Synthesis and Tautomerism of 1,5-Bis(alkylamino)-4*H*-benzo[*a*]phenothiazin-4-ones

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The equimolecular condensation of 2-aminobenzenethiol (**1**) with 4,8-bis(alkylamino)-1,5-naphthoquinones (**2**) in ethanol in the presence of HCl gave near-infrared-absorbing 1,5-bis(alkylamino)-4*H*-benzo[*a*]phenothiazin-4-ones (**3**), which existed as predominant tautomers in various solvents. The reaction mechanism was proposed to involve pathways through the *O*-protonation of **2**, followed by the attack of **1** on the resulting ion, the subsequent oxidation, and the acid-catalyzed intramolecular cyclization of the quinonoid intermediate. The tautomeric equilibria of **2**, **3**, and 5,8-dihydroxy-1,4-naphthoquinone favor the formation of an interconverting hydrogen atom of a higher electron density. The solvatochromic effect of **3** was analyzed by means of the linear solvation energy relationships.

There have been few investigations of 4*H*-benzo[*a*]-phenothiazin-4-ones, although extensive studies of the phenoxazine- and phenothiazine-ring systems have been done and many such compounds have been used as drugs, dyestuffs, and indicators.[1] In order to prepare near-infrared adsorbing quinone imine dyes for optically recording media, we focussed our attention upon the ring-closure reaction of 2-aminobenzenethiol (**1**) with 4,8-bis(alkylamino)-1,5-naphthoquinones (**2**) to give the corresponding 1,5-bis(alkylamino)-4*H*-benzo[*a*]phenothiazin-4-ones (**3**), for it is easy to form thin films of **3** on such substrates as plastics and glass by the use of vapor deposition or by coating solutions of **3** in various organic solvents; the resulting disk has the recording characteristics of a high reflectance and an excellent signal contrast.[2] Furthermore, the synthesis of **3** seems of interest with respect to the absorption characteristics and tautomerism of 1,5-naphthoquinone imines with intramolecularly hydrogen-bonded substituents. Peri-alkylamino groups introduced on unstable 1,5-naphthoquinone exert a high stabilizing effect involving a resonance effect and intramolecular hydrogen bonding. The effects of substituent and solvent on the tautomerism of **3** can be estimated spectroscopically.

As a part of our studies of both the syntheses of quinone imines and their structure-reactivity relationships,[3-9] this paper deals with the preparation of **3** as near-infrared dyes and with the tautomerism of **3** and related compounds on the basis of the spectral data and the semiempirical MNDO SCF MO results.

Theoretical

The MNDO SCF MO calculations[10-12] were carried out by the use of the MNDO program[13] and parametrizations,[10,11] without further modification. In order to shorten the computing time for the geometry optimization of a large molecule, the structural conditions were partly fixed by the following assumptions: (i) the benzenoid carbons and their adjacent hydrogens were coplanar; (ii) similar coplanar configurations held among quinonoid carbons and hydrogens, and (iii) the bond angle N–C–H of the *N*-methyl group was fixed at 109.5°. Computations were carried out on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science.

Results and Discussion

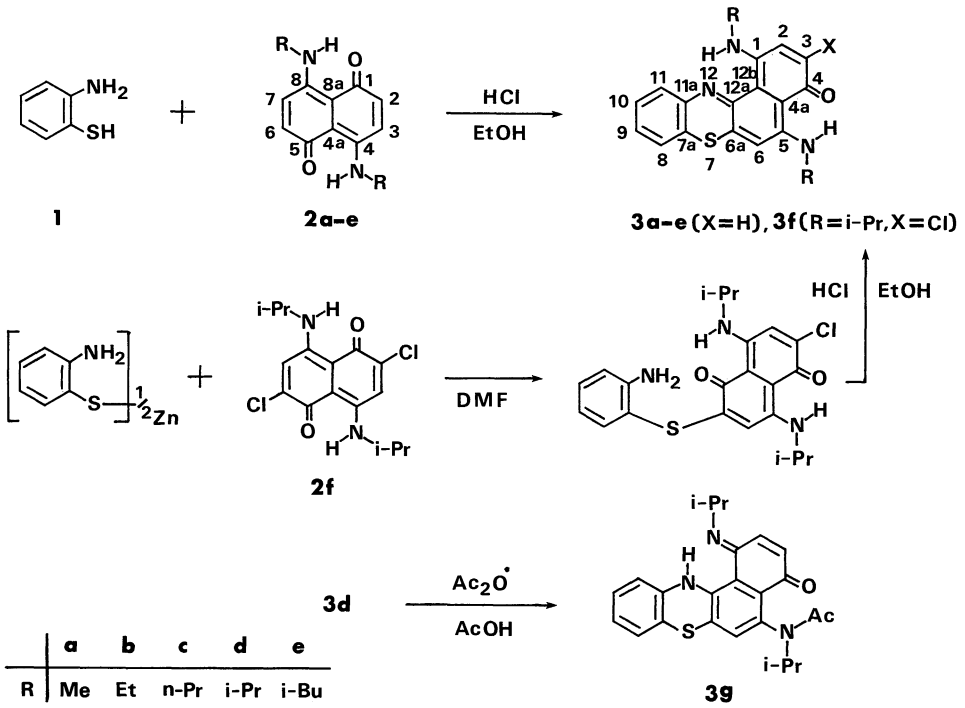
Synthesis of 1,5-Bis(alkylamino)-4*H*-benzo[*a*]phenothiazin-4-ones (3). The ring-closure reaction of an equimolecular mixture of **1** and **2a—e** in ethanol–6 M HCl(4:1, v/v) for 72 h at room temperature gave the corresponding **3a—e** in 45—73% yields (Scheme 1) (1 M=1 mol dm^{-1}). The synthesis of 1,5-bis(isopropylamino)-3-chloro-4*H*-benzo[*a*]phenothiazin-4-one (**3f**) was carried out by condensing zinc 2-aminobenzenethiolates with 2,6-dichloro-4,8-bis(isopropylamino)-1,5-naphthoquinone (**2f**) in *N*,*N*-dimethylformamide, followed by the cyclization of the resulting 2-chloro-4,8-bis(isopropylamino)-6-(2-aminophenylthio)-1,5-naphthoquinone (**4f**) in ethanol–6 M HCl (7:3, v/v) for 20 h at room temperature. The acetylation of **3d** with acetic anhydride in acetic acid for 1 h at room temperature afforded *N*,*N*′-diisopropyl-5-acetamido-4*H*-benzo[*a*]phenothiazin-4-one 1-imine(**3g**) in a yield of 86%.

