  Bull. Chem. Soc. Jpn., 65, 71—74 (1992)

Synthesis and Characterization of Mono-, Bis-, and Trissubstituted Pyridinium and Pyrylium Dyes

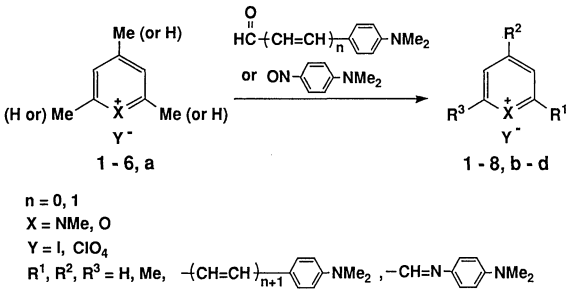
Masaki MATSUI,* Shigeo KAWAMURA, Katsuyoshi SHIBATA, and Hiroshige MURAMATSU
Department of Chemistry, Faculty of Engineering, Gifu University,
Yanagido 1-1, Gifu 501-11
(Received July 12, 1991)

A series of mono-, bis-, and trissubstituted pyridinium and pyrylium dyes have been synthesized by the condensation of methylpyridinium and methylpyrylium salts with aldehydes or nitroso compound. Large bathochromic shifts were observed in the following order, both in substituted azomethine pyridinium and pyrylium dyes, mono<bis<tris. The magnitude of the shift appeared in the order of multiple bonds, -CH=CH- < -CH=CH-CH=CH- < -CH=N-.

Much attention has been focused on the synthesis and characterization of functional dyes.[1] From the viewpoint of practical use, the synthesis of stable dyes for light, heat, oxygen, and ozone is important. Especially, much effort has been devoted to improve photostability of dyes. In order to depress the photofading of dyes, addition of UV absorbers, singlet oxygen quenchers, and antioxidants to the material and the introduction of halogen atoms or a trifluoromethyl group into a dye molecule have been proposed. The mechanism of photofading is complicated and both reductive and oxidative processes, depending on the circumstances, proceed to discolor dyes.[2] Indigo (CI Vat Blue 1),[3] Crystal Violet (CI Basic Violet 3),[4] quinophthalone dye,[5] and cyanine dye[6] were oxidized under UV irradiation to give the corresponding carbonyl compounds. Thus, one of the reactive moieties of dye molecules under an oxidative atmosphere is the olefinic bond. If a molecule has any substituted multiple bonds conjugated with the chromophore, the photostability of the molecule may be improved. In this report, the synthesis and absorption spectra of mono-, bis-, and trissubstituted pyridinium and pyrylium dyes have been examined.

Results and Discussion

Scheme 1 shows a synthetic path of pyridinium and pyrylium dyes. All dyes were synthesized by the condensation of methylpyridinium iodides or methylpyrylium perchlorate with an aldehyde or a nitroso compound and purified by column chromatography and/or recrystallization. Though all dyes showed only one spot by thin layer chromatography, to purify pyridinium dyes **4d**, **5b**, **5c**, **5d** and pyrylium dyes **7b**, **8c** was very difficult. The electron impact (EI) mass spectroscopy of pyridinium dyes **1**—**5** showed ion peaks m/z at M^+—MeI. The fast atom bombardment (FAB) mass spectroscopy of the pyridinium and pyrylium dyes showed the ion peaks m/z at M^+—I and M^+—ClO_4, respectively. The syntheses of pyridinium and pyrylium dyes are summarized in Table 1. The dyes were obtained in low to good yields.



Scheme 1.

