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Dyes Containing the Phenalene Ring System. I. Synthesis of Benzothiazole-Containing Dyes

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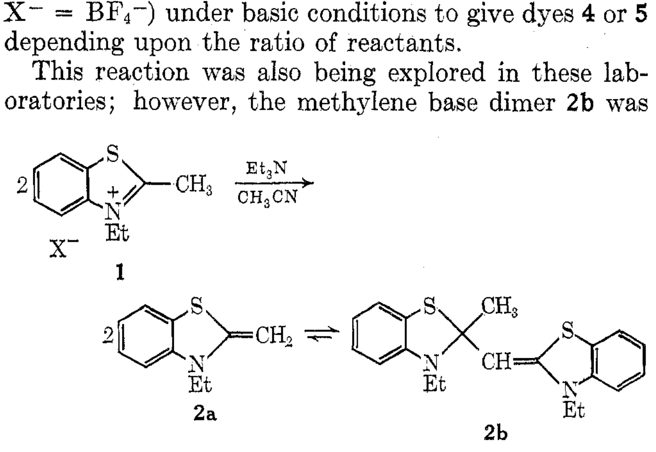
The reactions of 1,3-diethoxy-, 1,4-diethoxy-, 1,6-diethoxy-, 1,4,7-triethoxy-, and 1-ethoxy-6-methoxy-3-methylphenalenium fluoroborates with the methylene base of 3-ethyl-2-methylbenzothiazolium salts and with 3-methyl-2-iminobenzothiazoline gave a variety of dyes of potential photographic interest. The methylene base was found to attack the phenalenium rings at reactive positions bearing hydrogen as well as ethoxy, and to give dyes in the former case by a redox reaction. Some of the dyes absorbed strongly in the near-infrared with very little absorption in the visible. Some unusual chemistry was discovered involving reactions of certain of the alkoxyphenalenium fluoroborates with organic bases.

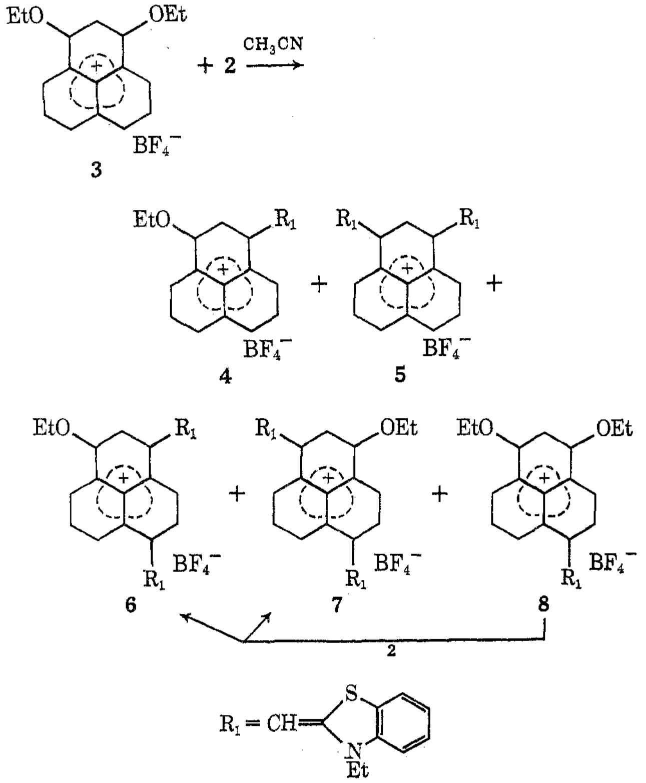
Although the phenalene ring system has been known for nearly a century, most of the interesting chemistry has appeared during the past 20 years.[1] Compounds containing the phenalene ring may be thought of as "dyes" in the sense that they are generally colored; however, dyes with the phenalene ring in direct conjugation with heterocyclic nuclei are less well known.[2-5]

Results and Discussion

In some recent publications by Hünig and Wolff[2-4] 1,3-diethoxyphenalenium fluoroborate (3) was treated with 3-ethyl-2-methylbenzothiazolium fluoroborate (1, $X^- = BF_4^-$) under basic conditions to give dyes 4 or 5 depending upon the ratio of reactants.

This reaction was also being explored in these laboratories; however, the methylene base dimer 2b was generally employed to avoid the need for an auxiliary base. In solution, dimer 2b is known to be in equilibrium with monomer 2a, which is presumably the reactive species.[6] When a large excess of 2 was employed in the reaction with 3, dye 6 and small amounts of dye 7 were obtained in addition to dyes 4 and 5. However, by the dropwise addition of an acetonitrile solution of 2 to a solution of 3 in large excess, the main product was the new dye 8 with 4 as a minor constituent.





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[1] D. H. Reid, *Quart. Rev., Chem. Soc.*, **19**, 274 (1965).

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

[3] S. Hünig and E. Wolff, *Justus Liebigs Ann. Chem.*, **732**, 7 (1970).

[4] S. Hünig and E. Wolff, *Justus Liebigs Ann. Chem.*, **732**, 26 (1970).

[5] E. Herrmann, A. Treibs, and E. Meissner, *Justus Liebigs Ann. Chem.*, **612**, 229 (1958).

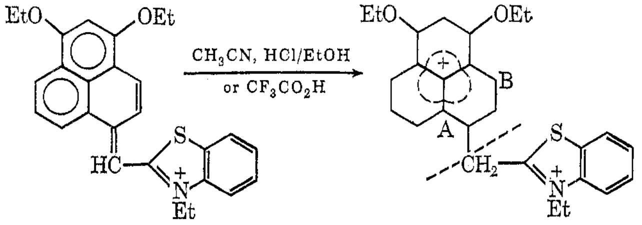
[6] J. R. Owen, *Tetrahedron Lett.*, 2709 (1969).