Spectrometric Identification of Products. The structures of the products thus obtained were confirmed by their ^{1}H NMR, IR, UV-visible, and high-resolution mass spectra (Tables 1—3). Scheme 2 shows four possible quinone monoimine (**I** and **III** forms) and quinone diimine (**II** and **IV** forms) tautomers and the plausible pathways of interconversion in the equilibria of **3a—f** in the various solvents used. In the ^{1}H NMR spectra of **3a—f** in $CDCl_3$, the observed multiplicities of the methine, methylene, or methyl protons adjacent to the nitrogen atoms in the 1- and 5-substituents suggest the existence of NH protons, indicating that the predominant tautomers in $CDCl_3$ are quinone monoimine forms bearing 1- and 5-

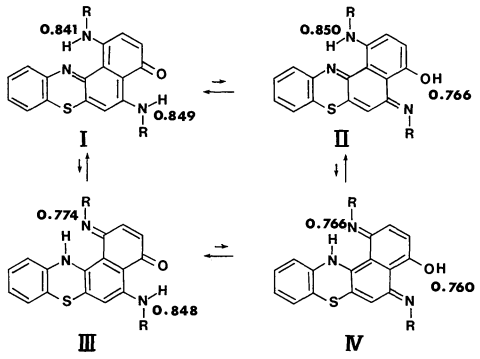
Table 1. Physical and Spectral Properties of 1,5-Bis(alkylamino)-4*H*-benzo[*a*]phenothiazin-4-ones (**3**)

Compd	Substituent[a]	Yield %	Mp °C	IR (KBr, cm^{-1}) C=O	IR (KBr, cm^{-1}) C=N	^1H NMR ($CDCl_3$)[b] δ	HRMS (M^+) Found (Calcd)
3a	-NHMe	58	135—137[c]	1612	1597	3.00 and 3.06 (d, 3H, Me, J=6 Hz)×2, 6.41 (s, 1H, H^6), 6.84—7.16 (m, 4H, arom), 6.93 (d, 1H, H^3, J=10 Hz), 7.06 (d, 1H, H^2, J=10 Hz), 13.34 (br, 2H, NH)	321.0934 (321.0938)
3b	-NHEt	47	209—211[c]	1617	1598	1.24 and 1.36 (t, 3H, Me, J=7 Hz)×2, 3.52 and 3.56 (qn, 2H, CH_2, J=7 Hz)×2, 6.56 (s, 1H, H^6), 6.88—7.22 (m, 4H, arom), 6.98 (d, 1H, H^3, J=10 Hz), 7.15 (d, 1H, H^2, J=10 Hz), 13.59 (br, 2H, NH)	349.1272 (349.1245)
3c	-NH(*n*-Pr)	45	138—139[c]	1618	1597	1.07 and 1.12 (t, 3H, Me, J=7 Hz)×2, 1.82 and 1.85 (qn, 2H, CH_2, J=7 Hz)×2, 3.38 and 3.46 (q, 2H, NCH_2, J=7 Hz), 6.58 (s, 1H, H^6), 6.88—7.35 (m, 4H, arom), 6.98 (d, 1H, H^3, J=10 Hz), 7.16 (d, 1H, H^2, J=10 Hz), 13.67 (br, 2H, NH)	377.1532 (377.1557)
3d	-NH(*i*-Pr)	68	121—122	1624	1595	1.36 and 1.43 (d, 6H, Me, J=6 Hz)×2, 3.90 and 4.09 (o, 1H, CH, J=6 Hz)×2, 6.65 (s, 1H, H^6), 6.89—7.30 (m, 4H, arom), 6.98 (d, 1H, H^3, J=10 Hz), 7.21 (d, 1H, H^2, J=10 Hz), 13.81 (br, 2H, NH)	377.1550 (377.1564)
3e	-NH(*i*-Bu)	73	147—149[c]	1618	1596	0.98 and 1.02 (d, 6H, Me, J=6 Hz)×2, 1.96 and 2.02 (n, 1H, J=6 Hz), 3.24 and 3.27 (t, 2H, J=6 Hz)×2, 6.57 (s, 1H, H^6), 6.88—7.25 (m, 4H, arom), 6.82 (d, 1H, H^3, J=10 Hz), 7.17 (d, 1H, H^2, J=10 Hz), 13.56 and 13.83 (br, 1H, NH)×2	405.1913 (405.1869)
3f	-NH(*i*-Pr) 3-Cl	72	152—154	1604	1593	1.36 and 1.42 (d, 6H, Me, J=6 Hz)×2, 3.92 and 3.98 (o, 1H, CH, J=6 Hz)×2, 6.64 (s, 1H, H^6), 6.90—7.30 (m, 4H, arom), 7.38 (s, 1H, H^2), 13.54 and 14.30 (br, 1H, NH)×2	411.1187 (411.1175)
3g	=N(*i*-Pr) -NAc(*i*-Pr)	86	157—159	1630	1581	0.76 and 1.16 (d, 3H, Me, J=6.5 Hz)×2, 1.43 and 1.52 (d, 3H, Me, J=6 Hz)×2, 1.73 (s, 3H, Ac), 4.37 (sp, 1H, CH, J=6 Hz), 4.80 (sp, 1H, CH, J=6.5 Hz), 6.52 (d, 1H, H^3, J=10 Hz), 6.70 (s, 1H, H^6), 6.43—7.10 (m, 4H, arom), 7.40 (d, 1H, H^2, J=10 Hz), 13.97 (br, 1H, NH)	419.1678 (419.1670)

a) For the predominant tautomer. b) Using the following abbreviations: s=singlet, d=doublet, t=triplet. q=quartet, qn=quintet, sp=septet, o=octet, n=nonet, m=multiplet, br=broad, arom=aromatic. c) Decomposition.



Scheme 1. Route for preparation of **3a—g**, illustrating the atomic numberings of **2** and **3** used in this paper.



Scheme 2. Generally possible tautomeric forms of **3** and the plausible pathways of interconversion, along with the MNDO electron densities (cf. Table 5) of their exchangeable hydrogen atoms.

bis(alkylamino) groups. The interconversion of the **I** form to the **II** or the **III** form in $CDCl_3$ was so slow that the NH proton was coupled to the adjacent CH protons on the ^1H NMR time scale.

The predominant tautomer for **3g** was confirmed to be *N,N'*-diisopropyl-5-acetamido-4*H*-benzo[*a*]phenothiazin-4-one 1-imine on the basis of the following results: (i) septet splits for both the *N*-isopropyl methine protons, indicating the absence of the neighboring NH proton; (ii) the chemical shift (δ 1.73) of acetyl protons bonded to heteroatom[14a]; (iii) two carbonyl stretching vibration bands at 1630 and 1655 cm^{-1}, indicating the presence of quinonoid oxygen and amides,[14b] and (iv) the upfield shift of the phenylene protons compared with those in **3d**, attributable to the electron-donating $N^{12}H$ group changed from the electron-accepting imino group.

However, the general coexistence of the other tautomers of **3a—g** was suggested by their IR and visible absorption spectra. In the IR spectra of **3a—f**, the C–O stretching vibration bands were observed near 1200 cm^{-1}, indicating the presence of phenolic OH groups;[14c] in the case of **3g**, the 5-substituent no longer bears any exchanging proton responsible for the tautomerism between the **I** and the **II** forms.