Table 2 summarizes the absorption data of pyridinium and pyrylium dyes. All dyes showed negative solvatochromism as has been known in the case of cyanine dyes. In a series of (4-dimethylaminostyryl)-1-methylpyridinium dyes **1b**, **2b**, **3b**, **4b**, and **5b**, the absorption band caused no remarkable shifts (Runs 1, 4, 7, 10, and 13). In the case of [(4-dimethylaminophenyl)-1,3-butadienyl]-1-pyridinium dyes **1c**, **2c**, **3c**, **4c**, and **5c**, the absorption bands of bis- and trissubstituted dyes were observed at longer wavelength than monosubstituted dyes (Runs 2, 5, 8, 11, and 14). In a series of mono-, bis-, and tris[(4-dimethylaminophenyl)iminomethyl]-1-methylpyridinium dyes **1d**, **2d**, **3d**, **4d**, and **5d**, the absorption bands in methanol were observed at λ_{max} 496, 503, 545, 540, and 567 nm, respectively (Runs 3, 6, 9, 12, and 15). Thus remarkable bathochromic shifts were observed in the order of iminomethyl substituted pyridinium dyes, mono<bis<tris. No drastic changes of molar extinction coefficients (log ε) of pyridinium dyes were observed. In a series of trissubstituted pyridinium dyes **5b**, **5c**, and **5d**, the absorption bands in methanol were observed at λ_{max} 490, 523, and 567 nm, respectively (Runs 13—15). Thus, larger bathochromic shifts of the absorption band was observed in the following order of multiple bands, -CH=CH- < -CH=CH-CH=CH- < -CH=N-. The same trend was observed in the cases of mono- and bissubstituted pyridinium dyes (Runs 1—12).

Pyrylium dyes **6**—**8** had longer absorption maxima than pyridinium dyes **1**—**5**. [4-(4-Dimethylaminophenyl)-1,3-butadienyl]pyrylium dyes had longer absorption maxima than the corresponding styryl dyes. Larger

Table 1. Syntheses of Pyridinium and Pyrylium Dyes

Run	Compd	Substituent					Yield[a]
		X	Y	R^1	R^2	R^3	%
1	**1b**	NMe	I	$CH=CHC_6H_4NMe_2$	H	H	57
2	**1c**	NMe	I	$(CH=CH)_2C_6H_4NMe_2$	H	H	75
3	**1d**	NMe	I	$CH=NC_6H_4NMe_2$	H	H	41
4	**2b**	NMe	I	H	$CH=CHC_6H_4NMe_2$	H	68
5	**2c**	NMe	I	H	$(CH=CH)_2C_6H_4NMe_2$	H	28
6	**2d**	NMe	I	H	$CH=NC_6H_4NMe_2$	H	30
7	**3b**	NMe	I	$CH=CHC_6H_4NMe_2$	$CH=CHC_6H_4NMe_2$	H	28
8	**3c**	NMe	I	$(CH=CH)_2C_6H_4NMe_2$	$(CH=CH)_2C_6H_4NMe_2$	H	13
9	**3d**	NMe	I	$CH=NC_6H_4NMe_2$	$CH=NC_6H_4NMe_2$	H	8
10	**4b**	NMe	I	$CH=CHC_6H_4NMe_2$	H	$CH=CHC_6H_4NMe_2$	15
11	**4c**	NMe	I	$(CH=CH)_2C_6H_4NMe_2$	H	$(CH=CH)_2C_6H_4NMe_2$	72
12	**4d**	NMe	I	$CH=NC_6H_4NMe_2$	H	$CH=NC_6H_4NMe_2$	10
13	**5b**	NMe	I	$CH=CHC_6H_4NMe_2$	$CH=CHC_6H_4NMe_2$	$CH=CHC_6H_4NMe_2$	9
14	**5c**	NMe	I	$(CH=CH)_2C_6H_4NMe_2$	$(CH=CH)_2C_6H_4NMe_2$	$(CH=CH)_2C_6H_4NMe_2$	10
15	**5d**	NMe	I	$CH=NC_6H_4NMe_2$	$CH=NC_6H_4NMe_2$	$CH=NC_6H_4NMe_2$	5
16	**6b**	O	ClO_4	Me	$CH=CHC_6H_4NMe_2$	Me	90
17	**6c**	O	ClO_4	Me	$(CH=CH)_2C_6H_4NMe_2$	Me	93
18	**7b**	O	ClO_4	$CH=CHC_6H_4NMe_2$	$CH=CHC_6H_4NMe_2$	Me	6
19	**8b**	O	ClO_4	$CH=CHC_6H_4NMe_2$	$CH=CHC_6H_4NMe_2$	$CH=CHC_6H_4NMe_2$	97
20	**8c**	O	ClO_4	$(CH=CH)_2C_6H_4NMe_2$	$(CH=CH)_2C_6H_4NMe_2$	$(CH=CH)_2C_6H_4NMe_2$	5

a) Isolated yield.

bathochromic shift of pyrylium dyes was observed in order of substituted dyes, mono<bis<tris. The absorption bands of **6b**, **7b**, and **8b** in methanol were observed at λ_{max} 570, 669, and 665 nm, respectivelly (Runs 16, 18, and 19).

