mol) were obtained by the procedure for **22**. Recrystallization from CH_3CN–EtOH gave 0.14 g (45%) of **23**: mp 181–184°; electronic (CH_3CN) λ_{max} 625 nm (ϵ 60,800), 520 (25,300), 420 (7500), 327 (26,000), 302 (26,000).

Anal. Calcd for $C_{31}H_{25}BF_4N_4OS_2$: C, 60.0; H, 4.06; N, 9.0; S, 10.3. Found: C, 59.8; H, 4.1; N, 8.9; S, 10.1.

3-Methyl-2-[4,7-bis(3-methyl-2-benzothiazolinylideneamino)-1-phenalenylideneamino]benzothiazolium Fluoroborate (24).—Compounds **19** (0.32 g, 0.002 mol) and **11** (0.19 g, 0.0005 mol) in $ClCH_2CH_2Cl$ for 2 days, recrystallized from CH_3CN, gave 0.3 g (81.4%) of **24** as fine bronze crystals: mp 310°; electronic (CH_3CN) λ_{max} 635 nm (ϵ 40,700), 332 (20,000).

Anal. Calcd for $C_{37}H_{27}BF_4N_6S_3$: C, 60.2; H, 3.7; N, 11.4; S, 13.0. Found: C, 60.2; H, 4.0; N, 11.6; S, 13.1.

1,3-Diethoxy-6-(2-diisopropylamino)vinylphenalenium Fluoroborate (25a).—Compound **3** (1.7 g, 0.005 mol) in CH_3CN (30 ml) was treated with diisopropylethylamine (3–4 ml) at room temperature for 1 day. The solution was concentrated to 10 ml and poured into ether. The dye was filtered and recrystallized from EtOH to give 0.24 g (20%) of **25a**: mp 220–223°; ir (KBr) 1623 (m), 1605 (m), 1540–1580 cm^{-1} (s); nmr (CD_3CN) δ *ca.* 1.5 (m, 18 H, all methyls), *ca.* 4.34 (m, 6 H, 2 $-OCH_2-$, 2 $=NHC<$), 6.84 (d, 1 H, $J = 12$ Hz, $=CH-$), 8.2 (d, 1 H, $J = 12$ Hz, other $=CH-$), 6.56 (s, 1 H, H_2), 7.9 (d, 1 H, $J = 10$ Hz, H_4), 7.6 (m, 2 H, H_5, H_8), 8.45 (d, 1 H, $J = 8$ Hz, H_7), 8.7 (d, 1 H, $J = 8$ Hz, H_9); electronic (CH_3CN, neutral) λ_{max} 667 nm (ϵ 43,000), 613 vibrational (40,000), 400 (3900), 347 (14,200), 310 (24,000).

25b had nmr (TFA)[9] δ 1.3–2.0 (m, 18 H, all methyls), 4.2–5.4 (m, 6 H, 2 $-OCH_2-$, 2 $=NC<$), 5.11 (d, 2 H, $J = 4$ Hz, $-CH_2-$), 8.75 (t, 1 H, $J = 4$ Hz, $-CH=N<)^+$, 7.0 (s, 1 H, H_2), 9.04 (d, 2 H, $J = 7.7$ Hz, H_4 or H_9), 9.11 (d, 2 H, $J = 7.7$ Hz, H_4 or H_9), 7.95 (d, 1 H, $J = 7.7$ Hz, H_5), 8.75 (d, 1 H, $J = 7.7$ Hz, H_7), 8.13 (t, 1 H, $J = 7.7$ Hz, H_8); electronic (CH_3CN, acidic)[15] λ_{max} 418, 400, 355, 253 nm.

Anal. Calcd for $C_{25}H_{32}BF_4NO_2$: C, 64.5; H, 6.9; N, 3.0. Found: C, 65.0; H, 6.7; N, 2.5.