Effect of Substituent on Visible Absorption Spectra of 1,5-Bis(alkylamino)-4*H*-benzo[*a*]phenothiazin-4-ones (3). In the visible spectrum of **3d** in chloroform, there were several diagnostic bands, together with a few shoulders; in the UV region, two absorption bands were observed at 306 and 256 nm. Table 2 lists the absorption characteristics of the main bands appearing in the visible spectra of **3a—g** in chloroform; their absorption maxima were named λ_1 to λ_5 in the order of increasing wavelengths. In general, 5,8-diamino-1,4-naphthoquinone,[15] 4,8-diamino-1,5-naphthoquinone,[15] 1,4-diaminoanthraquinone,[16] and their derivatives,[15,16] formed by replacing the amino group with the other intramolecularly hydrogen-bonded group, gave a double-headed peak, along with a shoulder, usually on the shorter wavelength side of the main band, in the visible region of their spectra. Therefore, the two most intense absorption bands at λ_1

Table 2. Substituent Effect on the Visible Absorption Spectra of **3** in Chloroform[a)]

Compound	λ_1 ($10^{-4}\varepsilon_1$)	λ_2 ($10^{-4}\varepsilon_2$)	λ_3 ($10^{-4}\varepsilon_3$)	λ_4 ($10^{-4}\varepsilon_4$)	λ_5 ($10^{-4}\varepsilon_5$)	$\varepsilon_2/\varepsilon_1$	$\varepsilon_3/\varepsilon_1$	$\varepsilon_5/\varepsilon_1$
3a	759.6	708.0	540.4	503.2	417.2			
	(1.82)	(1.53)	(0.422)	(0.510)	(0.608)	0.84	0.23	0.33
3b	760.8	707.2	540.0	503.2	419.4			
	(2.05)	(1.71)	(0.502)	(0.605)	(0.688)	0.83	0.24	0.34
3c	758.8	707.2	541.6	504.0	420.0			
	(1.80)	(1.44)	(0.422)	(0.510)	(0.590)	0.81	0.23	0.33
3d	754.0	703.6	539.2	501.2	417.0			
	(1.82)	(1.44)	(0.431)	(0.525)	(0.627)	0.79	0.24	0.34
3e	758.8	707.6	541.6	504.0	421.0			
	(1.94)	(1.55)	(0.457)	(0.563)	(0.647)	0.80	0.24	0.33
3f	772.4	708.8	537.6	503.0	406.4			
	(2.26)	(1.77)	(0.547)	(0.673)	(0.920)	0.78	0.24	0.41
3g	592.8	—	—	—	354.4			
	(0.379)				(0.531)	—	—	1.40

a) λ and ε represent the wavelength (nm) of the absorption maximum and the apparent molar absorption coefficient ($M^{-1}\,cm^{-1}$) because of tautomerism respectively.

and λ_2 were assigned to the **I** form existing as the predominant tautomer, and those at λ_3 and λ_4 to the **II** form as a minor tautomer. The absorption maxima, λ_1 and λ_2 for the **I** form of **3a**, designated by **3a(I)**, in chloroform were shifted bathochromically by 102—103 nm relative to those for **2a**[15] and by 10—23 nm compared with those for phenothiazino[2,1-*a*]phenothiazine-6,14-dione (**5**),[17] whereas the λ_3 and λ_4 maxima for **3a(II)** were shifted hypsochromically by 38—42 nm relative to those for 6-aminobenzo[*a*] [1,4] benzothiazino [3,2-*c*]phenothiazin-9-ol (**6**).[19]

Furthermore, in the absorption spectra of **3a—f**, two-headed peaks (longer absorption maxima λ_5) observed in the 370—430 nm region were assigned to their **III** forms. In the case of **3g**, which exists in the **III** form as the major tautomer, there were only two diagnostic bands of a medium intensity (a shoulder at 354 nm and a monotonous peak at 593 nm) in the 300—900 nm region; the absorption band at a longer wavelength may be attributable to the **I** form of **3g**, i.e., 1-isopropylamino-5-*N*-isopropylacetamido-4*H*-benzo-[*a*]phenothiazin-4-one. This large hypsochromic shift, suggesting the removal of practically all the electronic influence of the 5-substituent, was also observed in the visible absorption spectra of the *N*-methylacetamido compounds in 1-substituted anthraquinones[18] and *N*-*p*-substituted phenyl-2,6-di-*t*-butyl-*p*-benzoquinone monoimines.[19]

The visible absorption spectra of **3a—e** were little affected by the change in *N*-alkylation on going from *N*-methyl to *N*-isobutyl, except for the hypsochromic shifts of λ_1 and λ_2 by the *N*-isopropyl group. The introduction of the 3-Cl substituent on **3d(I)** resulted in a significant red shift, whereas it had little effect on the λ_{max} of **3d(II)**. The bathochromic effect (18 nm) of the 3-Cl substitution on the first π–π^* transition of **3d(I)** was similar to that (17 nm) for 1,5-bis (isopropylamino)-10-chloro-4*H*-benzo[*a*] phenoselenazin-4-one.[20]

Effect of Solvent on the Visible Absorption Spectra of 1,5-Bis(isopropylamino)-4*H*-benzo[*a*]phenothiazin-4-one (3d). Table 3 lists the solvent effects on the five absorption bands arising from **3d**. In all the solvents used, the predominant tautomer was the **I** form, although its proportion depended on the nature of the solvent. The effect of the solvent on both the absorption maxima and the ratio between their absorbances was analyzed by means of the linear solvation energy relationships of the solvatochromic π^*, δ, α, and β scales, which denote, respectively, the dipolarity–polarizability, the polarizability correction term, the hydrogen-bond-donor (HBD) acidity, and the hydrogen-bond-acceptor (HBA) basicity of the solvents proposed by Taft et al.,[21] and, if necessary, other solvent parameters.[22]

The absorption maxima from λ_1 to λ_5 were turned into the corresponding transition energies, from $E_T(1)$ to $E_T(5)$ in kcal mol^{-1} units[23] respectively, in order to compare their transition energies with those (E_T(PB), E_T(NBAO), and X_R) of phenol blue (PB)[24] nile blue A oxazone (NBAO)[25] and Brooker's dye VII:[26]

$$E_T(1) = 38.66 - 1.10(\pi^* - 0.25\mu) - 0.87\alpha \quad (n = 8,\ r = 0.933) \tag{1}$$

$$E_T(2) = 40.41 - 2.34(\pi^* + 0.18\delta) + 8.11(D - 1)/(2D + 1) - 2.46\alpha \quad (n = 7,^{27)}\ r = 0.999) \tag{2}$$

$$E_T(3) = 52.01 + 0.63(\pi^* - 0.62\delta) + 2.03\alpha \quad (n = 8,\ r = 0.991) \tag{3}$$

$$E_T(4) = 57.94 - 4.27(D - 1)/(2D + 1) + 0.22\mu + 1.37\alpha \quad (n = 8,\ r = 0.957) \tag{4}$$

$$E_T(5) = 69.31 - 1.10(D - 1)/(2D + 1) - 0.50\delta - 0.48\alpha + 1.12\beta \quad (n = 7,^{27)}\ r = 0.993) \tag{5}$$

$$E_T(PB) = 52.25 - 4.56\pi^* - 3.28\alpha \quad (n = 27,\ r = 0.962) \tag{6}$$

Table 3. Solvent Effect on the Visible Absorption Spectra of **3d**[a]

