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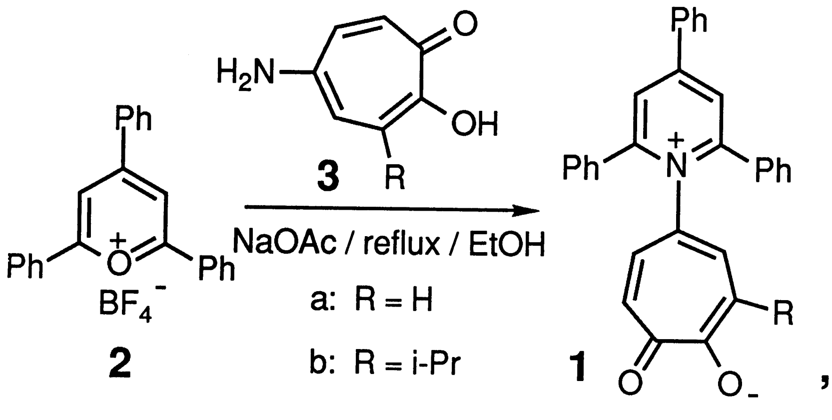
Novel Negative Solvatochromic Betaine Dyes, 5-(2,4,6-Triphenyl-*N*-pyridinio)tropolonates. Synthesis and Characterization

Hitoshi TAKESHITA,* Akira MORI, Nobuo KATO, Eiji WADA, Shuji KANEMASA,
Akira MORI,† Etsuo FUJIMOTO,† and Nobuaki NISHIYAMA††
Institute of Advanced Material Study, 86, Kyushu University,
Kasuga-koen, Kasuga, Fukuoka 816
†Graduate School of Engineering Sciences, 39, Kyushu University,
Kasuga-koen, Kasuga, Fukuoka 816
††Instrumental Analyses Center, Kyushu University,
Kasuga-koen, Kasuga, Fukuoka 816

5-(2,4,6-Triphenyl-*N*-pyridinio)tropolonates, troponoid betaine dyes, were prepared. These dyes were negatively solvatochromic and more blue-shifted than E_T 30 in all of the solvents. The dihedral angle between the pyridinium and the tropolonate rings was larger than that of E_T 30.

2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridinio)phenolate (E_T 30) is known as one of the largest solvatochromic dyes: this dye has an absorption at 453 nm in water and at 810 nm in diphenyl ether, a shift of 357 nm.1) This negative solvatochromism is explained in terms of the large polarity change on excitation from the more polar ground state to the less polar excited state.2) The structural modification of the electron-rich part of E_T 30 is, therefore, interesting in not only the theoretical but also the practical points of view. In this paper, we report the synthesis and the characterization of troponoid betaine dyes, 5-(2,4,6-triphenyl-*N*-pyridinio)tropolonates (**1**), which are expected to have the more polar ground state than E_T 30 since tropolone (3.53 D)3) is more polar than phenol (1.73 D).4)



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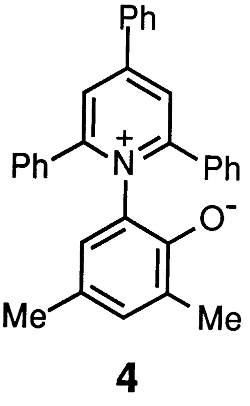

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Dyes **1** were prepared by essentially the same as that of E_T 30: an EtOH solution of 2,4,6-triphenylpyrillium tetrafluoroborate (**2**) and 5-aminotropolones (**3a**: R=H, **3b**: R=i-C_3H_7) was refluxed for 3 h in the presence of NaOAc to give pale yellow solids in 29 and 46% yields, respectively. The subsequent treatment with 10% aqueous NaOH gave red crystals **1a**5) and dark blue crystals **1b**.6) The solvatochromic data for **1**, E_T 30, and 2,4-dimethyl-6-(2,4,6-triphenyl-*N*-pyridinio)phenolate (**4**), an ortho betaine