1-Ethoxy-3-[2-(1-ethoxy-6-methoxy-3-phenalenylidene)ethylidene]-6-methoxy-3*H*-phenalene (26a).—Compound **17** (3.4 g, 0.01 mol) in 50 ml of dry, room-temperature pyridine was allowed to stand for 1 day. Crude **26a** was filtered, washed with pyridine, acetone, and ether, and dried. It was recrystallized twice from toluene to remove small amounts of another material: yield 0.3 g (19%); mp 277° dec; ir (KBr) 1610 (m), 1572 (s), 1578 cm^{-1} (s); nmr (TFA)[9] δ 1.74 (t, 6 H, $J = 7$ Hz),[10] 4.72 (q, 4 H, $J = 7$ Hz),[10] 4.47 (s, 6 H, 2 MeO), 4.05 (s, 4 H, $-CH_2CH_2-$), 7.53 (s, 2 H, 2 H_2), 9.06 (d, 2 H, $J = 9$ Hz, 2 H_4), 7.52 (d, 2 H, $J = 9$ Hz, 2 H_5), 9.36 (d, 4 H, $J = 8$ Hz, 2 H_7, 2 H_9), 8.22 (t, 2 H, $J = 8$ Hz, 2 H_8); electronic ($CHCl_3$) λ_{max} 626 nm (ϵ 60,200), 573 vibrational (30,600), 535 vibrational (14,000); (CH_3CN, acidic)[15] λ_{max} 495, 403, 355 nm.

Anal. Calcd for $C_{34}H_{30}O_4$: C, 81.4; H, 6.0. Found: C, 81.0; H, 6.0.

Registry No.—**1** (X = BF_4), 21800-42-0; **2**, 25082-84-2; **3**, 40082-98-2; **4**, 28275-93-6; **5**, 27906-68-9; **6**, 40084-75-1; **7**, 40084-76-2; **8**, 40084-77-3; **9**, 40082-99-3; **10**, 40083-00-9; **11**, 40083-01-0; **12**, 40084-78-4; **13**, 40084-79-5; **14**, 40084-80-8; **15**, 40084-81-9; **16**, 40084-82-0; **17**, 40083-02-1; **18**, 39981-66-3; **19**, 14779-16-9; **20**, 40084-83-1; **22**, 40084-84-2; **23**, 40084-85-3; **24**, 40084-86-4; **25a**, 40084-87-5; **26a**, 39981-68-5; 3-hydroxyphenalenone, 5472-84-4; triethyloxonium fluoroborate, 368-39-8; 6-hydroxyphenalenone, 3352-82-7; 1,3,3-trimethoxypropene, 17576-35-1; 6-ethoxyphenalenone, 39981-69-6; ethyl iodide, 75-03-6; 4-ethoxyphenalenone, 39981-70-9; 7-ethoxyphenalenone, 39981-71-0; 4-hydroxyphenalenone, 39981-72-1; 4,7-diethoxyphenalenone, 39981-73-2; 4,7-dihydroxyphenalenone, 19996-99-7; ethyl 1-(4-methoxy-1-naphthyl)ethylidenecyanoacetate (*E*), 39990-75-5; ethyl 1-(4-methoxy-1-naphthyl)ethylidenecyanoacetate (*Z*), 39990-76-6; acetyl-4-methoxynaphthalene, 24764-66-7; ethyl cyanoacetate, 105-56-6; 3-(4-methoxy-1-naphthyl)butanoic acid, 39981-76-5; 6-methoxy-3-methylphenalenone, 39981-77-6.

Acknowledgment.—The author is indebted to Dr. T. Regan and Mr. R. Young for providing the nmr spectra.

Dyes Containing the Phenalene Ring System. II. Electronic Spectra and Their Correlations with Hückel Molecular Orbital Theory[1]

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Received December 7, 1972

The electronic spectra of 21 closely related cationic compounds containing phenalene rings in conjugation with benzothiazole rings are discussed. Two transitions were observed in the 500–1000-nm region for all dyes containing two benzothiazole groups, and the relative intensities of these transitions were closely related to the substitution patterns on the phenalene rings. A good correlation was obtained between observed transition energies and those calculated by the Hückel molecular orbital method using optimized heteroatom parameters. Polarizations of the allowed transitions were determined from the molecular orbitals for selected cases.

Results

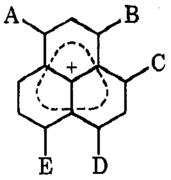
In paper I[1] syntheses were described for a number of dyes in which phenalene rings were in conjugation with benzothiazole rings. The availability of a number of closely related dyes provided a unique opportunity to examine their electronic spectral characteristics in relation to the patterns of substitution on the phenalene rings. Of particular interest were the energies of the transitions and their relative intensities. The compounds studied are summarized in Table I along with their longer wavelength absorption maxima. The transition energies for the transitions of lowest energy or two lowest energies in electron volts are included for comparison with calculated Hückel molecular orbital, (HMO) transition energies in units of β, the resonance integral.