Solvent	Scale[b]					Absorption characteristics[c] λ_{max}/nm, ε/M^{-1} cm^{-1}							
	π^*	α	β	D	μ	λ_1 (10^{-4} ε_1)	λ_2 (10^{-4} ε_2)	λ_3 (10^{-4} ε_3)	λ_4 (10^{-4} ε_4)	λ_5 (10^{-4} ε_5)	$\varepsilon_1/\varepsilon_T$	$\varepsilon_3/\varepsilon_T$	$\varepsilon_5/\varepsilon_T$
Acetic acid	0.62	1.09	—	6.19	1.73	761.2 (1.41)	696.0 (1.24)	520.8 (1.00)	490.0 (1.02)	410.8 (0.728)	0.45	0.32	0.23
Ethanol	0.54	0.86	0.77	24.3	1.67	758.8 (1.95)	698.0 (1.67)	530.8 (0.563)	497.6 (0.683)	412.6 (0.643)	0.62	0.18	0.20
Chloroform	0.76	0.34	Nil	4.70	1.06	754.0 (1.82)	703.6 (1.44)	539.2 (0.431)	501.2 (0.525)	417.0 (0.627)	0.63	0.15	0.22
Pyridine	0.87	Nil	0.64	12.3	2.20	747.2 (1.98)	688.0[d] (1.22)[d]	547.2 (0.338)	505.2 (0.391)	414.0 (0.594)	0.68	0.12	0.20
DMSO	1.00	Nil	0.76	48.9	4.30	742.4 (1.71)	680.0[d] (1.08)[d]	544.0 (0.343)	504.4 (0.390)	410.0 (0.578)	0.65	0.13	0.22
Hexane	−0.08	Nil	Nil	1.90	0.0	740.0 (1.59)	678.4 (1.18)	550.0 (0.231)	500.0 (0.214)	413.6 (0.587)	0.66	0.10	0.24
Ethyl acetate	0.55	Nil	0.45	6.03	1.76	734.8 (1.99)	676.0[d] (1.29)[d]	544.4 (0.335)	502.0 (0.358)	411.6 (0.676)	0.66	0.11	0.23
Acetonitrile	0.85	0.15	0.31	37.5	3.94	734.4 (1.97)	680.0[d] (1.41)[d]	539.6 (0.401)	500.0 (0.462)	414.2 (0.639)	0.65	0.13	0.21

a) The ranking of the solvents is the same order as for the magnitude of the bathochromic shifts of λ_1. b) Using Taft's solvatochromic parameters (π^*, α, and β), the dielectric constant (D), and the dipole moment (μ) taken from the literature.[21,22] The values of δ for chloroform and pyridine are 0.5 and 1.0 respectively, while those for the other solvents are equal to zero. c) λ, ε, and ε_T denote the wavelength of the absorption maximum, the apparent molar absorption coefficient, and the sum of ε_1, ε_3, and ε_5. d) λ and ε of the shoulder corrected by the curve-fitting method on the basis of the assumption that the shoulder and the neighboring strong peak are symmetrical curves.

$$E_T(\text{NBAO}) = 58.11 - 5.97\pi^* - 2.83\alpha \quad (n = 25,\ r = 0.969) \tag{7}$$

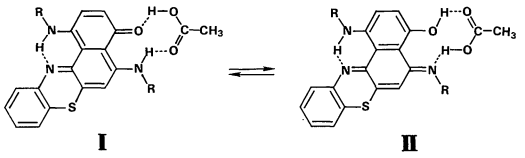
$$X_R = 50.65 - 7.52\pi^* - 3.27\alpha \quad (n = 38,\ r = 0.967) \tag{8}$$

where r, D, and μ represent the multiple correlation coefficient, the dielectric constant, and the dipole moment of the solvent respectively, and where the Kirkwood term,[28] $(D-1)/(2D+1)$, is primarily a measure of the permanent dipole–permanent dipole solvation.

One of the structural analogies among the **3d** tautomers — PB, NBAO, and Brooker's dye VII — is that they all include *N*- and *O*-basic sites, whereas the significantly structural difference is the intramolecular hydrogen bonding observed in only the tautomers. As the weighting coefficient of the α scale in Eqs. 1—8 shows, the intermolecular hydrogen-bonding interactions of the HBD solvent with the basic sites of **3d(II)** was greater in the ground state than in the excited state, while the reverse was observed in the other dyes described above. This interesting contrast is mainly to be ascribed to the difference between the π electron-donating hydroxyl group in **3d(II)** and the π electron-accepting carbonyl group in the other dyes. Equation 5 shows that the intermolecular hydrogen bonding of such hydrogen-donor sites as $N^{12}H$ and N^5H in **3d(III)** with the basic site in a solvent resulted in a hypsochromic shift. Although the first π–π^* transitions of PB, NBAO, and Brooker's dye VII were highly sensitive to changes in the π^* value of the solvent, the contribution of the polarity–polarizability term of $E_T(1)$–$E_T(5)$ responsible for the transition energies of **3d(I)**–**3d(III)** was relatively small and complex.

The visible spectra of **3a—f** suggest the general coexistence of three interconverting tautomeric forms. We will discuss, in a rough-and-ready way, the solvent effect on the tautomeric equilibria of **3d**, assuming that their molar absorptivities are approximately equal in a solution.[29] As Table 3 shows, the concentration of the **II** form increased with an increase in the HBD strength of the solvent in this order: hexane< acetonitrile<chloroform<ethanol<acetic acid; the HBA strength of a solvent was of less importance as a stabilizing factor of the **II** form. On the other hand, the concentration of the **I** form increased with an increase in the dipole–dipole interaction, as expressed by the Kirkwood term corrected by π^* and δ, but it decreased with an increase in the α value. Accordingly, the concentration of the **III** form decreased with an increase in the dipole–dipole interaction.

The concentration of the tautomeric **II** form of **3d** was more enhanced in acetic acid than in the other



Scheme 3. Tautomerism of **3** catalyzed by acetic acid.