The shifts of the absorption bands of pyridinium dyes were explained by the PPP MO calculation.[7] The results are summarized in Table 3. In the case of substituted iminomethyl-1-methylpyridinium dyes **1d**, **4d**, and **5d**, the proportion of the increase of HOMO energy level (ε_{HO}) was greater than that of LUMO energy level (ε_{LU}) in the order of substituted dyes, mono (**1d**)<bis (**4d**)<tris (**5d**) (Runs 1—3). Therefore, the calculated first-excited energies (ΔE_1) after configuration interaction treatment increased in the order of substituted dyes, tris (**5d**)<bis (**4d**)<mono (**1d**). In a series of trissubstituted pyridinium dyes **5b**, **5c**, and **5d**, the proportion of the increase of ε_{LU} was greater than that of ε_{HO} in the order of multiple bonds, -CH=N- (**5d**)< -CH=CH-CH=CH- (**5c**)< -CH=CH- (**5b**) (Runs 3—5). Therefore, the ΔE_1 values increased in the order of multiple bonds, -CH=N- (**5d**)< -CH=CH-CH=CH-

Table 2. Absorption Spectra of Pyridinium and Pyrylium Dyes

Run	Compd	in $CHCl_3$		in MeOH	
		λ_{max}/nm	log ε	λ_{max}/nm	log ε
1	**1b**	478	4.5	460	4.6
2	**1c**	508	4.5	480	4.6
3	**1d**	530	4.4	496	4.3
4	**2b**	502	4.8	475	4.6
5	**2c**	525	4.7	491	4.6
6	**2d**	539	4.5	503	4.3
7	**3b**	518	4.9	506	4.6
8	**3c**	557	4.8	532	4.8
9	**3d**	586	4.7	545	4.5
10	**4b**	515	4.8	492	4.8
11	**4c**	552	4.7	520	4.9
12	**4d**	578	4.5	540	4.5
13	**5b**	510	4.8	490	4.6
14	**5c**	559	4.6	523	4.5
15	**5d**	597	4.5	567	4.6
16	**6b**	590	4.5	570	4.6
17	**6c**	662	5.0	643	4.8
18	**7b**	683	4.8	669	4.7
19	**8b**	685	5.0	665	4.9
20	**8c**	781	4.9	745	4.7

Table 3. Calculated and Experimental Spectral Data for Pyridinium Dyes

Run	Compd	Calcd					Exp[a]	
		ε_{HO}/eV	ε_{LU}/eV	ΔE_1/eV	λ_{max}/nm	f[b]	λ_{max}/nm	log ε
1	**1d**	−9.036	−4.370	2.445	507	1.19	496	4.3
2	**3d**	−8.704	−4.396	2.145	578	1.08	545	4.5
3	**4d**	−8.697	−4.198	2.242	553	1.81	540	4.5
4	**5d**	−8.534	−4.198	2.222	558	1.36	567	4.6
5	**5b**	−8.541	−3.670	2.649	468	1.54	490	4.6
6	**5c**	−8.406	−3.916	2.407	515	1.77	523	4.5

a) In MeOH. b) Oscillator strength.

(**5c**)<–CH=CH– (**5b**). The similar trend was observed in the cases of mono- and bissubstituted pyridinium dyes.

Experimental

Instruments. NMR, mass, and UV spectra were recorded on JEOL JNM 270 GX, Shimadzu 9020-DF, and Hitachi 330 spectrophotometers, respectively. Melting points were measured with a Yanagimoto micro melting point apparatus and uncorrected.

Materials. Methylpyridinium iodides (**1a**, **2a**, **3a**, **4a**, and **5a**) and 2,4,6-trimethylpyrylium perchlorate (**6a**) were synthesized as described in the literatures. The physical and spectral data are as follows.