Clearly, nucleophilic attack can occur at positions of the phenalenium ring carrying hydrogen as well as ethoxy. In the former case, an oxidation–reduction reaction must occur, and the excess **3** presumably functions as a hydride acceptor. Hünig and Wolff have observed similar redox reactions in the reaction of 1-ethoxyphenalenium ions with nitromethane.[4]

It is interesting that in the electronic spectrum of **4** prepared by Hünig and Wolff[4] the absorption band maxima occurred in acetonitrile at 723 nm (ε 2620) as well as at 578 nm (ε 31,800), whereas in the present sample only the absorption at 577 nm (ε 35,200) was observed. It is likely that the former sample contained **8** as an impurity since **8** possesses a maximum at 712 nm (ε 59,400) in acetonitrile.

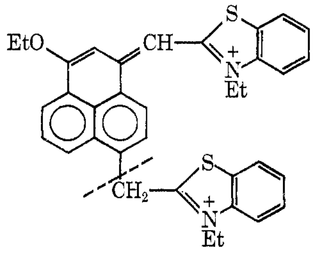
The products obtained in the two separate reactions of **2** with **3** may be explained as follows: (1) with an excess of the phenalenium ion **3**, methylene base **2** attacked either a ring carbon bearing an ethoxy to give **4** or a ring carbon bearing a hydrogen to give **8** *via* a redox reaction; (2) with an excess of **2**, dyes **4** and **5** were readily formed; however, **4** was not the main intermediate in the formation of **5**, since dye **4** was rather unreactive toward **2** and gave only very small amounts of **5** after several days. The other two dyes **6** and **7** were undoubtedly formed from the reaction of **2** with **8**, which was known to be fast. The transient formation of **8** might be expected: although dimer **2b** was in excess relative to **3**, the reactive monomer **2a** probably was not in excess, at least at the point of addition of **3** to the solution.

The electronic spectrum of the protonated species **8b** resembled that of **3** and **1** superimposed and lent support to the structure assigned to **8a**. The nmr in CF_3CO_2H of **8b** in comparison with **3** showed a loss of one of the resonances at δ 8.9, suggesting attachment at position A in **8b**, since attachment at position B would have resulted in loss of a low-field resonance at δ 9.17, attributed to the hydrogen peri to the ethoxy groups.

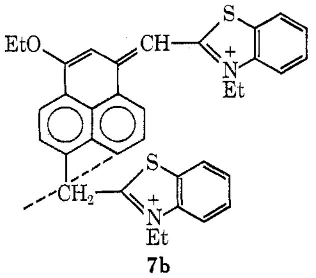


8a **8b**

The electronic spectra of acidic solutions of **6** and **7** were nearly identical and resembled remarkably the superimposed spectra of dyes **4** and **1**. However, a distinction could not be made without further evidence.

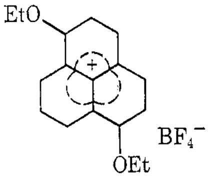


6b

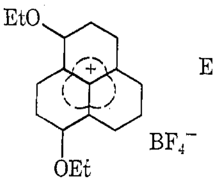


7b

The work was extended by preparing the ethoxyphenalenium salts **9–11** and treating them with methylene base **2** to give, respectively, the three isomeric blue dyes **12–14** (Scheme I). These dyes were separated from others by column chromatography and recrystallization. The three isomeric dyes (**12–14**), together with a fourth isomer, **8**, provided the necessary intermediates for establishing the structures of the dyes *via* the interrelationships outlined in Scheme I. Each of the four isomers was treated with **2** to give different pairs of isomeric dyes containing two heterocyclic moieties per molecule. Only **14** gave a single secondary dye, since attack at either carbon bearing an ethoxy group led to the same dye. These results, coupled with the analytical and spectral data, were sufficient to allow confidence in the structural assignments.



9



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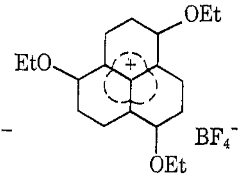
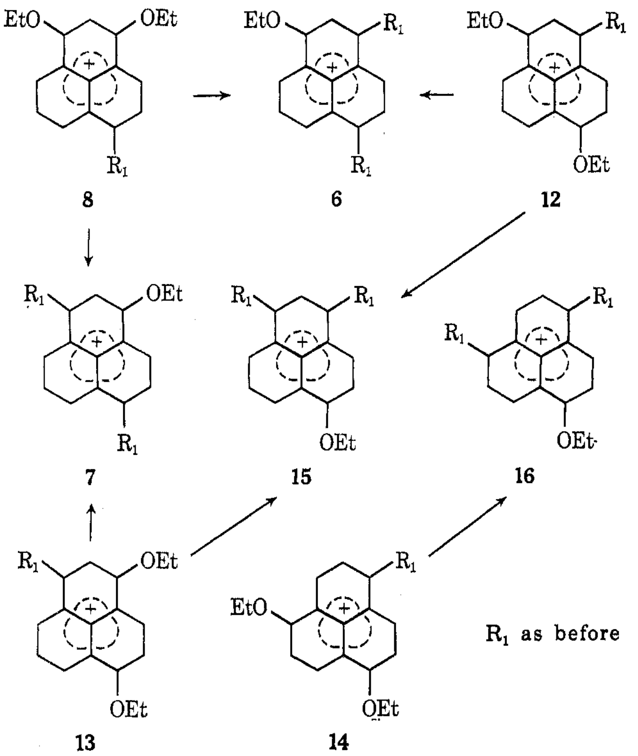
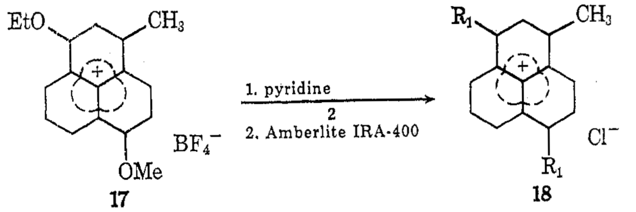