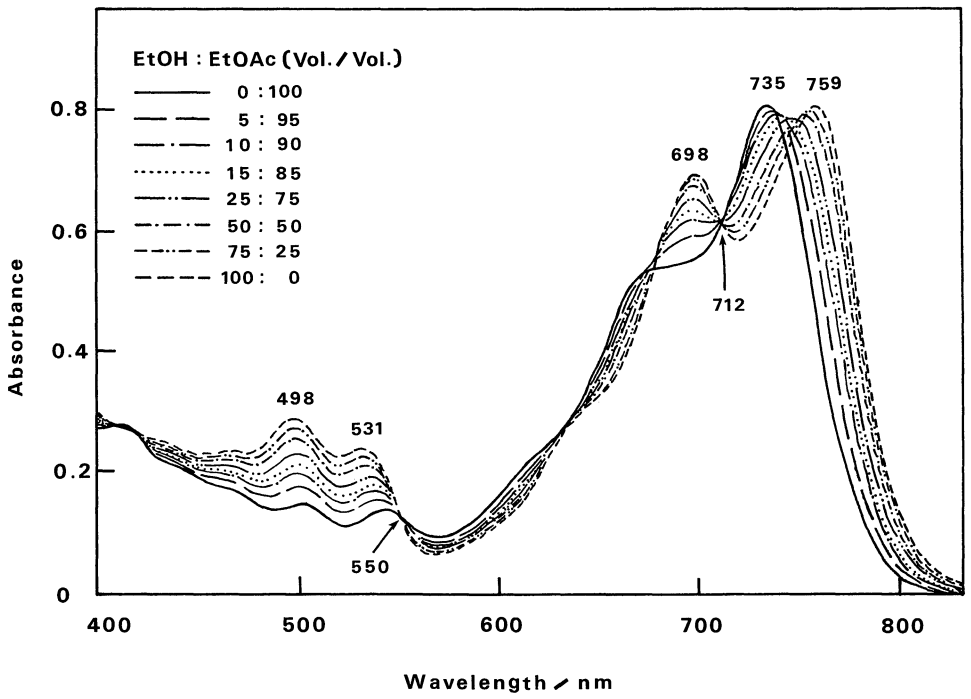


Fig. 1. Solvatochromism of **3d** in the ethanol–ethyl acetate solvent system: The concentration of **3d**= 4.24×10^{-5} mol dm^{-3}. Isobetic points were observed at 712 and 550 nm.

solvent used. In the ^{1}H NMR spectrum[30] of **3d** in an acetic acid-d_4 solution, both amine hydrogens were replaced by the carboxylic D atoms. The signals for the *N*-isopropyl methine proton on the higher-field side became noticeably broad compared with those in $CDCl_3$, suggesting that the rate of exchange between the **I** and the **II** forms is faster in acetic acid-d_4 than in $CDCl_3$. The behavior of acetic acid may ascribed to the two-proton transfer process between the tautomer and the solvent, as is illustrated by Scheme 3.

The influence of the solvent composition on the solvatochromism of **3d** was examined in the ethanol–ethyl acetate system as a suitable model pair of hydrogen-bond donor and acceptor (Fig. 1). The spectral shifts for **3d(I)** and **3d(II)** were more sensitive to the addition of ethanol in larger composition of ethyl acetate. Therefore, the major contributions to the spectral shifts of the tautomers are attributed to the hydrogen bonding between their basic sites with the hydroxyl groups of the ethanol monomer and of the linear oligomer ends.[31] In the lower-concentration range of ethanol, the enhanced ratio of the ethanol monomers to the total ethanol species made the solvatochromic shift more sensitive.

Tautomeric Equilibria of 1,5-Bis(alkylamino)-4*H*-benzo[*a*]phenothiazin-4-ones (3) and Related Compounds. It is interesting to obtain information on the tautomeric equilibria of naphthoquinones and naphthoquinone imines bearing intramolecularly hydrogen-bonded substituents at peri-positions. Figure 2 illustrates the molecular structures of some major tautomers. The general rules controlling their tautomerisms may be briefly summarized as follows:

(1) From successive comparisons among **2**, **3**, **5**, **7**, **8**, and **10**, the probability of proton transfer from a peri-substituent is shown to increase generally in the order of: $NH_2 \leq NHR < NHC_6H_4SR < OH$. This order may be explained primarily in terms of the proton-transfer ability of the substituents.

(2) The probability of attracting quinonoid properties to a ring is enhanced by a π electron-donating substituent conjugated to a carbonyl-oxygen or imino-nitrogen atom. This assumption is supported by the tautomerisms[32] of 2,6- and 2,7-disubstituted 5,8-dihydroxy-1,4-naphthoquinones (**9**), where the attraction of quinonoid properties to a ring by a substituent was decreased in the order of: $OH > OCH_3 \gg OCOCH_3 > CH_2CH_3 \gg H \gg COCH_3$. Accordingly, it is reasonable to assume, on the basis of the π electron-donating character of the thiophenylene(SC_6H_4R) group, that the 1,4-quinonoid form increased in the order of: **2**<**3**<**6**.

(3) In general, the 1,4-quinonoid form is more stable than the 1,5-quinonoid form unless strongly π electron-donating substituents, such as amino and alkylamino groups, are set at the 4- and 8-positions in the latter form. The stability of **2** and **3** in the 1,5-quinonoid form can be explained in terms of the large resonance effect of the peri-alkylamino groups and the intramolecular hydrogen bonds.

In two interconverting tautomeric forms, a more electropositive hydrogen atom in a polar group such as -OH can separate readily from the heteroatom to a conjugated anion, whereas a less electropositive hydro-

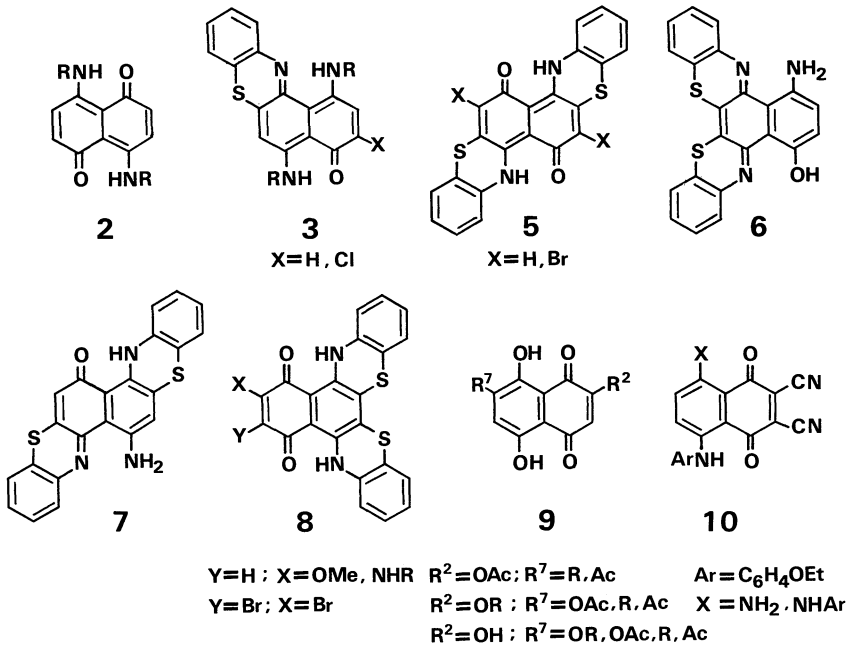
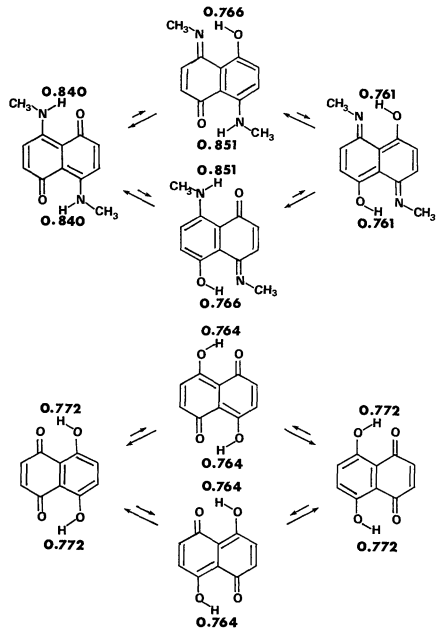