1,2-Dimethylpyridinium Iodide (1a): Yield 83%; mp 228.0—229.0 °C (lit,[8] 229—231 °C); ^{1}H NMR ($CDCl_3$) δ=2.97 (s, 3H), 4.56 (s, 3H), 7.90 (d, J=8.4 Hz, 1H), 7.94 (t, J=7.0 Hz, 1H), 8.36 (t, J=7.9 Hz, 1H), and 9.45 (d, J=6.6 Hz, 1H).

1,4-Dimethylpyridinium Iodide (2a): Yield 48%; mp 153.0—155.0 °C (lit,[8] 153.3—154.3 °C); ^{1}H NMR ($CDCl_3$) δ=2.70 (s, 3H), 4.64 (s, 3H), 7.89 (d, J=6.6 Hz, 2H), and 9.17 (d, J=6.6 Hz, 2H).

1,2,4-Trimethylpyridinium Iodide (3a): Yield 62%; mp 112.0—114.0 °C (lit,[9] 105.5—106.5 °C); ^{1}H NMR ($CDCl_3$) δ=2.63 (s, 3H), 2.92 (s, 3H), 4.48 (s, 3H), 7.71 (d, J=6.2 Hz, 1H), 7.73 (s, 1H), and 9.21 (d, J=6.2 Hz, 1H).

1,2,6-Trimethylpyridinium Iodide (4a): Yield 40%; mp 240.0—243.0 °C (lit,[8] 239—240 °C); ^{1}H NMR ($CDCl_3$) δ=2.97 (s, 6H), 4.30 (s, 3H), 7.78 (d, J=7.7 Hz, 2H), and 8.20 (t, J=7.7 Hz, 1H).

1,2,4,6-Tetramethylpyridinium Iodide (5a): Yield 75%; mp 216.0—218.0 °C (lit,[8] 213—214 °C); ^{1}H NMR ($CDCl_3$) δ=2.55 (s, 3H), 2.90 (s, 6H), 4.30 (s, 3H), and 7.61 (s, 2H).

2,4,6-Trimethylpyrylium Perchlorate (6a): Yield 13%; mp 240 °C (decomp) (lit,[10] 240 °C (decomp)); EIMS (70 eV) m/z (rel intensity) 122 (M^+—ClO_4, 49) and 43 (100).

Synthesis of Mono- and Bissubstituted Pyridinium Dyes (1b—d, 2b—d, 3b—d, 4b—d). In a general procedure, to a methanol solution of methylpyridinium iodide and the corresponding molar equivalent of an aldehyde or a nitroso compound was added piperidine (a few drops). After refluxing the mixture, the solution was cooled to room temperature. The resulting precipitate was filtered and recrystallized from methanol. Physical and spectral data of the pyridinium dyes are as follows.

2-(4-Dimethylaminostyryl)-1-methylpyridinium Iodide (1b): Mp 282.0—283.0 °C; ^{1}H NMR (DMSO-d_6) δ=3.04 (s, 6H), 4.29 (s, 3H), 6.79 (d, J=8.5 Hz, 2H), 7.23 (d, J=15.6 Hz, 1H), 7.69 (t, J=7.0 Hz, 1H), 7.71 (d, J=8.5 Hz, 2H), 7.91 (d, J=15.6 Hz, 1H), 8.34 (t, J=7.9 Hz, 1H), 8.44 (d, J=7.9 Hz, 1H), and 8.74 (d, J=6.1 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 224 (M^+—MeI, 100). Found: C, 52.58; H, 5.28; N, 7.51%. Calcd for $C_{16}H_{19}IN_2$: C, 52.47; H, 5.23; N, 7.65%.

2-[4-(4-Dimethylaminophenyl)-1,3-butadienyl]-1-methylpyridinium Iodide (1c): Mp 224.0—246.0 °C; ^{1}H NMR (DMSO-d_6) δ=2.99 (s, 6H), 4.21 (s, 3H), 6.75 (d, J=9.0 Hz, 2H), 6.95 (d, J=14.9 Hz, 1H), 7.10 (d, J=8.4 Hz, 2H), 7.47 (d, J=9.0 Hz, 2H), 7.73 (t, J=6.8 Hz, 1H), 7.81 (dd, J=14.9 and 9.7 Hz, 1H), 8.35 (t, J=9.2 Hz, 1H), 8.39 (d, J=8.8 Hz, 1H), and 8.77 (d, J=5.9 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 250 (M^+—MeI, 100). Found: C, 54.92; H, 5.47; N, 7.10%. Calcd for $C_{18}H_{21}IN_2$: C, 55.09; H, 5.40; N, 7.14%.