11

SCHEME I

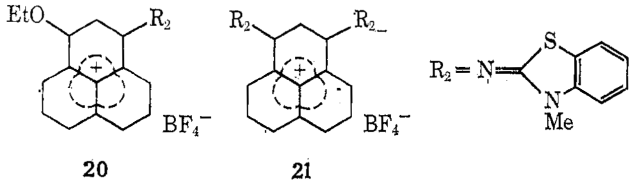


Since **3** reacted with methylene base **2** to give **5**, it was of interest to look for the isomers of **5** derived from **9** and **10**. Strong evidence for the presence of these compounds in the reaction mixtures of **9** and **10** with **2** was obtained, but the quantities of these isomers obtained were insufficient for characterization. By treating the blocked phenalenium ion **17** with **2** the secondary dye **18** was readily produced which had λ_{max} (MeOH) 905 nm (ε 125,000).



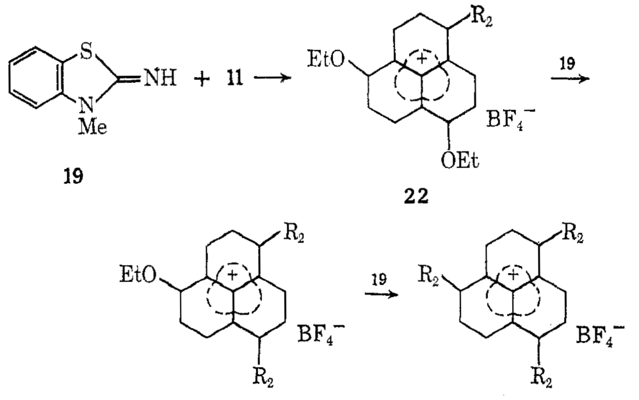
17 18

The reactions of the ethoxyphenalenium ions with 3-methyl-2-iminobenzothiazoline (**19**) differed considerably from their reactions with **2**. Compound **3** proceeded to react cleanly in a stepwise fashion with **19** to give **20** and **21** in agreement with the work of Hünig and Wolff,[3] who prepared the methoxy analog of **20**.



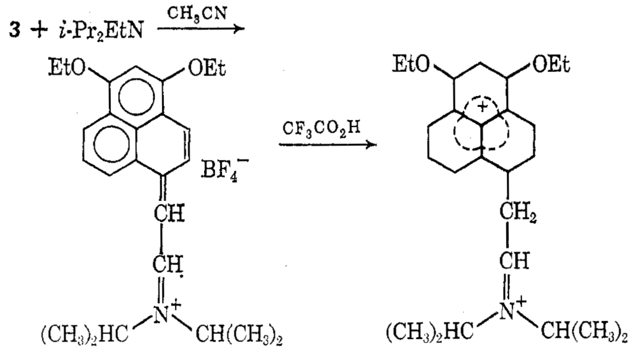
20 21

No products were obtained from attack at ring carbons bearing hydrogen, even when a large excess of **3** was present. This agreed with the findings that strong nitrogen nucleophiles gave no redox products.[4] Likewise, 1,4,7-triethoxyphenalenium fluoroborate (**11**) underwent stepwise attack at the ethoxy carbons, leading to **22**–**24**. In reactions with methylene base **2**, the reactivity of the phenalenium rings toward **2** dropped off rapidly with increasing numbers of R_1 groups in the dye molecules. This was in marked contrast with the reactivity of the phenalenium rings toward **19**. Dye **24** was easily formed from **11** and excess **19** in essentially quantitative yields at room temperature.



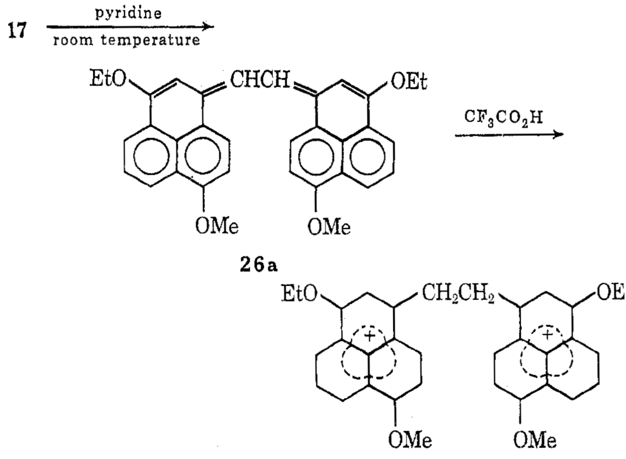
19 22 23 24

As mentioned previously, one of the reasons for using the methylene base **2** instead of **1** was to avoid auxiliary bases which sometimes gave unexpected products. At room temperature, **3** reacted with diisopropylethylamine to give **25a**. Both **25a** and its protonated form **25b** were characterized *via* nmr and their electronic spectra. Other tertiary aliphatic amines with at least one ethyl group reacted similarly.



25a 25b

The methyl group of the blocked phenalenium salt **17** underwent an oxidative coupling reaction in pyridine to give **26a**. The spectra of the doubly protonated form **26b** were in complete agreement with the structure when compared with **17**.



26a 26b

Experimental Section

All melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. The ir spectra were measured as potassium bromide pressings on a Perkin-Elmer 257 grating spectrophotometer. The nmr spectra were recorded with a Varian A-60, Varian T-60, or Brüker 90-MHz instrument, and absorption values are given in parts per million downfield from tetramethylsilane added as the internal standard. The electronic spectra were run on a Perkin-Elmer 350 or 450 UV-VIS-NIR spectrophotometer.