Fig. 2. Predominant tautomers of **2**, **3**, and their related compounds. Their tautomeric forms except for **3** were taken from literatures: **2**, Ref. 15; **5**—**8**, Ref. 17; **9**, Ref. 32; **10**, Ref. 33.



Scheme 4. Tautomeric equilibria of **2a** and 5,8-dihydroxy-1,4-naphthoquinone, together with the MNDO electron densities (cf. Table 4) of their exchangeable hydrogen atoms.

gen atom tends to stay there. From successive comparisons between the MNDO electron densities of the interconverting hydrogen atoms in two tautomers on the pathway shown in Scheme 2, the predominant tautomer is suggested to be the **I** form, bearing electron-rich hydrogen atoms. Similar arguments can be applied to the tautomerisms of **2a** and 5,8-dihydroxy-1,4-naphthoquinone (Scheme 4). Their equilibria favor tautomers bearing exchangeable hydrogen atoms of higher electron densities. In the case of cytosine,[34] the ab initio electron density (0.691) of the 4-amino hydrogen atom in the 4-amino-2-oxo form, the most stable tautomer in DNA, was higher than that (0.666) of the hydrogen atom bonded to the N^3 in the 4-imino-2-oxo form as a rare tautomer, supporting the above assumption. Therefore, the electron density of an interconverting hydrogen atom is a useful index for qualitatively predicting the equilibrium of prototropic tautomerism.

The Mechanism for the Ring-closure Reaction of 2-Aminobenzenethiol (1) with 4,8-Bis(alkylamino)-1,5-naphthoquinone (2a—e) in Ethanol in the Presence of HCl. Figure 3 shows the effect of the HCl concentration on the visible absorption spectra of **2d** in ethanol–water(4:1, v/v). The absorbances of the two bands (λ_{max}=649 and 598 nm) originating from **2d(I)** decreased with the increase in the HCl concentration, and new bands appeared near 688, 637, 586, and 544 nm. These new bands may be responsible for the protonated compounds[35] of **2d**. In the ethanol–6 M HCl(4:1, v/v) system bearing pH 0.18, it is estimated

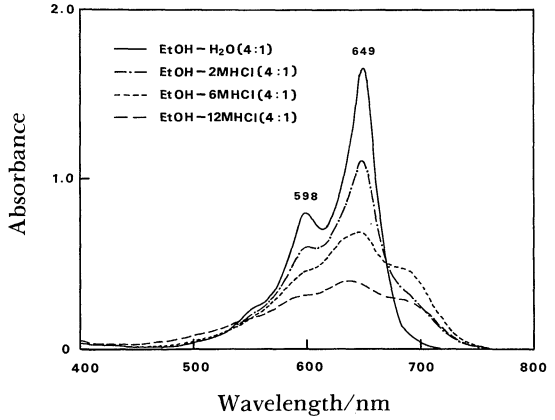


Fig. 3. Effect of HCl concentration on the visible absorption spectra of **2d** in ethanol–water (4:1, v/v): The initial concentration of **2d**=6.00×10^{-5} mol dm^{-3}. The pH values for ethanol–2, 6, and 12 M HCl (4:1, v/v) solutions at 20°C were 0.65, 0.18, and −0.12, respectively.

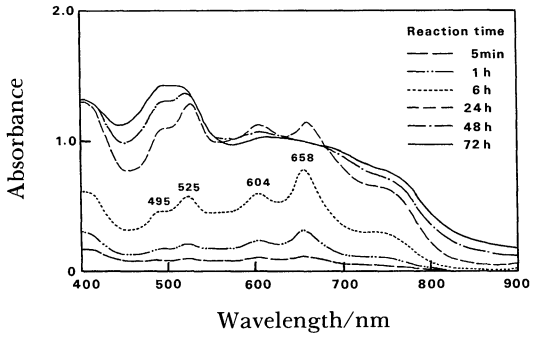


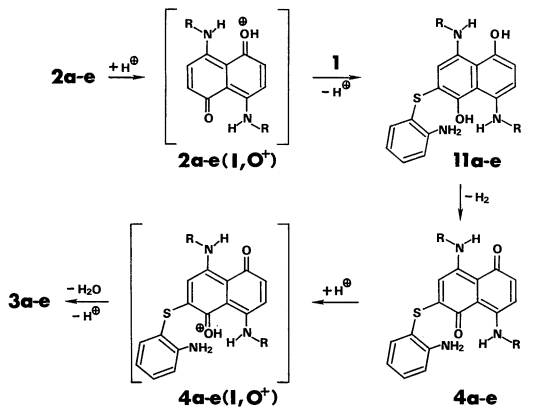
Fig. 4. Visible absorption spectra of the equimolecular mixture of **1** with **2d** in ethanol–6M HCl (4:1, v/v): The initial concentration of **2d**=7.34×10^{-5} mol dm^{-3}.

from the decrease in absorbance that about three quarters of the **2d** were converted to other species, e.g., the protonated ions. The protonation of **2d** would occur predominantly at the oxygen atom rather that at the nitrogen atom to give conjugated cations. From a comparison of the UV absorption spectra[36] of **1** in neutral, acidic, and basic ethanol solutions, the conversion of **1** to its cation was estimated to be more than 79% in the same solvent system.