Table 1. Solvatochromic Data of E_T 30, **1**, and **4**

	λmax/ nm			
Solvent	E_T30	**1a**	**1b**	**4**
Chloroform	731.2	602.4	646.7	
Tetrahydrofuran	764.5	654.0	—b)	
Dichloromethane	695.6	588.0	624.0	652
Pyridine	711.2	594.0	629.1	653
Acetone	677.5	566.0	596.2	636
Ethanol	550.9 (553.6)a)	474.4	504.8	530
Methanol	515.1	408.0	411.7	500
Acetonitrile	621.5	525.6	560.2	622
Water	453.1	406.4	—b)	

a) The values in parentheses were measured in this work. b) Not observed.

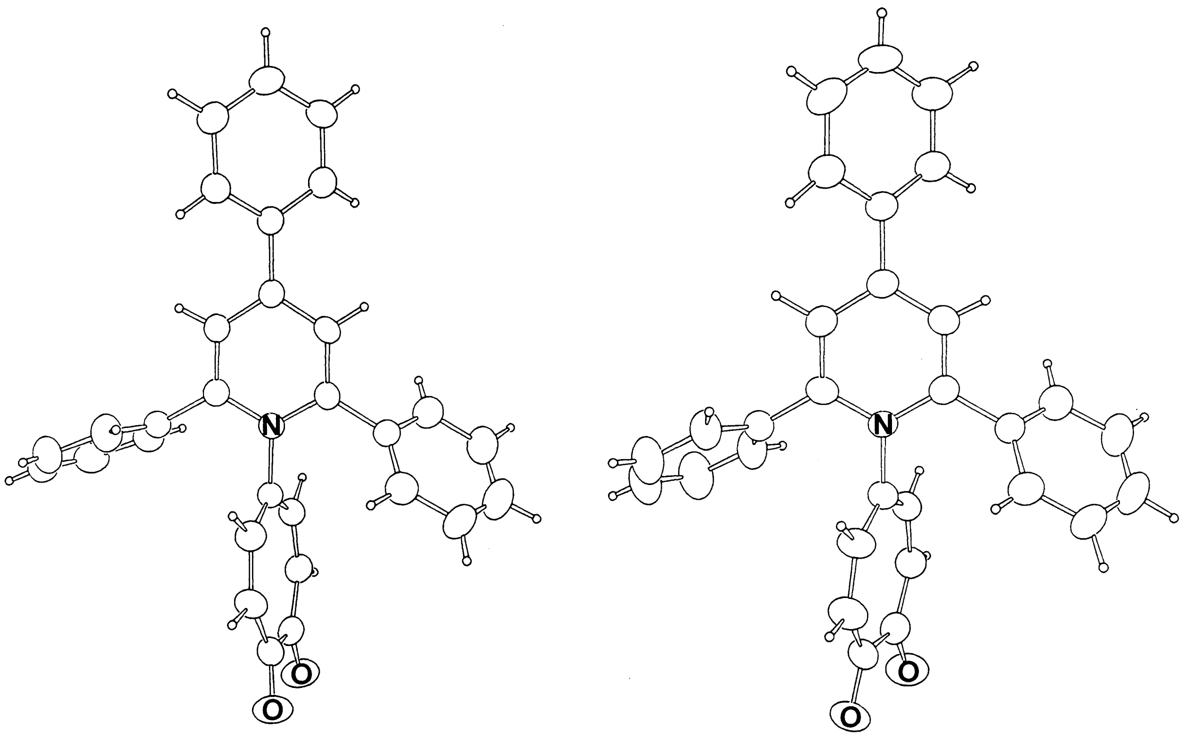

Fig. 1. ORTEP representations of **1aA** (left) and **1aB** (right).

dye,7) are summarized in Table 1. Absorption bands of **1** were shorter than those of E_T 30 and **4** in all of the solvents showing a negative solvatochromism. The blue-shifted absorption maxima of **1** are explained by that the ground state of **1** was more polar than those of E_T 30 and **4** and that the excited state of **1** was less stable than those of E_T 30 and **4** since **1** has an α-diketone structure in the both states. Absorption bands of **1a** were more blue-shifted than **1b**. The extinction coefficient of **1a** is 2650 in acetonitrile, while about 1270 for E_T 30.7) Hence **1a** is more than twice as sensitive for detection of water as E_T 30.