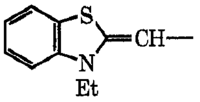
In Figure 1 a plot of observed transition energies (eV) *vs.* those calculated by the HMO method shows, in general, a very good correlation considering the gross approximations inherent in the simple method. The success of the treatment may be attributed largely to two factors: (1) the similarities of the dyes, and (2) the use of optimized heteroatom parameters (see Experimental Section). The line in Figure 1 was that established previously for a large number of cyanine dyes.[2]

[1] Paper I: J. K. Elwood, *J. Org. Chem.*, **38**, 2425 (1973).

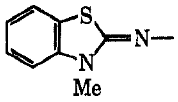
[2] D. M. Sturmer, personal communication.

TABLE I.—ELECTRONIC SPECTRA OF THE PHENALENE COMPOUNDS





R_1



R_2

Compd	A	B	C	D	E	Electronic spectra,[a] λ_{max}, nm (ϵ[b])	E_{max}, eV[c]	Calcd[d] transition energies β	eV
3[e]	EtO	EtO	H	H	H	390 (s)	~3.06[f]	0.828	2.75
						353 (s)			
4	EtO	R_1	H	H	H	577 (35,200)	~2.00[f]	0.508	1.69
						402 (m)	3.08	0.908	3.02
5	R_1	R_1	H	H	H	780 (46,600)	1.59	0.428	1.42
						539 (51,600)	2.30	0.647	2.15
						380 (s)			
6	EtO	R_1	H	R_1	H	812 (97,600)	1.525	0.447	1.49
						558 (18,100)	2.22	0.641	2.13
						398 (21,000)			
7	R_1	EtO	H	R_1	H	840 (106,500)	1.475	0.437	1.45
						540 (vw)	2.29	0.673	2.24
						400 (7700)			
						340 (40,000)			
8[g]	EtO	EtO	H	R_1	H	712 (59,400)	1.74	0.508	1.69
						415 (4750)	2.99	0.921	3.06
9[e]	EtO	H	H	EtO	H	505 (s)	2.46	0.735	2.44
						395 (m)			
10[e]	EtO	H	EtO	H	H	460 (s)	2.69	0.778	2.58
						360 (m)			
11[e]	EtO	H	EtO	H	EtO	450 (s)	2.75	0.826[h]	2.73
						246 (m)			
12	EtO	R_1	H	EtO	H	635 (37,400)	1.95	0.523	1.74
						590 v (46,400)	2.10		
						425 (13,000)	2.92	0.825	2.74
13	R_1	EtO	H	EtO	H	646 (40,200)	1.915	0.514	1.71
						604 v (43,800)	2.05		
						412 (7200)	3.01	0.878	2.92
14	R_1	H	EtO	H	EtO	700 (42,300)	1.77	0.516	1.73
						642 v (48,500)	1.93		
						410 (14,500)	3.02	0.868	2.88
15	R_1	R_1	H	EtO	H	757 (40,000)	1.635	0.459	1.52
						573 (52,700)	2.16	0.615	2.04
						363 (23,000)			
16	R_1	H	R_1	H	EtO	845 (93,800)	1.465	0.447	1.48
						572 (22,600)	2.17	0.641	2.13
						417 (26,000)			
17	EtO	Me	H	MeO	H	495 (s)	2.50	0.749	2.49
						405 (m)			
18	R_1	Me	H	R_1	H	905 (125,000)	1.37	0.418	1.39
						510 (6800)	2.43	0.698	2.32
						430 (4300)			
20	EtO	R_2	H	H	H	517 (24,500)	2.40	0.631	2.10
						395 (12,200)	3.14	0.868	2.88
21	R_2	R_2	H	H	H	592 (23,100)	2.09	0.586	1.95
						499 (33,500)	2.48	0.706	2.35
						358 (9000)			
22	R_2	H	EtO	H	EtO	567 (34,900)	2.185	0.644	2.14
						436 (23,100)	2.84	0.834	2.77
						327 (13,000)			
23	R_2	H	R_2	H	EtO	625 (60,800)	1.98	0.600	1.99
						520 (25,300)	2.38	0.710	2.36
						420 (7500)			
24	R_2	H	R_2	H	R_2	635 (40,700)	1.95	0.605[h]	2.01
						332 (20,000)			