In order to obtain information regarding the condensation mechanism of **1** with **2a—e** in acidic ethanol, the visible absorption spectra of diluted reaction solutions were followed at suitable time intervals (Fig. 4). Almost immediately after the mixing of **1** and **2d** in ethanol–6 M HCl(4:1, v/v), the absorbances of the diagnostic bands arising from **2d(I)** were remarkably low. As the reaction proceeded, however, various absorption bands emerged at approximately 410, 495, 525, 604, and 658 nm, along with shoulders longer than 700 nm. The absorption bands

appearing at 604 and 658 nm were assigned to **2d** and/or 2-(2-aminophenylthio)-4,8-bis(isopropylamino)-1,5-naphthoquinone (**4d**); the absorption maxima of the other peaks were similar to those of peaks observed in the visible absorption spectra of **3d** in ethanol in the presence of HCl. In addition, the absorption bands due to the protonated ions produced from **2d**, **3d**, and **4d** complicated the spectral characteristics.

It is possible that the addition of **1** to **2a—e** passes through various reaction mechanisms, depending on the pH of the solution and the nature of the solvent. Figures 3 and 4 favor the assumption that protonation plays an important role in the ring-closure reaction of **1** with **2a—e** to give **3a—e** in the acidic ethanol. Furthermore, the intermediates **4a—e** were also isolated from the reaction mixture and could readily be converted into **3a—e** in the same solvent system. Therefore, it may be suggested that the major pathways for the equimolecular condensation of **1** with **2a—e** in ethanol in the presence of HCl at room temperature involve the oxidation of 2-(2-aminophenylthio)-4,8-bis(alkylamino)-1,5-naphthalenediol (**11a—e**) and the subsequent ring-closure reaction of the resulting quinone **4a—e** to yield **3a—e** (Scheme 5). The O^1-protonation of **2a—e** brought about the subsequent attack of **1** on the C^6 atom of the cation and a hydrogen migration from the C^6 to the O^5 atom.



Scheme 5. Proposed mechanism for the ring-closure reaction of **1** with **2a—e** in ethanol in the presence of HCl.

Tables 4 and 5 list the MNDO electron densities of **2a**, **3a**, and related compounds. In the O^1-protonated **2a(I)**, shown by **2a(I, O^{1+})**, the O^1 atom lost only 0.064 electron relative to the unprotonated **2a(I)**, although 0.761 electron was transferred to the proton; therefore, a significant charge redistribution occurred through the σ- and π-frameworks. This suggests that the cation bears a delocalized positive charge on the C^1, C^4, C^5, and C^8 and smaller π-electron densities on the C^1, C^3, C^4, C^5, C^6, and C^8. In the frontier orbital, i.e., the LUMO, of the cation, the MNDO results suggest that the π-electron densities of the quinonoid carbons

Table 4. MNDO Electron Densities of **2a** and Related Compounds in the Ground State[a)]

No.[b)]	**2a(I)**		**2a(I,O^{1+})**[c)]		**2a(II)**[d)]	**2a(III)**[e)]	4,8-diOH-1,5-NQ[f)]	5,8-diOH-1,4-NQ[g)]
	Total	π	Total	π	Total	Total	Total	Total
C^1	3.702	0.748	3.814	0.900	3.814	3.809	3.694	3.694
C^2	4.116	1.009	4.099	1.037	4.080	4.020	4.095	4.083
C^3	4.014	0.953	4.004	0.931	4.010	4.095	4.028	4.083
C^4	3.847	0.892	3.771	0.872	3.923	3.832	3.789	3.694
C^{4a}	4.158	1.126	4.195	1.201	4.110	4.146	4.214	4.173
C^5	3.724	0.748	3.724	0.777	3.704	3.809	3.694	3.834
C^6	4.116	1.009	3.959	0.816	4.089	4.020	4.095	4.045
C^7	4.014	0.953	4.158	1.097	4.066	4.095	4.028	4.045
C^8	3.847	0.892	3.637	0.684	3.842	3.832	3.789	3.835
C^{8a}	4.158	1.126	4.134	1.189	4.128	4.146	4.214	4.173
O^1	6.322	1.335	6.269	1.877	6.253	6.252	6.345	6.322
H^2	0.915		0.905		0.918	0.918	0.912	0.913
H^3	0.920		0.904		0.919	0.932	0.913	0.913
$N^4(O^4)$	5.332	1.257	5.367	1.665	5.327	5.371	6.245	6.322
O^5	6.322	1.335	6.258	1.285	6.305	6.252	6.345	6.252
H^6	0.915		0.886		0.916	0.918	0.912	0.912
H^7	0.920		0.903		0.932	0.932	0.913	0.912
$N^8(O^8)$	5.332	1.257	5.249	1.558	5.345	5.371	6.245	6.252
H^{18}	0.840		0.761 (OH) 0.769 (NH)		0.766	0.761	0.764	0.772
H^{45}	0.840		0.784		0.851	0.761	0.764	0.772

a) In examples of **2a(I)**, **2a(III)**, and 4,8-dihydroxy-1,5-naphthoquinone, the MNDO electron densities calculated on the basis of the C_2 symmetry were in fair agreement with those calculated on the basis of the S_2 symmetry. b) The atomic numberings for the **2a** tautomers are the same as those for **2a(I)** shown in Scheme 1 and those in parentheses for the other compounds; H^{18} denotes an exchangeable H atom linked to the heteroatom in the 1- or 8-substituent, and H^{45}, one linked to the heteroatom in the 4- or 5-substituent. c) O^1-protonated ion produced from **2a(I)**. d) *N'*,*N'*-dimethyl-8-amino-5-hydroxy-1,4-naphthoquinone-4-imine. e) *N*,*N'*-dimethyl-4,8-dihydroxy-1,5-naphthoquinone diimine. f) 4,8-Dihydroxy-1,5-naphthoquinone. g) 5,8-Dihydroxy-1,4-naphthoquinone.

Table 5. MNDO Total Electron Densities of **3a** Tautomers in the Ground State

No.[a)]	**3a**(**I**)	**3a**(**II**)	**3a**(**III**)	**3a**(**IV**)
C^1	3.865	3.927	3.841	3.831
C^2	4.007	4.010	4.067	4.096
C^3	4.128	4.087	4.092	4.024
C^4	3.698	3.813	3.703	3.808
C^{4a}	4.165	4.141	4.112	4.151
C^5	3.837	3.832	3.917	3.830
C^6	4.013	4.065	3.990	4.074
C^{6a}	4.154	4.125	4.159	4.095
S^7	5.879	5.882	5.892	5.893
C^{7a}	4.135	4.133	4.174	4.179
C^8	4.030	4.032	3.997	3.996
C^9	4.047	4.043	4.093	4.092
C^{10}	4.062	4.063	4.020	4.019
C^{11}	4.010	4.005	4.106	4.102
C^{11a}	3.972	3.979	3.861	3.865
N^{12}	5.259	5.240	5.304	5.290
C^{12a}	3.847	3.856	3.792	3.800
C^{12b}	4.078	4.031	4.097	4.115
N^1	5.334	5.329	5.345	5.375
N^5	5.343	5.360	5.339	5.380
O^4	6.327	6.256	6.304	6.252
H^{112}	0.841	0.850	0.774	0.766
H^{45}	0.849	0.766	0.848	0.760

a) The atomic numberings are the same as that for **3a**(**I**) shown in Scheme 1; H^{112} denotes the exchangeable H atom linked to either the N^1 or N^{12} atom, and H^{45}, that linked to either the O^4 or the N^5 atom.

decreased in the order of; $0.638(C^8)>0.293(C^6)>0.227(C^1)>0.169(C^3)>0.075(C^5)$. One of the reasons why **1** attacks the C^6 atom rather than the C^8 atom of **2a**—**e**(**I**,O^{+1}) may be the steric hindrance between the reactants in the transition state.