The crystal structure of **1a** in Fig. 1 showed the presence of two conformers (**1aA** and **1aB**) in the crystal lattice, whose dihedral angles between pyridinium and tropolonate rings were 74.6° for **1aA** and 67.9° for **1aB**.8) These angles are larger than that (65°) of the bromo derivative **5** of E_T 309) and smaller than that (90°) of **4**.7) The difference of the dihedral angles seems to mainly depend on the molecular width of the electron-rich part. The C-O bond lengths, 1.255 and 1.240 Å for **1aA** and 1.259 and 1.255 Å for **1aB**, are shorter than those (1.329 and 1.268 Å) of tropolone,10) those of sodium tropolonate (1.285 and 1.279 Å),11) **4** (1.29 Å)7) and **5** (1.29 Å).9) This means that both C-O bonds of **1a** have a significant carbonyl character and that a considerable amount of negative charge is located on the seven-membered ring in the ground state. On the other hand, the C-N bond lengths, 1.474 Å for **1aA** and 1.467 Å for **1aB**, are similar to those of **4** (1.47 Å) and **5** (1.479 Å), suggesting little conjugation between the tropolonate and pyridine rings in the ground state.

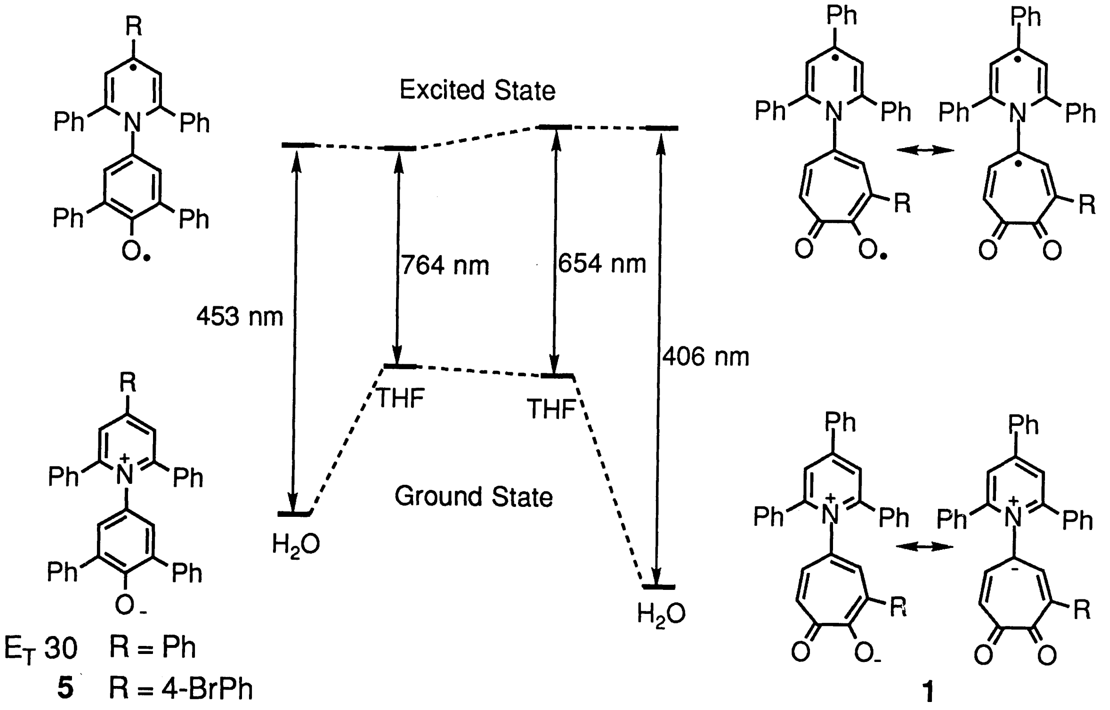

Fig. 2. Energy diagrams of the electronic ground and excited states of **1** and E_T 30.