[a] Electronic spectra were run in CH_3CN, unless otherwise specified, on a Perkin-Elmer 350 or 450 UV-VIS-NIR spectrophotometer. At the suggestion of a referee, compounds **4**, **5**, **8**, and **16** were examined in methanol and 2,6-lutidine. The very unsymmetrical dyes **4** and **8** did not show any greater solvent sensitivity than did the relatively symmetrical dyes **5** and **16**. These compounds were shifted bathochromically by *ca.* 10 nm in going from methanol to 2,6-lutidine. [b] Extinction coefficient or letters denoting s = strong, m = moderate, w = weak, v = very. [c] Transition energy in electron volts. [d] Calculated transition energies in units of β, the HMO resonance integral, and in electron volts using the conversion 3.32 eV/β. [e] Spectra run in methylene chloride. [f] The transition was a long-wavelength shoulder on the main absorption. [g] Spectrum run in ethanol. [h] Degenerate highest filled orbitals.

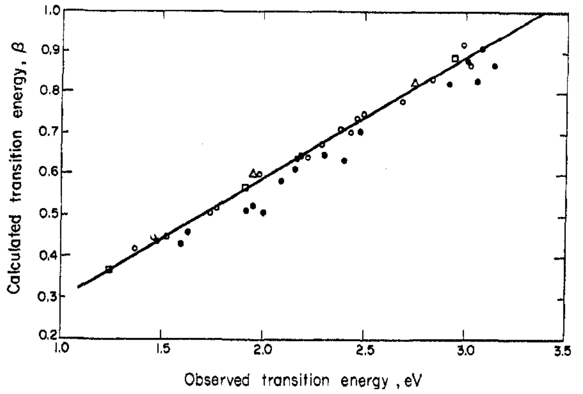
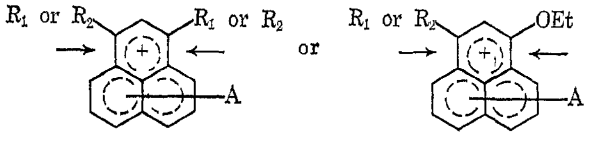


Figure 1.—Plot of observed first or first two transition energies against values calculated by the HMO method. Open squares are for 3,3′-diethylthiacyanine, 3,3′-diethylthiadicarbocyanine, and 3,3′-diethylthiapentacarbocyanine, and serve as reference points. Open circles are for the bulk of the phenalene compounds. Solid circles and open triangles are for the compounds which show deviations for the reasons discussed in the text. Heteroatom parameters used in the calculations are discussed in the Experimental Section.

Discussion

The points for a number of dyes fell somewhat below the line. Examination revealed that these dyes possessed either two R groups or one R group and one ethoxy group joined to the same ring of the phenalene ring system with no other R groups present, as illustrated below (see Table I for definition of R_1 and R_2). These dyes are represented by solid circles in Figure 1.

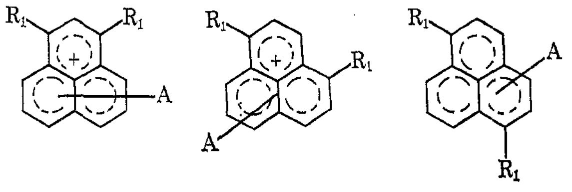


A = H or EtO

A reasonable explanation for this consistent deviation is that the bonds indicated by the arrows have considerably reduced bond order. The bond-order calculations clearly show this; however, the HMO treatment underestimates the reduction. Hünig and Wolff[3] have concluded similarly from nmr and electronic spectral studies on 1,3-disubstituted phenalenium compounds that these bonds are of reduced order and that the compounds should be considered as something intermediate between a completely delocalized system and one in which a naphthalene moiety is fused onto the chromophore chain. When the resonance integrals for these bonds were reduced by 20%, the points were made to move near the line for the cases tried.

Two of the points which fell somewhat above the line for their lowest energy transition are represented by open triangles in Figure 1. These dyes had degenerate highest filled levels of appropriate symmetry to be split by configuration interaction. The spectra appeared as rather broad absorptions consisting of two overlapping bands; however, whether these were due to transitions from different orbitals or from one orbital to different vibrational levels of the excited state is not known.