It is considered that **11a**—**e** was easily oxidized with electron acceptors, such as quinones and dissolved oxygen, in the system. In the acidic ethanol, the equilibrium in oxidation-reduction process lay finally on the quinone side in the presence of dissolved oxygen.

Experimental

The ^{1}H NMR spectrum was measured in chloroform-*d*, using tetramethylsilane as the internal standard, on a Varian XL-200 or a JOEL JNM-PMX 60SI NMR spectrometer. The melting points were determined with a Yanako micromelting-point apparatus and were uncorrected. The IR spectrum was recorded using a potassium bromide disk on a JASCO A-102 spectrometer. The UV and visible absorption spectra were obtained with a Hitachi 150-20 UV spectrometer using 1-cm quartz cells. The mass and high-resolution mass spectra were recorded on ESCO EMD-05B and Hitachi M-2000 spectrometers respectively. The pH value of a solvent was determined with a TOA HM-30S pH meter. For column chromatography, silica gel (Kieselgel 60, Merck, 70—230 mesh) was used.

Compounds 2a—e. According to the method of Bloom and Dudek,[15] **2a**—**e** were synthesized from leuco-5,8-dihydroxy-1,4-naphthoquinone and the corresponding alkylamine. They were purified on a silica-gel column, thus eluting toluene–ethyl acetate(4:1, v/v).

Compound 2f. The 10 M HCl (10 ml) involving bromine (0.16 ml) was stirred, drop by drop, into a solution of **2d** (210 mg) in 10 M HCl (10 ml) at 0 °C. After 2 h of stirring, the reaction mixture was poured into 150 ml of water, and the resulting precipitate was chromatographed on a silica-gel column, using toluene–ethyl acetate(4:1, v/v) as the eluent.

Compounds 3a—e. To a suspension of **2a—e** (0.5 mmol) in ethanol (20 ml) we added a solution of **1** in 6 M HCl (5 ml); the mixture was then stirred for 72 h at room temperature. The reaction mixture was neutralized by a 5% aqueous sodium hydrogencarbonate solution, diluted by an excess of water, and extracted with benzene–ethyl acetate (4:1, v/v). The extracts were dried on magnesium sulfate and chromatographed on a silica-gel column. Further purification was carried out on a silica-gel column, thus eluting benzene–ethyl acetate (3:1, v/v).

Compound 3f. A mixture of **2f** (30 mg) and zinc 2-aminobenzenethiolates (65 mg, 2.5 mol equiv. to **2f**) in *N*,*N*-dimethylformamide (2 ml) was stirred for 7 h at 40 °C The dark green solid separated by adding an excess of water was filtered off and chromatographed on a silica-gel column, thus eluting toluene–ethyl acetate (4:1, v/v), to prepare **4f**. The solution of **4f** in ethanol (7 ml)–6 M HCl (3 ml) was stirred for 20 h at room temperature and then neutralized by a 5% aqueous sodium carbonate solution, diluted, and extracted with benzene. The extracts were dried on magnesium sulfate and evaporated. The residue was dissolved in toluene–ethyl acetate (4:1, v/v) and chromatographed on a silica-gel column, followed by elution with toluene–ethyl acetate (8:1, v/v), to give **3f** (26 mg) in a 72% yield.

Compound 3g. A deaerated solution of **3d** (10 mg) in acetic anhydride (3 ml) and acetic acid (1 ml) was stirred for 1 h at room temperature. The solution was then treated with an excess of water and extracted with benzene. The residue thus evaporated was chromatographed on a silica-gel column, using toluene–ethyl acetate (2:1, v/v), to afford **3g** (9.6 mg) in an 86% yield.

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27) The $E_T(2)$ and $E_T(4)$ values in acetic acid were excluded because of the uncertain λ_2 value, which is proportional to the concentration of the **II** form, and its unknown β value respectively.

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30) ^{1}H NMR spectrum of **3d** in acetic acid-d_4: δ=1.42 and 1.44 (d, 6H, Me, J=6 Hz)×2, 4.03 (m, 1H, CH), 4.16 (sp, 1H, CH, J=6 Hz), 7.10 (s, 1H, H^6), 7.20—7.57 (m, 4H, arom), 7.32 (d, 1H, H^3, J=8 Hz), and 7.50 (d, 1H, H^2, J=8 Hz).

31) From the near-infrared study of the ethanol-*d* solution, it is estimated that the hydrogen-bonded molecular structure of pure ethanol-*d* at 25 °C consists primarily of a monomer, an acyclic tetramer, and cyclic tetramer in a molar ratio of 1:3. 4:10.9; see, A. N. Fletcher, *J. Phys. Chem.*, **76**, 2562 (1972).

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34) M. H. Palmer, J. R. Wheeler, J. S. Kwiatkowski, and B. Lesyng, *J. Mol. Struct., Theochem.*, **92**, 283 (1983).

35) As the formation of protonated species from quinones in acidic solutions has been polarographically demonstrated (see J. Q. Chambers, "Electrochemistry of Quinones," Chap. 14 in Ref. 1c), the ^{1}H NMR and visible spectra of **2a** in CF_3COOH were measured: ^{1}H NMR δ=3.61 (s, 6H, Me), 7.68 (d, 2H, J=10 Hz), 7.85 (d, 2H, J=10 Hz), and 11.2 (s, 2H,); UV(nm) λ_{max}=322 (ε=9400), 674 (ε=8100), and λ_{sh}=717 (ε=7800). These results suggest that **2a**(**I**) is converted to another symmetrical structure, such as a diprotonated cation of **2a**(**III**).

36) The absorption characteristics for the E_2- and B-bands (nm) originating from the π-π^* transitions of **1** and its ions were: in ethanol-water (4:1), λ_{sh}=230 (ε=11600), λ_{max}=340 (ε=2600); in ethanol-6 M HCl (4:1), λ_{sh}=234 (ε=6600), λ_{sh}=313 (ε=730); in ethanol-12 M HCl (4:1), λ_{sh}=234 (ε=6500), λ_{sh}=313 (ε=700); in ethanol-12 M $NaOH_{aq}$ (4:1), λ_{max}=262 (ε=7300), λ_{max}=306 (ε=3500).