2-[(4-Dimethylaminophenyl)iminomethyl]-1-methylpyridinium Iodide (1d): Mp 208.0—210.0 °C; ^{1}H NMR (DMSO-d_6) δ=3.04 (s, 6H), 4.55 (s, 3H), 6.83 (d, J=9.2 Hz, 2H), 7.62 (d, J=9.2 Hz, 2H), 8.04 (t, J=7.3 Hz, 1H), 8.53 (t, J=7.9 Hz, 1H), 8.66 (d, J=7.9 Hz, 1H), 8.93 (d, J=6.1 Hz, 1H), and 9.02 (s, 1H); EIMS (70 eV) m/z (rel intensity) 225 (M^+—MeI, 100). Found: C, 49.28; H, 5.30; N, 11.18%. Calcd for $C_{15}H_{18}IN_3$: C, 49.04; H, 4.94; N, 11.44%.

4-(4-Dimethylaminostyryl)-1-methylpyridinium Iodide (2b): Mp 260.0—263.0 °C (lit,[11] 256—258 °C); ^{1}H NMR (DMSO-d_6) δ=3.02 (s, 6H), 4.17 (s, 3H), 6.79 (d, J=9.2 Hz, 2H), 7.17 (d, J=15.9 Hz, 1H), 7.59 (d, J=9.2 Hz, 2H), 7.91 (d, J=15.9 Hz, 1H), 8.04 (d, J=7.0 Hz, 2H), and 8.68 (d, J=7.0 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 224 (M^+—MeI, 100).

4-[4-(4-Dimethylaminophenyl)-1,3-butadienyl]-1-methylpyridinium Iodide (2c): Mp 254.0—255.0 °C; ^{1}H NMR (DMSO-d_6) δ=2.98 (s, 6H), 4.18 (s, 3H), 6.72 (d, J=15.3 Hz, 1H), 6.73 (d, J=9.2 Hz, 2H), 7.01 (d, J=5.5 Hz, 2H), 7.45 (d, J=9.2 Hz, 2H), 7.79 (dt, J=15.3 and 5.5 Hz, 1H), 8.02 (d, J=6.7 Hz, 2H), and 8.69 (d, J=6.7 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 250 (M^+—MeI, 98) and 142 (100). Found: C, 55.01; H, 5.43; N, 7.06%. Calcd for $C_{18}H_{21}IN_2$: C, 55.09; H, 5.40; N, 7.14%.

4-[(4-Dimethylaminophenyl)iminomethyl]-1-methylpyridinium Iodide (2d): Mp 164.0—166.0 °C; ^{1}H NMR (DMSO-d_6) δ=3.02 (s, 6H), 4.33 (s, 3H), 6.82 (d, J=9.2 Hz, 2H), 7.51 (d, J=9.2 Hz, 2H), 8.36 (d, J=6.4 Hz, 2H), 8.93 (s, 1H), and 8.96 (d, J=6.4 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 225 (M^+—MeI, 100). Found: C, 48.88; H, 5.29; N, 11.73%. Calcd for $C_{15}H_{18}I_3N$: C, 49.04; H, 4.94; N, 11.44%.

2,4-Bis(4-dimethylaminostyryl)-1-methylpyridinium Iodide (3b): Mp>300 °C; ^{1}H NMR ($CDCl_3$) δ=3.02 (s, 6H), 3.04 (s, 6H), 4.16 (s, 3H), 6.81 (d, J=8.4 Hz, 4H), 7.12 (d, J=16.1 Hz, 1H), 7.19 (d, J=16.1 Hz, 1H), 7.58 (d, J=8.4 Hz, 2H), 7.70 (d, J=8.4 Hz, 2H), 7.76 (d, J=7.0 Hz, 1H), 7.87 (d, J=16.1 Hz, 1H), 7.89 (d, J=16.1 Hz, 1H), 8.35 (s, 1H), and 8.53 (d, J=7.0 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 369 (M^+—MeI, 100).