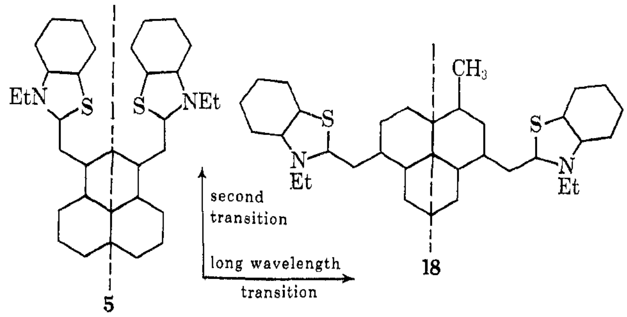
The intensities of the two longest wavelength transitions for the dyes containing two R_1 groups were of particular interest. A comparison of molecular extinction coefficients at λ_{max} revealed that, for the dyes with R_1 groups substituted in 1,3 positions, the intensities of the two transitions were comparable. For dyes with a 1,4-substitution pattern, the long-wavelength transition was much stronger, while those with 1,6 substitution showed only a very weak second transition.



A = H or EtO

longer wavelength ε	4.0-4.7 × 10^4	9.3-9.8 × 10^4	10.5-12.5 × 10^4
shorter wavelength ε	5.1-5.3 × 10^4	1.8-2.3 × 10^4	*ca.* 0.6 × 10^4

An examination of the orbitals for dyes **5** and **18**, which have C_{2v} symmetry (neglecting the small effect of the methyl in **18**), showed that the polarizations of the allowed transitions are as drawn below.[4] Models suggested that the molecules can achieve planarity only by assuming the geometry indicated. In dye **5** the horizontal and vertical dimensions of the molecule are comparable and, hence, the transition moment vectors for the two transitions can have appreciable components along the allowed polarizations.[5] Dye **18** has a long horizontal dimension, and so the long-wavelength transition should be intense; however, the second transition is only allowed with vertical polarization and this component of its transition moment vector must be small. Dyes possessing a 1,4-substitution pattern might be expected to fall in between these two extremes. In fact, an examination of the absorption spectra of all the dyes containing two R groups revealed a clear-cut correlation of relative band intensities to substitution pattern, thus supporting the structural assignments in paper I.[1]



Kiprianov and coworkers[6,7] have studied extensively the spectra of biscyanines containing two conjugated chromophores and have found that the relative intensities of the two longest wavelength absorption bands depended upon the angle formed between the

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[3] S. Hünig and E. Wolff, *Chimia*, **22**, 33 (1968).

[4] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 204-207.

[5] K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, pp 169-176.

[6] V. I. Permagarov, G. G. Dyadyusha, F. A. Mikhailenko, and A. I. Kiprianov, *Dokl. Akad. Nauk SSSR*, **188**, 1098 (1969).

[7] A. I. Kiprianov, *Ind. Chim. Belg.*, **32**, special number 100-2 (1967).

two interacting chromophores. They interpreted these results as being due to the reciprocal influence of two oscillators. This is another way of looking at the phenomenon, and it leads to the same conclusions as derived from the molecular orbital approach.

Experimental Section

The molecular orbital calculations were carried out on an IBM 360-65 computer for molecules requiring over a 41 × 41 matrix or when vectors were required; otherwise, a program written by the author for the IBM-1130 was used. The standard convention was adopted for heteroatoms (x) in which h_x and k_{cx} were related, respectively, to the Coulomb integral (α_x) and the resonance integral (β_{cx}) by the relationships $\alpha_x = \alpha_o + h_x\beta_o$ and $\beta_{cx} = k_{cx}\beta_o$.[8] An auxiliary inductive parameter, AIP = 0.1 Σ_x h_x, was used for all carbon atoms adjacent to heteroatoms.

Heteroatom Parameter Optimization.—Dr. D. M. Sturmer, of the Kodak Research Laboratories, supplied the heteroatom parameters used in this work, which he optimized as follows. A special program was used to calculate transition energies (in units of β_o) for a large number of compounds using an initial set of values (h_x and k_{cx}) for the heteroatom. The calculations for all the compounds were then repeated with another set of values for h_x and k_{cx}. The procedure was repeated continuously while varying h_x and k_{cx} systematically. After each set of calculations a linear correlation was made between the observed transition energies and those calculated with that particular set of values. A contour surface was generated when both h_x and k_{cx} were plotted against the standard deviations of the linear correlations. This produced the best set of values for the heteroatom in those compounds.

The values for sulfur were optimized for a large number of cyanine dyes using for ring nitrogen h_x = 1.5 and k_{cx} = 1.0. The values used for the chain nitrogen in the R_2 groups were optimized for a limited number of 8-azacarbocyanines and 8-azadicarbocyanines. The oxygen parameters were chosen to correlate with the spectra of the 1,6-diethoxy-, 1,4-diethoxy-, and 1,4,7-triethoxyphenalenium ions. The values are summarized below in the order $h_x(k_{cx})$.