1,3-Diethoxyphenalenium Fluoroborate[7] (3).—To 3-hydroxyphenalenone[8] (98.1 g, 0.50 mol) in methylene chloride (600 ml) was added diisopropylethylamine (67.9 g, 0.525 mol). After all the material was in solution, triethyloxonium fluoroborate (200 g, 1.05 mol) was added in several portions with swirling. The resulting warm solution was refrigerated for several hours, and the crude **3** was filtered, washed with cold CH_2Cl_2 and then cold water, and dried. Recrystallization of **3** from ethanol–acetonitrile (2:1) gave 55.3 g (32.5%): mp 228° dec (lit.[3] mp 226–228° dec); nmr (TFA)[9] δ 1.9 (t, 6 H, $J = 7$ Hz),[10] 4.95 (q, 4 H, $J = 7$ Hz), 7.1 (s, 1 H, H_2),[11] 9.16 (d, 2 H, $J = 8$ Hz, H_4, H_9), 8.17 (t, 2 H, $J = 8$ Hz, H_5, H_8), 8.83 (d, 2 H, $J = 8$ Hz, H_6, H_7); electronic (CH_2Cl_2) λ_{max} 390, 353, 249 nm.

2-[3-Ethoxy-7-(3-ethyl-2-benzothiazolinylidenemethyl)-1-phenalenylidenemethyl]-3-ethylbenzothiazolium Fluoroborate (6).—A solution of **3** (1.02 g, 0.003 mol) in 20 ml of anhydrous CH_3CN was added dropwise over several hours to a stirring room-temperature solution of **2** (1.2 g, 0.007 mol) in anhydrous CH_3CN.

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(7) In view of some discrepancies with the spectral data as described in ref 3, the current results are reported.

(8) B. Iestert, W. Eifler, and H. Göth, *Chem. Ber.*, **101**, 2162 (1968).

(9) TFA is trifluoroacetic acid.

(10) The nmr values in parentheses are for multiplicities, abundancies, coupling constants, and assignments, respectively. Where assignments are not given the values are for the methyl or methylene of an ethyl group.

(11) Assignment of the absorption to the hydrogen at position 2 of the phenalenium ring is denoted by H_2, etc.

The next day the solution was evaporated and the residue was extracted in a Soxhlet apparatus for a day with ether. The ether was discarded and extraction was continued for another day with methanol. Crude **6** was filtered from the cooled methanol solution and some additional crude **6** was removed from the thimble of the Soxhlet extractor. Recrystallization from CH_3CN gave 160 mg (8.3%): mp 260–263°; ir (KBr)[12] 1617 (m), 1565 cm^{-1} (m); nmr (TFA)[9] δ 1.83 (t, 9 H, J = 7 Hz),[10] 4.7–5.4 (m, 6 H), 5.85 (s, 4 H, 2 $-CH_2-$),[13] 7.7–8.6 (m, 11 H, B,[14] H_2, H_5, H_8), 9.17–9.55 (m, 2 H, H_6, H_9), 9.7 (d, 1 H, J = 8 Hz, H_4); electronic (CH_3CN, neutral) λ_{max} 812 nm (ϵ 97,600), 558 (18,100), 398 (21,000); (CH_3CN, acidic)[15] λ_{max} 577, 404, 332, 280 nm.

Anal. Calcd for $C_{35}H_{31}BF_4N_2OS_2$: C, 65.1; H, 4.84; N, 4.3; S, 9.9; F, 11.7. Found: C, 65.1; H, 5.2; N, 4.1; S, 10.1; F, 11.3.

The methanolic filtrate, consisting of a mixture of **4** and **5** with traces of **6** and **7**, was evaporated, and the residue in CH_3CN was chromatographed on a 3-ft column of Fischer neutral alumina partially deactivated by the addition of 20 ml of water/lb. Elution with CH_3CN gave blue dye **4**, magenta dye **5**, and traces of grayish **6** and **7**, in that order. Recrystallization of **4** from EtOH gave 250 mg (17.7%): mp 315°; ir[12] (KBr) 1625 (m), 1565 cm^{-1} (s); nmr (TFA)[9] δ 1.6–2.2 (m, 6 H),[10] 4.9–5.5 (m, 4 H), 5.93 (s, 2 H, $-CH_2-$),[13] 7.9–8.5 (m, 5 H, H_2, B),[14] 9.77 (d, 1 H, J = 7.5 Hz, H_4), 8.6 (t, 2 H, J = 7 Hz, H_5, H_8), 9.0–9.5 (m, 3 H, H_6, H_7, H_9); electronic[7] (CH_3CN, neutral) λ_{max} 577 nm (ϵ 35,200), 402, 332, 282.

Anal. Calcd for $C_{25}H_{22}BF_4NOS$: C, 63.7; H, 4.7; N, 3.0; S, 6.8; F, 16.1; B, 2.3. Found: C, 63.7; H, 4.9; N, 3.3; S, 7.1; F, 16.0; B, 2.4.

Recrystallization of **5** from EtOH gave 50 mg (3%): mp 278–280°; ir (KBr) 1617 (vw), 1585 cm^{-1} (vw).

For specific preparations of **4** and **5** see ref 3.