2,4-Bis[4-(4-dimethylaminophenyl)-1,3-butadienyl]-1-methylpyridinium Iodide (3c): Mp 256.0—257.0 °C; ^{1}H NMR (DMSO-d_6) δ=2.99 (s, 6H), 3.00 (s, 6H), 4.09 (s, 3H), 6.68 (d, J=15.2 Hz, 1H), 6.74 (d, J=8.8 Hz, 2H), 6.76 (d, J=8.8 Hz, 2H), 6.89 (d, J=15.2 Hz, 1H), 6.99—7.10 (m, 5H), 7.47 (d, J=8.8 Hz, 4H), 7.71—7.85 (m, 2H), 8.29 (s, 1H), and 8.53 (d, J=7.0 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 421 (M^+—MeI, 100). Found: C, 61.46; H, 5.93; N, 7.16%. Calcd for $C_{30}H_{34}IN_3 \cdot H_2O$: C, 61.96; H, 6.23; N, 7.23%.

2,4-Bis[(4-dimethylaminophenyl)iminomethyl]-1-methylpyridinium Iodide (3d): Mp 238.0—239.0 °C; ^{1}H NMR ($CDCl_3$) δ=3.03 (s, 6H), 3.06 (s, 6H), 4.53 (s, 3H), 6.83 (d, J=9.2 Hz, 4H), 7.55 (d, J=9.2 Hz, 2H), 7.63 (d, J=8.2 Hz, 1H), 7.66 (d, J=8.2 Hz, 1H), 7.92 (d, J=9.2 Hz, 2H), 9.01 (s, 2H), and 9.03 (s, 1H); EIMS (70 eV) m/z (rel intensity) 371 (M^+—MeI, 100). Found: C, 54.01; H, 5.46; N, 13.09%. Calcd for $C_{24}H_{28}IN_5 \cdot H_2O$: C, 54.24; H, 5.69; N, 13.18%.

2,6-Bis(4-dimethylaminostyryl)-1-methylpyridinium Iodide (4b): Mp 247.0—248.0 °C (lit,[12] 242—244 °C); ^{1}H NMR ($CDCl_3$) δ=3.04 (s, 12H), 4.41 (s, 3H), 6.69 (d, J=8.8 Hz, 4H), 7.19 (d, J=15.6 Hz, 2H), 7.36 (d, J=15.6 Hz, 2H), 7.64 (d, J=8.8 Hz, 4H), 7.78 (d, J=8.0 Hz, 2H), and 8.08 (t, J=8.0 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 369 (M^+—MeI, 100).

2,6-Bis[4-(4-dimethylaminophenyl)-1,3-butadienyl]-1-

methylpyridinium Iodide (4c): Mp 256.0—257.0 °C; ^{1}H NMR (DMSO-d_6) δ=2.99 (s, 12H), 4.08 (s, 3H), 6.75 (d, J=8.8 Hz, 4H), 6.96—7.14 (m, 6H), 7.45 (d, J=8.8 Hz, 4H), 7.59 (dd, J=15.2 and 9.3 Hz, 2H), 8.05 (d, J=8.1 Hz, 2H), and 8.21 (t, J=8.1 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 421 (M^+—MeI, 22) and 287 (100). Found: C, 61.51; H, 6.03; N, 7.12%. Calcd for $C_{30}H_{34}IN_3 \cdot H_2O$: C, 61.96; H, 6.23; N, 7.23%.

2,6-Bis[(4-dimethylaminophenyl)iminomethyl]-1-methylpyridinium Iodide (4d): Mp 227.0—229.0 °C; ^{1}H NMR (DMSO-d_6) δ=3.05 (s, 12H), 4.64 (s, 3H), 6.84 (d, J=9.2 Hz, 4H), 6.66 (d, J=9.2 Hz, 4H), 8.50 (m, 1H), 8.62 (d, J=8.5 Hz, 2H), and 9.15 (s, 2H); EIMS (70 eV) m/z (rel intensity) 371 (M^+—MeI, 100).

Synthesis of Trissubstituted Pyridinium Methine Dyes (5b, 5c). In a general procedure, to a methanol solution of 1,2,4,6-tetramethylpyridinium iodide (**5a**, 0.5 g, 2 mmol) were added an aldehyde (6 mmol) and piperidine (6 mmol). The mixture was refluxed for 5 h. After evaporation of the solvent, the product was isolated using a column chromatograph (SiO_2, MeOH : CH_2Cl_2=1 : 30).