An isopropyl group at C-3 of the tropolonate ring made the absorption red-shifted. This is attributable to the inductive effect of isopropyl group, since it is hard to assume a steric inhibition by an isopropyl group at C-3 of the conjugated system. Consequently, the isopropyl group destabilizes the negatively charged tropolonate in the ground state and stabilizes the diradical species in the excited state. In parallel, this red shift of **1b** is also explained by the difference of the dipole moment of 3-isopropyltropolone (3.37 D)12) and tropolone (3.53 D).3)

References

1) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Liebigs Ann. Chem.*, **661**, 1 (1963).
2) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York (1968), p. 293.
3) Y. Kurita, *Sci. Repts. Tohoku Univ., Ser. I*, **38**, 85 (1954); *Nature*, **167**, 688 (1951).
4) C. P. Smyth and S. O. Morgan, *J. Am. Chem. Soc.*, **49**, 1030 (1927).
5) **1a**: mp >300 °C; ^{1}H NMR (270 MHz, CD_3OD) δ6.39 (2H, d, *J*=12 Hz), 6.91 (2H, d, *J*=12 Hz), 7.35-7.5 (10H, m), 7.6-7.7 (3H, m), 8.1-8.2 (2H, m), and 8.34 (2H, s). Found: C, 77.54; H, 5.25; N, 2.97%. Calcd for $C_{30}H_{21}NO_2{\cdot}2H_2O$: C, 77.74; H, 5.44; N, 3.02%.
6) **1b**: mp 255-257 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ0.76 (6H, d, *J*=6.8 Hz), 3.56 (1H, sept, *J*=6.8 Hz), 6.21 (1H, d, *J*=11.7 Hz), 6.27 (2H, dd, *J*=11.7, 2.2 Hz), 6.36 (2H, d, *J*=2.2 Hz), 7.3-7.35 (10H, m), 7.6-7.7 (3H, m), 7.9-7.95 (2H, m), and 8.14 (2H, s). Found: C, 82.99; H, 5.78; N, 2.98%. Calcd for $C_{33}H_{27}NO_2{\cdot}1/2H_2O$: C, 82.82; H, 5.90; N, 2.93%.
7) M. S. Paley, E. J. Meehan, C. D. Smith, F. E. Rosenberger, S. C. Howard, and J. M. Harris, *J. Org. Chem.*, **54**, 3432 (1989).
8) The crystal belonged to the monoclinic space group $P2_1/n$ with a=17.827(6) Å, b=19.023(4) Å, c=15.290(5) Å, V=4943.4(7) Å^3, β=107.56(3)°, Z=8, D_{calcd}=1.154 g/cm^3. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.67 cm^{-1}). A total of 11827 reflections was collected by ω-2θ scan technique up to $2\theta \leq 56°$, among which 4138 ($I>3\sigma(I)$) were obtained reflections. The structure was solved by direct methods (*MULTAN* 78) and positions of H were determined by difference Fourier syntheses. Refinement was carried out by full-matrix least squares using F. Thermal parameters for C and O were anisotropic and that of H was fixed at 4.0 Å^2. The final conventional R was 0.071 and Rw=0.096 was obtained for $w=4(F_o)^2/[(F_o)^2]^2$. Atomic scattering factors were taken from International Tables for X-ray Crystallography.13) Computation on PDP11/23 computer was performed by using Enraf-Nonius *SDP* and *ORTEP* II programs.14)
9) R. Allmann, *Z. Kristallogr.*, **128**, 115 (1969).
10) H. Shimanouchi and Y. Sasada, *Tetrahedron Lett.*, **1970**, 2421.
11) Y. Sasada and I. Nitta, *Acta Crystallogr.*, **9**, 205 (1956).
12) Y. Kurita, T. Nozoe, and M. Kubo, *Bull. Chem. Soc. Jpn.*, **26**, 242 (1953).
13) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, (1974), Vol. IV.
14) C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, (1976).

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