.00	−11.5	0.999	MeO,Me,Cl,H[g]
VI: 2-Benzothienyl–$\underset{\text{OPNB}}{\underset{\vert}{\text{CH}}}$–Me, Solv[23]	80E, 75 °C	4-X-2	B	−4.99	−7.15	0.993	MeO,Me,Cl,H
		5-X-2	B	−4.19	−4.81	0.997	MeO,Me,Cl,H[h]
		6-X-2	B	−3.88	−11.0	0.999	MeO,Me,Cl,H
		7-X-2	B	−4.61	−3.10	0.992	MeO,Me,Cl,H
VII: 1-Azulenyl–CH$_2$CH$_2$–OTs, Solv[56a]	AcOH, 25 °C	2-X-1	B	−4.49	−5.17	0.999	MeO,Me,Cl,Br,H
		3-X-1	A	−3.70	−3.80	0.995	MeO,Me,Br,H,CN,Ac,NO$_2$[i]
		6-X-1	B	−3.16	−4.39	0.993	MeO,Me,Br,H
VIII: 1-Azulene–COOH, pK_a[56b]	50E, 25 °C	2-X-1	B	2.23	2.53	0.999	MeO,Me,Cl,Br,H
		3-X-1	A	1.58	0.89	0.999	MeO,Me,Cl,H,CN,Ac,NO$_2$[j]
		6-X-1	B	1.29	1.48	0.997	MeO,Me,Br,H

a) See text. b) A: Analysis with LSFE Eq. 2, B: with LSFE Eq. 5, C: calculation by means of the parameters of LArSR Eq. 1. c) $\rho_\pi^-=(0.96)$. d) Without OH; $\rho_\pi^-=(0.56)$. e) $r^+=0.17$[1] was used for the interconversion. f) Without NH$_2$; too limited data set. g) Too limited data sets for the 5-X-3 and 6-X-3 benzofuryl systems;[57] further, the data for the pK_a of 5,6-X-benzofurancarboxylic acids are not sufficient.[60] h) The log k/k_0 value for MeO ($=0.53$) was corrected and used; $(\log k/k_0)_{\text{benzofuryl}}=0.9842(\log k/k_0)_{\text{benzothienyl}}+0.013$. i) $\rho_\pi^-=-3.3$. j) $\rho_\pi^-=1.9$.

On the other hand, the $-\rho_i$ values for the 4- and 7-positions in the benzothienyl system are also nearly the same as the value of 4.9±0.2 for VI. The ratio of the values is calculated to be 0.84 (by 4.1/4.9), identical with the position constant in the 2-naphthyl system. The ρ_i values thus obtained by the use of LSFE Eq. 5 may again be concluded to furnish the simple $1/r$ dependency well. Previously, Wells and Adcock argued for the requirement of some angle function, $(\cos\theta)/R^2$, in particular for the dissociation of the 8-X-2 naphthalenecarboxylic acids.[20] The orientational effect, if operative, may be expected to be relatively more important in the 4-X-2 benzothienyl system than in the 8-X-2 naphthyl system because of the larger angle of θ.[23a] However, no orientational factor can be detected in the present results. Further, the azulyl system gives a constant ratio of $\rho_{i,6\text{-X-1}}/\rho_{i,3\text{-X-1}}$ (0.84 for VII and VIII), independent of the different *Pi* effects. Since the reactivities are concerned with nonconjugate positions in the azulyl ring, more data at the conjugate positions would be of much interest.

From the values of ρ_π^+ relative to ρ_i in the series of the 2-benzothienyl system in Table 6, the 6-X-2 system ($\rho_\pi^+/\rho_i=2.8$) can be regarded as a system involving a strong *Pi* exaltation effect. Though the 7-X-2 benzothienyl system (0.7) also shows less exaltation than σ_p^0, as in the case of the 7-X-2 naphthyl, the 4-X-2 (1.4) and 5-X-2 (1.2) systems belong to the intermediate class, with a moderate *Pi* exaltation. These observations indicate the requirement of different resonance parameters of σ_R^+, σ_R^0, and σ_R(BA) for the respective sets to achieve the best fit to Taft's DSP Eq. 4. Generally speaking, however, there is no definite rule for the choice of the most appropriate parameters, especially for any intermediate class of reactivity ($\rho_\pi^+/\rho_i=2$—2.5). Since a different choice of $\bar{\sigma}_R$ causes different $\bar{\rho}_R$ values, the comparison of $\bar{\rho}_I$ and $\bar{\rho}_R$ between different sets of reactivity classes may be difficult. The present ρ_π^+ values, obtained for VI, satisfy not only the sequence, but also the magnitude of Δq, Forsyth's charge difference.[23a]

As has been mentioned before by us[18] and by others,[4] Dewar's FM[3] and many other modified methods for extended *pi*-systems[19,20,23] have, *a priori*, assumed transmission coefficients, especially for *Pi* effects, obtained by means of MO calculations and have then defined the substituent constants to fit the corresponding original phenyl set of reactivities. Although this kind of approach is successful with a very limited reactivity class, the approach can never handle variations in *Pi* effects depending on the types of reactions without any changes in substituent constants and/or model calculations.

In summary, it may be concluded that the electrophilic reactivity sets at B-ring positions in the 2-naphthyl and relevant extended systems can be adequately described by means of the LSFE equation. The resulting empirical ρ_i and ρ_π^+ parameters are reasonably correlated with certain physical properties characteristic of the system and are not inconsistent with our earlier conclusions with regard to the 1-naphthyl and other reactivities. The present discussion has been concerned with the *pi*-donor substituents in electrophilic reactivities, but the treatment seems likewise promising for *pi*-acceptor substituents in nucleophilic reactivities.[50] We believe the present results provide further evidence for the significance of the LSFE equation as well as for the applicability of the universal substituent constants, independent of the reactivity classes.

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The proton NMR spectra were obtained using a Hitachi R-20 or R-24 spectrometer (60 MHz, CW) or JEOL JNM-FX100 (100 MHz, FT), with TMS as the internal standard. The carbon-13 NMR spectra were also obtained with the latter spectrometer at 25 MHz (FT). The chemical shifts are given in ppm downfield from TMS (δ value).

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