An Exceptionally-Large Negative Halochromism in 2-(4-Ethoxycarbonylphenyl)-2,3-dihydro-3,3-dimethyl-5,6-cycloheptapyrazoledione, a Hinopurpurin Derivative

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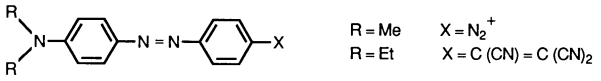
Synopsis. 2-Aryl-2,3-dihydro-3,3-dimethyl-5,6-cycloheptapyrazolediones with an electron-releasing group at C-4 on the benzene ring showed a bathochromic shift in acid solution, whereas the 4-ethoxycarbonylphenyl derivative showed a negative halochromism; 484 nm in ethyl acetate, 517, 566, and 600(sh) nm in trifluoroacetic acid, and 455 nm in concd sulfuric acid.

It is well-known that azo compounds in acidic solution show absorption maxima normally at longer wavelengths than those in neutral solution.[1] However, 4′-diazonio-4-(dimethylamino)azobenzene[2] and 4-(diethylamino)-4′-(tricyanovinyl)azobenzene[3] are outstanding in view of their negative halochromism, i.e., the absorption in acidic solution is at shorter wavelengths than that in neutral solution. We will describe here a new example showing a remarkably large negative halochromism.



Scheme 1.

2-Aryl-2,3-dihydro-3,3-dimethyl-5,6-cycloheptapyrazolediones, hinopurpurins (**1**), prepared from 4-isopropyltropolone and benzene diazonium salts,[4] are known to be stable dyes. Table 1 summarizes the oxidation-reduction potentials ($E^1_{1/2}$ and $E^2_{1/2}$), determined by cyclic voltammetry (CV), and the maxima of the visible absorption spectra. The remote substituents on the benzene ring influence both the potentials and the maxima. Since **1** can be regarded as a masked *p*-tropoquinone, the shapes of the voltammograms, as shown in Fig. 1, might be similar to those of *p*-tropoquinone derivatives.[5,6] This was indeed observed and the more electron-attractive the substituent, the higher were the potentials $E^1_{1/2}$ and $E^2_{1/2}$.

The absorption of **1a** did not change much on changing the solvent. However, the positions of the absorption of **1c** and **1d** were largely dependent on the solvent. Compounds **1b** and **1c** showed positive halochromism; i.e., 13 nm for **1b** and ca. 70 nm for **1c** between chloroform and concd sulfuric acid.

On the other hand, the absorption of **1d** showed a bathochromic shift (ca. 60 nm) in trifluoroacetic acid, whereas in concd sulfuric acid an unusually large negative shift was observed (111 nm between trifluoroacetic acid and concd sulfuric acid and 29 nm between ethyl acetate and concd sulfuric acid) with a decrease of the peak intensity. The wavelength of the absorption peak was ca. 30 nm shorter than that of **1a** in concd sulfuric acid and that of **1d** in ethyl acetate. This negative halochromism of **1d** was also observed in acidic methanol solutions. The reversibility of this color change was confirmed by changes of the acidity of methanol solutions.