2-[3-Ethoxy-6-(3-ethyl-2-benzothiazolinylidenemethyl)-1-phenalenylidenemethyl]-3-ethylbenzothiazolium Fluoroborate (7).—To dye **8** (0.52 g, 0.001 mol) in pyridine (200 ml) and ether (100 ml) at −60° was added all at once **2** (0.5 g, 0.003 mol) in a little pyridine. The Dry Ice bath was removed, and the stirring reaction mixture was allowed to come to room temperature (3 hr). The mixture of **7**, **6**, and **8** was filtered and recrystallized from CH_3CN to give a gelatinous suspension to which an equal volume of $CHCl_3$ was added. After this suspension was stirred in the $CHCl_3$–CH_3CN mixture for 10 min, the solid was filtered. A second recrystallization and $CHCl_3$ treatment gave, after filtering, 50 mg of **7** (15% based upon unrecovered **8**): mp 320°; ir (KBr) 1610 (mw), 1565 cm^{-1} (w); nmr (TFA)[9] δ 1.6–2.2 (m, 9 H),[10] 4.9–5.4 (m, 6 H), 5.93 (s, 4 H, 2 $-CH_2-$);[13] electronic (CH_3CN, neutral) λ_{max} 840 nm (ϵ 106,500), 400 (7700), 340 (40,000); (CH_3CN, acidic)[15] λ_{max} 577, 405, 332 nm.

Anal. Calcd for $C_{35}H_{31}BF_4N_2OS_2$: C, 65.1; H, 4.8; S, 9.9; N, 4.3. Found: C, 64.1; H, 4.9; S, 10.2; N, 4.7.

Isomer **7** was almost completely insoluble in $CHCl_3$, whereas **6** had appreciable solubility. Tlc (Eastman cellulose–$CHCl_3$) moved **6**, but **7** remained at the origin.

2-(4,6-Diethoxy-1-phenalenylidenemethyl)-3-ethylbenzothiazolium Fluoroborate (8).—To **3** (7.48 g, 0.022 mol) in stirring, room-temperature CH_3CN (250 ml) was added dropwise over 1 hr **2** (1.77 g, 0.01 mol) in CH_3CN (75 ml). The solution was stirred for an additional 1 hr, concentrated to 50 ml, and added to 1 l. of stirring ether. The solid was filtered, washed with ether, and dissolved in CH_3CN (200 ml). The solution was filtered, and treated while stirring with diisopropylethylamine (10 ml). Soon **8** began separating and after being refrigerated for several hours was filtered, washed with ethanol, and recrystallized from CH_3CN to give 3.1 g (60%) of **8** free of **4**, **5**, **6**, and **7**: mp 290°; ir (KBr) 1619 (m), 1560 (m), 1573 (m), 1587 cm^{-1} (m); nmr (TFA)[9] δ 1.6–2.1 (m, 9 H),[10] 4.6–5.4 (m, 6 H), 5.67 (s, 2 H, $-CH_2-$),[13] 7.8–8.3 (m, 6 H, B,[14] H_2, H_8), 9.17 (d, 2 H, J = 7.5 Hz, H_3, H_7), 7.07 (s, 1 H, H_5), 8.9 (d, 1 H, J = 8 Hz, H_9); electronic (EtOH, neutral) λ_{max} 712 nm (ϵ 59,400), 657 vibrational (51,000), 415 (4750), 362 (16,000), 316 (16,000); (EtOH, acidic)[15] λ_{max} 420, 405, 360 nm.

Anal. Calcd for $C_{27}H_{26}BF_4NO_2S$: C, 62.9; H, 5.1; N, 2.7; B, 2.1; F, 14.75. Found: C, 62.9; H, 5.0; N, 2.5; B, 2.1; F, 14.6.

6-Hydroxyphenalenone[16] was prepared by a modification of the procedure of Cooke, Johnson, and Segal[17] in which 1,3,3-trimethoxypropene was substituted for glycerol and sodium nitrobenzenesulfonate. Yields varied up to 50%; mp >230°.

6-Ethoxyphenalenone.—6-Hydroxyphenalenone (4.9 g, 0.025 mol), ethyl iodide (40 g), and K_2CO_3 (20 g) were refluxed in 500 ml of acetone for 24 hr. After the residue was evaporated, 500 ml each of water and ether were added to dissolve all materials. After the ethereal layer was separated, the aqueous layer was washed twice with ether, and the combined ethereal layers were washed twice with water and dried ($MgSO_4$). Slow evaporation of the ether caused the 6-ethoxyphenalenone to crystallize, giving 4.35 g (77.6%), mp 117–121°.

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4. Found: C, 79.9; H, 5.5.

4-Ethoxyphenalenone and 7-Ethoxyphenalenone.—4-Hydroxyphenalenone was prepared by the synthesis of Cooke and Segal[18] on a 0.2-mol scale and gave 18.2 g (46.4%), mp 267° (lit.[18] mp 260°).

The alkylation of 4-hydroxyphenalenone (5.9 g, 0.03 mol) gave a mixture of the 4- and 7-ethoxy isomers, which were not separated. Recrystallization from ether gave 6.3 g (93.6%).

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4. Found: C, 80.6; H, 5.7.

4,7-Diethoxyphenalenone.—4,7-Dihydroxyphenalenone was prepared by the synthesis of Jarcho[19] and alkylation (21.2 g, 0.1 mol) with ethyl sulfate and 2 *N* NaOH gave 25.5 g (97%) on the alkylation step. Recrystallization from ethanol gave 23.4 g (89%), mp 155–156°.

Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0. Found: C, 76.4; H, 6.3.

1,4,7-Triethoxyphenalenium Fluoroborate (11).—4,7-Diethoxyphenalenone (13.17 g, 0.05 mol) was dissolved in a minimum of warm CH_2Cl_2. To this solution was added triethyloxonium fluoroborate (11.4 g, 0.06 mol) with swirling to dissolve. The flask was stoppered and refrigerated overnight; the solution was filtered and gave yellow-orange **11**. The crystals were washed with CH_2Cl_2 and dried to give 13.12 g (69.3%): mp >270° dec; nmr (CD_3CN) δ 1.64 (t, 9 H, J = 7 Hz),[10] 4.62 (q, 6 H, J = 7 Hz), 7.4 (d, 3 H, J = 9 Hz, H_2, H_5, H_8), 8.86 (d, 3 H, J = 9 Hz, H_3, H_6, H_9); electronic (CH_2Cl_2) λ_{max} 450, 246 nm.