2,4,6-Tis(4-dimethylaminostyryl)-1-methylpyridinium Iodide (5b): Mp 219.0—222.0 °C; ^{1}H NMR (DMSO-d_6) δ=3.02 (s, 18 H), 4.09 (s, 3H), 6.79 (d, J=8.8 Hz, 4H), 6.80 (d, J=8.8 Hz, 2H), 7.12 (d, J=16.1 Hz, 1H), 7.27 (d, J=16.1 Hz, 2H), 7.59 (d, J=8.8 Hz, 2H), 7.68 (d, J=16.1 Hz, 2H), 7.69 (d, J=8.8 Hz, 4H), 7.97 (d, J=16.1 Hz, 1H), and 8.10 (s, 2H); EIMS (70 eV) m/z (rel intensity) 514 (M^+—MeI, 61) and 142 (100).

2,4,6-Tris[4-(4-dimethylaminophenyl)-1,3-butadienyl]-1-methylpyridinium Iodide (5c): Mp 181.0—183.0 °C; ^{1}H NMR (DMSO-d_6) δ=2.99 (s, 18H), 3.97 (s, 3H), 6.65 (d, J=15.4 Hz, 1H), 6.74 (d, J=9.0 Hz, 2H), 6.75 (d, J=9.0 Hz, 4H), 6.92 (d, J=15.1 Hz, 2H), 6.95—7.12 (m, 7H), 7.45 (d, J=9.0 Hz, 4H), 7.47 (d, J=9.0 Hz, 2H), 7.61 (dd, J=15.1 and 9.5 Hz, 2H), and 8.02 (s, 2H); FABMS m/z 607 (M^+—I).

Synthesis of 2,4,6-Tris[(4-dimethylaminophenyl)iminomethyl]-1-methylpyridinium Iodide (5d). To a methanol solution (10 ml) of 1,2,4,6-tetramethylpyridinium iodide (**5a**, 0.5 g, 2 mmol) were added *N*,*N*-dimethyl-*p*-nitrosoaniline (0.9 g, 6 mmol) and piperidine (a few drops). The mixture was refluxed for 3 h. After the reaction, the solvent was evaporated. The product was isolated using a column chromatograph (SiO_2, MeOH : $CHCl_3$=1 : 3 and SiO_2, MeOH : $CHCl_3$=3 : 20). Mp 134.0—138.0 °C; ^{1}H NMR (DMSO-d_6) δ=3.04 (s, 6H), 3.06 (s, 12H), 4.62 (s, 3H), 6.84 (d, J=9.2 Hz, 2H), 6.86 (d, J=9.2 Hz, 4H), 7.58 (d, J=9.2 Hz, 2H), 7.69 (d, J=9.2 Hz, 4H), 8.89 (s, 2H), 9.08 (s, 1H), and 9.17 (s, 2H); EIMS (70 eV) m/z (rel intensity) 517 (M^+—MeI, 5) and 135 (100).

Synthesis of Pyrylium Dyes 6b, 6c, 7b, 8b, and 8c. In a general procedure, to an ethanol solution (1.5 ml) of 2,4,6-trimethylpyrylium perchlorate was added the corresponding molar equivalents of aldehyde. The mixture was refluxed for 5 h. After cooling to room temperature, the resulting precipitate was filtered and chromatographed (SiO_2, MeOH : CH_2Cl_2=1 : 5).

2,6-Dimethyl-4-(4-dimethylaminostyryl)pyrylium Perchlorate (6b): Mp 190.0—192.0 °C; ^{1}H NMR ($CDCl_3$) δ=2.56 (s, 6H), 3.16 (s, 6H), 6.70 (d, J=9.2 Hz, 2H), 6.84 (d, J=15.3 Hz, 1H), 7.49 (s, 2H), 7.74 (d, J=9.2 Hz, 2H), and 8.23 (d, J=15.3 Hz, 1H); FABMS m/z 254 (M^+—ClO_4).