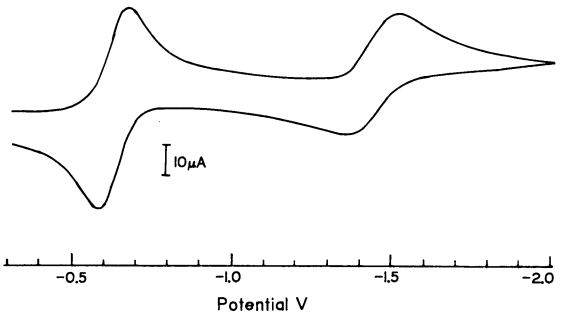
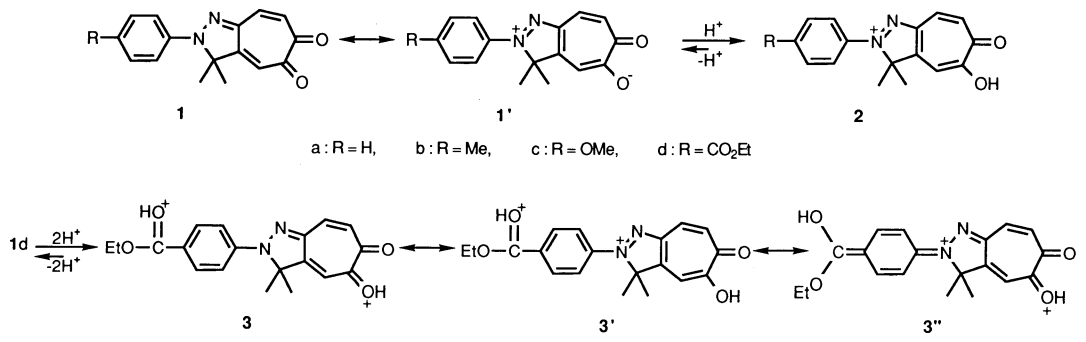


Fig. 1. CV curve of **1d**.



Scheme 2.

Table 1. Oxidation-Reduction Potentials[a] and Maxima of Visible Absorption Bands

	1a	1b	1c	1d
$E^1_{1/2}$	−0.73	−0.75	−0.81	−0.62
$E^2_{1/2}$	−1.45	−1.59	−1.69	−1.43
H_2SO_4	488(25000)	523(35100)	588(46700)	455(27200)
	468(28100)	511(33900)	577(40600)	
CF_3COOH	585(9900, sh)	604(11700, sh)	634(13000, sh)	600(20300, sh)
	500(28200)	516(33400)	562(31400)	566(26600)
				517(31600)
$CHCl_3$	502(34900)	510(34300)	517(24100)	507(42400)
CH_3OH	503(37100)	510(35800)	520(11100)	505(41400)
AcOEt	483(32400)	490(28200)	495(16800)	484(40900)

a) The CV were measured in anhydrous DMF with 0.1 M $(n\text{-Bu})_4NBF_4$ using Pyrex-glass sealed Pt wire as working and counter electrodes and standard Ag/AgCl as a reference electrode at 22—23 °C under N_2 atmosphere with a scan rate of 100 mV s^{-1}.

These phenomena could be explained as follows: There exist the following mesomeric forms (**1** and **1′**). In the ground state, the neutral form is predominant, whereas the ionic form is favored in the excited state. Since a large increase in the dipole moment of the molecule can be expected during the excitation, the energy level of the excited state will be markedly lowered, causing a bathochromic shift.[7] Furthermore, the protonated form (**2**) of **1** seems to be more stable than the neutral one due to the disappearance of the dipole repulsion on the α-diketone part and the formation of a tropolone structure. The electron-releasing substituents on the benzene ring assist this protonation to cause a bathochromic shift as observed in **1b** and **1c**. In the case of **1d**, the ethoxycarbonyl part might be also protonated in concd sulfuric acid. The doubly protonated species **3**, where charges are located at two terminal oxygens, has mesomeric forms such as **3′** and **3″**, the latter of which is a polar and less stable *p*-benzoquinone methide derivative. Accordingly, the excited state is more strongly destabilized than the ground state and the maxima of the absorption would become shorter than those of the neutral form.[7]

In view of recent interest in organic dyes for functional compounds, a rare negative halochromism with exceptionally large differences observed in easily available nonbenzenoid dyes is particularly noteworthy. Furthermore, azo compounds as functional dyes, recently became less attractive in view of their chemical instability; however, the present dyes, hinopurpurins, are stable towards air, light, and acid and base under ordinary conditions, having ring-closed to 5*H*-pyrazole system, and are promising materials.