Anal. Calcd for $C_{19}H_{21}BF_4O_3$: C, 59.4; H, 5.5. Found: C, 59.8; H, 5.2.

1,6-Diethoxyphenalenium fluoroborate (9) and 1,4-diethoxyphenalenium fluoroborate (10) were prepared by the same procedure as for **11**; however, dilution with ether was required to separate the products, which were hygroscopic.

9 had nmr (CD_3CN) δ 1.67 (t, 6 H, J = 7 Hz), 4.66 (q, 4 H, J = 7 Hz),[10] 7.4 (d, 2 H, J = 9 Hz, H_2, H_5), 8.65 (d, 2 H, J = 9 Hz, H_3, H_4), 9.0 (d, 2 H, J = 8 Hz, H_7, H_9), 8.0 (t, 1 H, J = 8 Hz, H_8); electronic (CH_2Cl_2) λ_{max} 505, 395, 345, 270 nm.

10 had nmr (CD_3CN) δ 1.7 (t, 6 H, J = 7 Hz), 4.7 (q, 4 H, J = 7 Hz),[10] 7.44 (d, 1 H, J = 9 Hz, H_2 or H_5), 7.57 (d, 1 H, J = 9 Hz, H_2 or H_5), 8.9 (d, 1 H, J = 9 Hz, H_3), 8.66 (d, 1 H, J = 9 Hz, H_6), 8.6 (m, 1 H, H_7), 7.9 (t, 1 H, J = 7.5 Hz, H_8), 8.8 (m, 1 H, H_9); electronic (CH_2Cl_2) λ_{max} 460, 360, 256 nm.

2-(3,7-Diethoxy-1-phenalenylidenemethyl)-3-ethylbenzothiazolium Fluoroborate (12).—To **9** (0.68 g, 0.002 mol) in 50 ml of stirring CH_3CN was added dropwise over 1 hr **2** (0.18 g, 0.001 mol) in 40 ml of CH_3CN. The next day the solution was evaporated to dryness, treated with EtOH, and filtered. Recrystallization from 2:1 EtOH–CH_3CN gave 0.16 g (31%) of **12**: mp 322°; ir (KBr) 1623 (ms), 1565 cm^{-1} (s); nmr (TFA)[9] δ 1.6–2.1 (m, 9 H),[10] 4.6–5.4 (m, 6 H), 5.7 (s, 2 H, $-CH_2-$),[13] 7.8–8.3 (m, 4 H, B),[14] 7.8 (s, 1 H, H_2), 9.63 (d, 2 H, J = 8 Hz, H_4, H_6), 8.4 (t, 1 H, J = 8 Hz, H_5), 7.63 (d, 1 H, J = 9 Hz, H_8), 9.1 (d, 1 H, J = 9 Hz, H_9); electronic (CH_3CN, neutral) λ_{max} 635 nm (ϵ

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[12] Ir bands are reported only for the 1560–1630-cm^{-1} region. Dyes containing ethoxy groups generally gave bands of moderate intensity in the 1600–1630-cm^{-1} and in the 1560–1600-cm^{-1} regions. In the absence of ethoxy groups only weak bands were found in these regions. s = strong, m = medium, w = weak, v = very.

[13] Nmr spectra run in TFA are for protonated dyes. The $-CH_2-$ links the phenalenium ring with the benzothiazolium ring.

[14] B denotes the aromatic hydrogens of the benzothiazolium ring.

[15] Anhydrous solvents were always used. For the acidic spectra in CH_3CN a drop or two of absolute ethanol saturated with HCl was added.

[16] For a more recent preparation see A. L. Das Gupta and R. M. Chatterje, *J. Chem. Soc.*, 1619 (1971).

[17] R. G. Cooke, B. L. Johnson, and W. Segal, *Aust. J. Chem.*, **11**, 233 (1958).

[18] R. G. Cooke and W. Segal, *Aust. J. Chem.*, **8**, 420 (1955).

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37,400), 590 (46,400), 425 (13,000), 367 (13,400), 344 (13,700), 337 (13,700); (CH_3CN, acidic)[15] λ_{max} 510, 402, 355 nm.

Anal. Calcd for $C_{27}H_{26}BF_4NO_2S$: C, 62.9; H, 5.1; S, 6.2; F, 14.75. Found: C, 63.3; H, 5.1; S, 6.3; F, 14.6.

The procedure used for **8** would probably be superior.

2-(3,6-Diethoxy-1-phenalenylidenemethyl)-3-ethylbenzothiazolium Fluoroborate (13).—Using the procedure for **12**, compound **10** (0.68 g, 0.002 mol) and **2** (0.18 g, 0.001 mol) gave 0.12 g (23%) of **13** after chromatography (neutral alumina–CH_3CN): mp 300°; ir (KBr) 1621 (ms), 1560 (ms), and 1575 cm^{-1} (ms); electronic (CH_3CN, neutral) λ_{max} 646 nm (ϵ 40,200), 604 (43,800), 412 (7200), 343 (11,000); (CH_3CN, acidic)[15] λ_{max} 460, 358 nm.

Anal. Calcd for $C_{27}H_{26}BF_4NO_2S$: C, 62.9; H, 5.1; N, 2.7; F, 14.75. Found: C, 63.4; H, 5.5; N, 3.1; F, 14.6.