S = 0.75 (0.6)
ring alkyl N = 1.5 (1.0)
O = 1.0 (0.7)
chain N = 0.7 (1.0)
CH_3C = −0.1 (inductive model)

Registry No.—**3,** 40083-03-2; **4,** 40083-04-3; **5,** 40083-05-4; **6,** 40083-06-5; **7,** 40036-99-5; **8,** 40083-07-6; **9,** 40083-08-7; **10,** 40083-09-8; **11,** 40083-10-1; **12,** 40083-11-2; **13,** 40083-12-3; **14,** 40083-13-4; **15,** 40083-14-5; **16,** 40083-15-6; **17,** 40083-16-7; **18,** 40083-17-8; **20,** 40037-00-1; **21,** 40083-18-9; **22,** 40083-19-0; **23,** 40083-20-3; **24,** 40083-21-4.

Acknowledgment.—The author is greatly indebted to Dr. D. M. Sturmer for supplying the optimized parameters and for those calculations requiring the use of the IBM 360-65 computer.

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[8] A. Streitwieser, Jr., *Ind. Chim. Belg.*, 117 (1967).

Transmission of Substituent Effects in Heterocyclic Systems. Evidence for Coplanarity in 2-Phenylthiazole, and a Determination of $\sigma_p{}^+$ for the Coplanar Phenyl Substituent[1]

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Received March 26, 1973

The rate of solvolysis of 1-(2-phenyl-5-thiazolyl)ethyl chloride has been studied and compared with other solvolysis data in the thiazole system. The rate of solvolysis is 20 times that expected for a substituent having a $\sigma_p{}^+$ value of −0.179. This rate is, however, consistent with a $\sigma_p{}^+$ value of −0.34. These results are explained in terms of a coplanar thiazole–phenyl system.

In conjunction with studies from these laboratories of the transmission of substituent effects in heterocyclic systems[2–4] we have had occasion to observe the same substituent in several different electronic and geometric environments. Data on the phenyl substituent in the thiazole system are unique and can be used to understand more fully this versatile substituent. In earlier studies of electrophilic substitution reactions it has been observed that the effect of the *p*-phenyl substituent is variable and inconsistent.[5–7] Stock and Brown have pointed out that the σ^+ substituent constant for phenyl is variable[7,8] and shows much more scatter as evaluated from a variety of reactions than do most electrophilic substituent constants, and that this is probably the result of noncoplanarity.

Berliner and Shieh[9] studied the constrained system 1-(2-fluorenyl)ethyl chloride and found its rate of solvolysis to be 700 times that of 1-phenylethyl chloride. In evaluating the large rate acceleration in this system and in 2-(2-fluorenyl)-2-chloropropane, Brown and Inukai[10] pointed out that a phenyl moiety constrained to coplanarity is much more effective in electron release than a typical biphenyl system. They calculated a replacement constant, $\sigma_{Ar}{}^+$, for the fluorenyl moiety of −0.49. It may be concluded that a *p*-phenyl substituent held to a planar geometry should result in a $\sigma_p{}^+$ value of approximately −0.37 (correcting for *m*-CH_2 and *o'*-CH_2).

In our studies of the transmission of substituent effects in thiazoles, we have analyzed the 1-(2-x-5-thiazolyl)ethanol system where x = H, CH_3, Cl, SCH_3, and OCH_3. These data gave excellent correla-

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[1] Supported in part by a grant from the National Science Foundation, GP-6133X.

[2] D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, **34**, 1008 (1969).

[3] D. S. Noyce and R. W. Nichols, *J. Org. Chem.*, **37**, 4306, 4311 (1972).

[4] D. S. Noyce, C. A. Lipinski, and R. W. Nichols, *J. Org. Chem.*, **37**, 2615 (1972).

[5] P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954); P. B. D. de la Mare and M. Hassan, *ibid.*, 3004 (1957).

[6] F. B. Deans, C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 3031 (1959).

[7] L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, **84**, 1242 (1962).

[8] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

[9] E. Berliner and Shieh, *J. Amer. Chem. Soc.*, **79**, 3849 (1957).

[10] H. C. Brown and T. Inukai, *J. Amer. Chem. Soc.*, **83**, 4825 (1961).