Experimental

Preparation of Hinopurpurins. To a pyridine solution (5 cm^3) of 4-isopropyltropolone (400 mg, 2.44 mmol) was added drop by drop an aqueous solution of a diazotized amine (3 mmol) at 0 °C to 5 °C with stirring for 2 h. After the solution was diluted with water (40 cm^3), the precipitate was filtered and dried. An EtOH solution of 5-diazonio-4-isopropyltropolone was refluxed for 4 h and cooled to yield crystals by filtration.

1a: Reddish needles, 42%, mp 154—155 °C (from acetone-hexane; lit,[4] mp 148 °C); ^1H NMR ($CDCl_3$)[8] δ=1.75 (6H, s), 6.42 (1H, s), 6.75 (1H, d, *J*=12.1 Hz), 7.32 (1H, t, *J*=7.3 Hz), 7.46 (2H, dd, *J*=9.2, 7.3 Hz), 7.56 (2H, d, *J*=9.2 Hz), and 7.57 (1H, d, *J*=12.1 Hz); ^{13}C NMR ($CDCl_3$) δ=27.8 (2C), 75.7, 116.3, 119.4 (2C), 126.8, 127.4, 129.8 (2C), 132.7, 139.5, 142.9, 157.4, 182.7, and 184.3.

1b: Greenish needles, 52%, mp 256—267 °C (decomp) (from EtOH; lit,[4] mp 244 °C); ^1H NMR (pyridine-d_5) δ=1.60 (6H, s), 2.28 (3H, s), 6.70 (1H, s), 6.83 (1H, d, *J*=12.1 Hz), 7.27 (2H, d, *J*=8.4 Hz), 7.57 (2H, d, *J*=8.4 Hz), and 7.62 (1H, d, *J*=12.1 Hz); ^{13}C NMR (pyridine-d_5) δ=20.7, 27.2 (2C), 76.0, 116.7, 119.9 (2C), 127.3, 130.5 (2C), 132.6, 136.7, 137.7, 142.8, 157.4, 183.3, and 185.1.

1c: Greenish needles, 47%, mp 228—229 °C (from EtOH; lit,[4] 228—229 °C); ^1H NMR ($CDCl_3$) δ=1.69 (6H, s), 3.86 (3H, s), 6.40 (1H, s), 6.72 (1H, d, *J*=12.5 Hz), 6.99 (2H, d, *J*=9.2 Hz), 7.45 (2H, d, *J*=9.2 Hz), and 7.55 (1H, d, *J*=12.5 Hz); ^{13}C NMR ($CDCl_3$) δ=27.7 (2C), 55.7, 76.3, 114.9 (2C), 116.0, 122.2 (2C), 126.8, 132.6, 132.8, 142.5, 156.9, 159.0, 182.7, and 184.3.

1d: Greenish needles, 56%, mp 200—201 °C (from AcOEt-hexane); ^1H NMR ($CDCl_3$) δ=1.41 (3H, t, *J*=7.3 Hz), 1.81 (6H, s), 4.40 (2H, q, *J*=7.3 Hz), 6.43 (1H, s), 6.73 (1H, d, *J*=12.1 Hz), 7.57 (1H, d, *J*=12.1 Hz), 7.62 (2H, d, *J*=9.2 Hz), and 8.11 (2H, d, *J*=9.2 Hz); ^{13}C NMR ($CDCl_3$) δ=14.4, 27.7 (2C), 61.2, 74.9, 117.0, 117.3 (2C), 127.4, 128.4, 131.3 (2C), 132.5, 142.7, 143,7, 157.4, 165.7, 182.7, and 184.2; IR (KBr) 3000—2850, 1700, 1600, 1375, 1275, and 910 cm^{-1}; UV (MeOH) 283 (ε 9600), 302 (5900), 326 (7000), 384 (1400), and 505 nm (41400).

Found: C, 67.61; H, 5.27; N, 8.28%. Calcd for $C_{19}H_{18}N_2O_4$: C, 67.44; H, 5.36; N, 8.28%.

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8) NMR spectra were measured with JEOL FX 100 Model and GSX 270 H Model spectrometers.