2-(4,7-Diethoxy-1-phenalenylidenemethyl)-3-ethylbenzothiazolium Fluoroborate (14).—Compounds **11** (1.9 g, 0.005 mol) and **1** ($X^- = BF_4^-$) (1.46 g, 0.0055 mol) were refluxed for 10 min in 30 ml of acetic acid containing diisopropylethylamine (2 ml), cooled, poured into ether, and filtered. Recrystallization twice from CH_3CN gave 1.6 g (62.2%) of **14**: mp 310°; ir (KBr) 1613 (ms), 1564 (m), 1588 cm^{-1} (m); nmr (TFA)[9] δ 1.5–2.1 (m, 9 H),[10] 4.6–5.4 (m, 6 H), 5.7 (s, 2 H, $-CH_2-$),[13] 7.9–8.4 (m, 5 H, B, H_2),[14] 9.38 (d, 1 H, J = 8.5 Hz, H_3), 7.8 (d, 1 H, J = 9.5 Hz, H_5 or H_8), 7.7 (d, 1 H, J = 9.5 Hz, H_5 or H_8), 9.52 (d, 1 H, J = 9 Hz, H_6), 9.09 (d, 1 H, J = 9.5 Hz, H_9); electronic (CH_3CN, neutral) λ_{max} 700 nm (ϵ 42,300), 642 (48,500), 410 (14,500), 385 (13,700), 341 (11,300), 312 (13,300); (CH_3CN, acidic)[15] λ_{max} 480, 370, 261 nm.

Anal. Calcd for $C_{27}H_{26}BF_4NO_2S$: C, 62.9; H, 5.1; N, 2.7; S, 6.2. Found: C, 62.5; H, 5.0; N, 2.9; S, 6.5.

2-[6-Ethoxy-3-(3-ethyl-2-benzothiazolinylidenemethyl)-1-phenalenylidenemethyl]-3-ethylbenzothiazolium Fluoroborate (15).—A mixture of **9** (0.68 g, 0.002 mol) and **2** (1.77 g, 0.01 mol) was stirred at room temperature for 4 days in CH_3CN (90 ml). Filtration removed **6** (0.05 g, 7.7%); the filtrate was concentrated and chromatographed (alumina–CH_3CN) with a 3-ft column as described under the preparation for **6**. After the yellow materials and blue dyes were eluted, the magenta dye **15** was obtained and recrystallized from EtOH–CH_3CN to give 0.12 g (18.6%): mp 313–315°; ir (KBr) 1615 (w), 1580 cm^{-1} (m); nmr (TFA)[9] δ 1.93 (t, 9 H, J = 7 Hz),[10] 4.9–5.4 (m, 6 H), 5.9 (s, 4 H, 2 $-CH_2-$),[13] 8.68 (s, 1 H, H_2), 9.2–9.9 (m, 3 H, H_4, H_7, H_9), 7.8–8.6 (m, 10 H, H_5, H_8, B);[14] electronic (CH_3CN, neutral) λ_{max} 757 nm (ϵ 40,000), 573 (52,700), 362 (23,000), 291 (21,000); (CH_3CN, acidic)[15] λ_{max} 590, 350, 287 nm.

Anal. Calcd for $C_{35}H_{31}BF_4N_2OS_2$: C, 65.1; H, 4.8; S, 9.9. Found: C, 64.8; H, 4.8; S, 9.6.

2-[7-Ethoxy-4-(3-ethyl-2-benzothiazolinylidenemethyl)-1-phenalenylidenemethyl]-3-ethylbenzothiazolium Fluoroborate (16).—Compounds **11** (0.76 g, 0.002 mol) and **1** ($X^- = BF_4^-$) (1.33 g, 0.005 mol) were refluxed for 3 hr in pyridine, cooled, and poured into ether. The dye was filtered and chromatographed as described previously, and the bluish-magenta fraction was retained. Recrystallization from EtOH gave 0.06 g (4.6%): mp 170–175°; ir (KBr) 1605 (mw), 1584 cm^{-1} (mw); electronic (CH_3CN, neutral) λ_{max} 845 nm (ϵ 93,800), 572 (22,600), 417 (26,000), 335 (20,000); (CH_3CN, acidic)[15] λ_{max} 580, 296, 255 nm.

Anal. Calcd for $C_{35}H_{31}BF_4N_2OS_2$: C, 65.1; H, 4.8. Found: C, 65.4; H, 5.2.

Ethyl 1-(4-Methoxy-1-naphthyl)ethylidenecyanoacetate.—1-Acetyl-4-methoxynaphthalene[20] (100.12 g, 0.5 mol), ethyl cyanoacetate (56.6 g, 0.5 mol), acetic acid (30 g, 0.5 mol), ammonium acetate (9.2 g), and benzene (150 ml) were refluxed with stirring for 24 hr; 20–21 ml of water and acetic acid were collected in a Dean–Stark trap. The mixture was evaporated and distilled at 187–205° (2 mm) to give 124 g (84%) of golden syrup as a *ca.* 40:60 mixture of geometric isomers as indicated by nmr.

3-(4-Methoxy-1-naphthyl)butanoic Acid.—The isomer mixture from above (118 g, 0.4 mol) was dissolved in EtOH to give 350 ml. The solution was reduced in a Paar bottle with palladium on charcoal (5 g of 20%) for 14 hr at 35° and 20–40 psi, warmed, and catalyst filtered, and the filtrate was evaporated.

The residue was hydrolyzed by refluxing for 2 days in water (400 ml), $CH_3OCH_2CH_2OH$ (150 ml), and KOH (100 g). The solution was diluted with water (100 ml) and filtered; the filtrate was acidified (HCl). The gummy product was treated several times with fresh water (scratching) and finally with warm petroleum ether (bp 30–60°) to crystallize it.