2,6-Dimethyl-4-[4-(4-dimethylaminophenyl)-1,3-butadienyl]pyrylium Perchlorate (6c): Mp 145 °C (decomp); ^{1}H NMR ($CDCl_3$) δ=2.58 (s, 6H), 3.12 (s, 6H), 6.44 (d, J=15.0 Hz, 1H), 6.80 (d, J=8.5 Hz, 2H), 6.96 (dd, J=15.0 and 11.7 Hz, 1H), 7.40 (s, 2H), 7.53 (d, J=8.5 Hz, 2H), 7.54 (d, J=15.0 Hz, 1H), and 8.26 (dd, J=15.0 and 11.7 Hz, 1H); FABMS m/z 280 (M^+—ClO_4).

2,4-Bis(4-dimethylaminostyryl)-6-methylpyrylium Perchlorate (7b): Mp 182.0—183.0 °C; ^{1}H NMR (DMSO-d_6) δ=2.61 (s, 3H), 3.06 (s, 6H), 3.11 (s, 6H), 6.80 (d, J=8.6 Hz, 2H), 6.85 (d, J=9.2 Hz, 2H), 7.03 (d, J=15.9 Hz, 1H), 7.07 (d, J=15.9 Hz, 1H), 7.52 (s, 1H), 7.56 (s, 1H), 7.66 (d, J=9.2 Hz, 2H), 7.69 (d, J=8.6 Hz, 2H), 7.84 (d, J=15.9 Hz, 1H), and 8.13 (d, J=15.9 Hz, 1H); FABMS m/z 385 (M^+—ClO_4).

2,4,6-Tris(4-dimethylaminostyryl)pyrylium Perchlorate (8b)[13]: Mp 259 °C (decomp); ^{1}H NMR (DMSO-d_6) δ=3.07 (s, 12H), 3.10 (s, 6H), 6.83 (d, J=8.5 Hz, 4H), 6.85 (d, J=8.5 Hz, 2H), 7.04 (d, J=15.5 Hz, 2H), 7.08 (d, J=15.5 Hz, 1H), 7.52 (s, 2H), 7.69 (d, J=8.5 Hz, 2H), 7.73 (d, J=8.5 Hz, 4H), 7.95 (d, J=15.5 Hz, 2H), and 8.04 (d, J=15.5 Hz, 1H); FABMS m/z 516 (M^+—ClO_4).

2,4,6-Tris[4-(4-dimethylaminophenyl)-1,3-butadienyl]pyrylium Perchlorate (8c): Mp 195 °C (decomp); FABMS m/z 594 (M^+—ClO_4).

PPP-MO Calculation. PPP-MO program available from Maruzen was used for the calculation.[14]

References

1) Z. Yoshida and T. Kitao, "Chemistry of Functional Dyes," Mita Press, Tokyo (1989).
2) R. Nakamura and M. Hida, *Sen'i Gakkai Shi,* **38**, T183 (1982).
3) N. Kuramoto and T. Kitao, *J. Soc. Dyers Colour.,* **95**, 257 (1979).
4) N. Kuramoto and T. Kitao, *Dyes Pigm.,* **3**, 49 (1982).
5) N. Kuramoto and T. Kitao, *J. Chem. Soc., Perkin Trans. 2,* **1980**, 1569.
6) G. W. Byers, S. Gross, and P. M. Henrichs, *Photochem. Photobiol.,* **23**, 37 (1976).
7) S. Tokita, M. Matsuoka, Y. Kogo, and H. Kihara, "Kinoseishikiso no Bunsisekkei (Molecular Design of Functional Dyes)," Maruzen, Tokyo (1989).
8) E. M. Koser and P. E. Klinedinst, Jr., *J. Am. Chem. Soc.,* **78**, 3493 (1956).
9) G. V. Boyd, A. W. Ellis, and M. D. Harms, *J. Chem. Soc. C,* **1970**, 800.
10) K. Hauser and H. Kaiser, *Org. Synth.,* Coll. Vol. 5, 1108 (1973).
11) D. N. Kramer, L. P. Bisanta, and R. Bato, *J. Org. Chem.,* **39**, 3132 (1974).
12) R. Wizinger and K. Wagner, *Helv. Chim. Acta,* **34**, 2290 (1951).
13) H. Khedija, H. Strzelecka, and M. Simalty, *Bull. Soc. Chim. Fr.,* **1972**, 3173.
14) H. Kihara and S. Tokita, "PPP-PC," Maruzen, Tokyo (1989).