The crystalline product was melted in a porcelain dish until CO_2 evolution ceased, it was then cooled, and the residue was recrystallized from high-boiling ligroin to give 64 g (65.5%), mp 126–128°.

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.6. Found: C, 73.9; H, 6.5.

6-Methoxy-3-methylphenalenone.—To 3-(4-methoxy-1-naphthyl)butanoic acid (24.4 g, 0.1 mol) in a polyethylene bottle was added cautiously liquid HF (150 ml). After 3 hr at room temperature the solution was slowly poured with stirring onto crushed ice in a large beaker. The dark gummy material became crystalline in an hour or so. Lumps were broken up and the material was finally filtered, washed with water, and dried to give 21.9 g (96.7%) of mixed, ring-closed products (*ca.* 84:16 ratio of six- to five-membered ring components as indicated by nmr). A repeat using 0.15 mol gave 32.9 g (97%).

The isomeric mixture (49.8 g, 0.22 mol) in warm benzene was filtered to remove a little solid, and to the filtrate was added dichlorodicyanoquinone (50 g, 0.22 mol) in a minimum of benzene. The mixture was refrigerated overnight and filtered to give 87.7 g of solids[21] which were stirred for 30 min with aqueous NaOH to dissolve out dichlorodicyanohydroquinone. Filtration gave 33.4 g of crude product, which was recrystallized from methanol to give 31.3 g (75.5%) based upon correct isomer present, mp 166–168°.

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4. Found: C, 79.9; H, 5.8.

1-Ethoxy-6-methoxy-3-methylphenalenium Fluoroborate (17).—6-Methoxy-3-methylphenalenone (29.15 g, 0.13 mol) was alkylated by the procedure for **11** to give 40.2 g (91%) of **17** as a somewhat hygroscopic red-orange powder: mp 225–7° dec; nmr (CD_3CN) δ 1.58 (t, 3 H, J = 7 Hz),[10] 4.38 (q, 2 H, J = 7 Hz), 2.7 (s, 3 H, Me), 4.17 (s, 3 H, MeO), 6.87 (s, 1 H, H_2), 8.34 (d, 1 H, J = 8.7 Hz, H_4), 7.0 (d, 1 H, J = 8.7 Hz, H_5), 8.3 (d, 2 H, J = 7.5 Hz, H_7, H_9), 7.45 (t, 1 H, J = 7.5 Hz, H_8); electronic (CH_3CN) λ_{max} 500, 405, 353, 271 nm.

3-Ethyl-2-[6-(3-ethyl-2-benzothiazolinylidenemethyl)-3-methyl-1-phenalenylidenemethyl]benzothiazolium Chloride (18).—Compounds **17** (3.4 g, 0.01 mol) and **2** (5.3 g, 0.03 mol) were stirred for 3 days at room temperature in pyridine (100 ml). The solid (1.8 g) was filtered and stirred in MeOH (400 ml) with Amberlite IRA-400 resin for 3 hr. The resin and some **26a** were filtered from the cool methanol and the filtrate was evaporated. Recrystallization of the residue from MeCN–H_2O (9:1) gave 1.3 g (22.6%) of **18**: mp 218–220°; ir (KBr) 1606 (w), 1570 cm^{-1} (w); electronic (CH_3CN, neutral) λ_{max} 905 nm (ϵ 125,000), 510 (6800), 430 (4300), 348 (31,700), 327 (33,400); (CH_3CN, acidic)[15] λ_{max} 535, 277 nm.

Anal. Calcd for $C_{34}H_{29}ClN_2S_2\cdot 6H_2O$: C, 70.9; H, 5.28; Cl, 6.1; S, 11.1; N, 4.86. Found: C, 70.9; H, 5.0; Cl, 5.9; S, 10.9; N, 4.5.

2-(3-Ethoxy-1-phenalenylideneamino)-3-methylbenzothiazolium Fluoroborate (20).—Compounds **3** (1.02 g, 0.003 mol) and **19** (0.49 g, 0.003 mol) were stirred for 1 day at room temperature in 1,2-dichloroethane (20 ml). Crude **20** was filtered, washed with ether, and dried to give 0.9 g (65.5%). Recrystallization from CH_3CN gave 0.6 g (43.6%): mp 275°; electronic (CH_3CN) λ_{max} 517 nm (ϵ 24,500), 395 (12,200), 356 (13,200), 304 (11,100).

Anal. Calcd for $C_{23}H_{19}BF_4N_2OS$: C, 60.3; H, 4.2; N, 6.1; S, 7.0. Found: C, 60.1; H, 4.4; N, 6.3; S, 7.0.

2-(4,7-Diethoxy-1-phenalenylideneamino)-3-methylbenzothiazolium Fluoroborate (22).—Compound **19** (0.08 g, 0.0005 mol) in 1,2-dichloroethane was added dropwise to a stirring solution of **11** (0.3 g, 0.00075 mol). After a few hours the solution was poured into ether and filtered. Crude **22** was recrystallized twice from EtOH to give 0.16 g (64%): mp 280–282° dec; electronic (CH_3CN) λ_{max} 567 nm (ϵ 34,900), 436 (23,100), 327 (13,000).

Anal. Calcd for $C_{25}H_{23}BF_4N_2O_2S$: C, 59.8; H, 4.6; N, 5.6; S, 6.4. Found: C, 60.2; H, 4.7; N, 5.2; S, 6.0.

2-[7-Ethoxy-4-(3-methyl-2-benzothiazolinylideneamino)-1-phenalenylideneamino]-3-methylbenzothiazolium Fluoroborate (23).—Compounds **19** (0.16 g, 0.001 mol) and **11** (0.21 g, 0.00055

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[21] Some of the 5-methoxy-1-methylbenz[*e*]indanone may be recovered from the benzene filtrate, mp 119–121°.

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.

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

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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]

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

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