Syntheses and Properties of Quinonoid Mesoionic Compounds

Shuki ARAKI,* Naomitsu AOYAMA, and Yasuo BUTSUGAN
Department of Applied Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466
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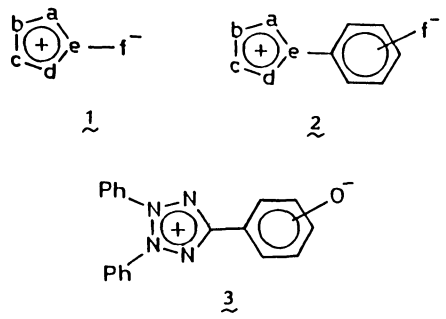
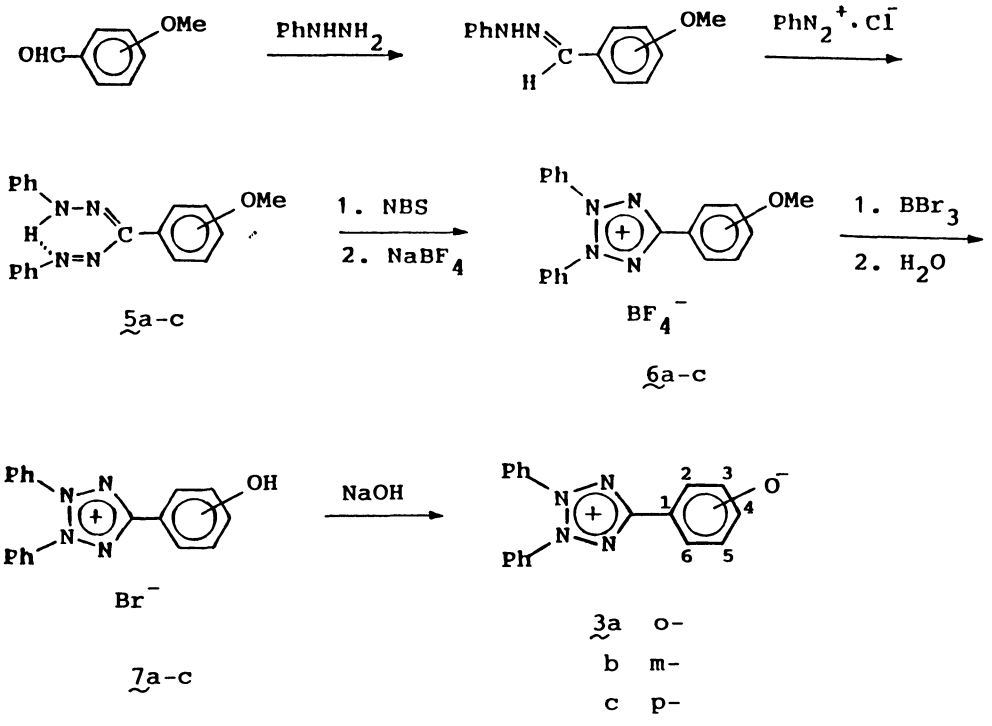
Quinonoid mesoionic compounds having a 2,3-diphenyltetrazolium ring were synthesized and characterized spectroscopically. Compounds possessing an inserted benzene ring were found that a dipolar (5-tetrazolylio)-phenolate structure contributes importantly to the ground state of the mesoions. On the contrary, a mesoion having an inserted anthracene ring is a less polar compound, anthraquinone methide structures being dominant in its ground state electronic structure.

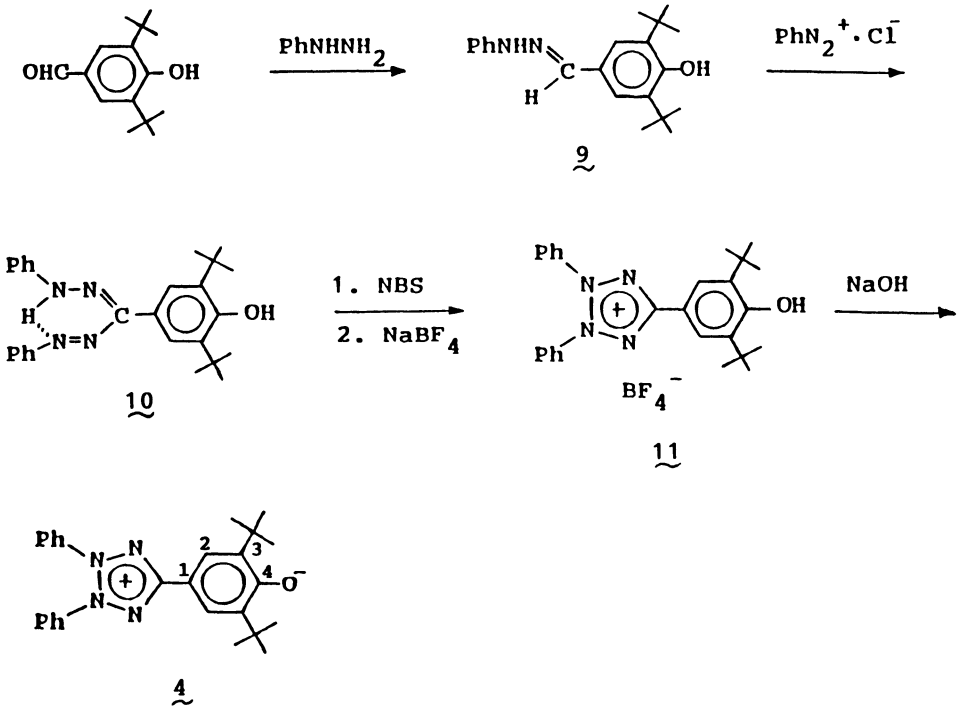
Mesoionic compounds of the general formula **1**, where a—f are suitably substituted carbons or heteroatoms, are an interesting family of heterocycles because of their unique structure, reaction behavior, and pharmaceutical activity; and numerous works have been focused on the chemistry of these novel electronic systems.[1] Quinonoid mesoionic compounds **2**, derived from **1** by insertion of a benzene ring into the exocyclic e–f bond of **1**, are one of unique modifications of mesoions, and their properties are intriguting in connection with those of the original mesoions **1**. Recently, we reported[2] the preparation of (2,3-diphenyl-5-tetrazolylio)phenolates (**3a—c**) as the first representatives of such quinonoid mesoions. Now, we describe here the synthesis and physicochemical properties of the further examples of the related quinonoid mesoions possessing a tetrazolium ring, together with a full account of the study on **3a—c**.



Synthesis. The synthetic pathway of the tetrazoliums **3a—c** is illustrated in Scheme 1. Phenylhydrazones of anisaldehydes (*o*, *m*, and *p*) were reacted with benzenediazonium chloride to give formazanes **5a—c**. Oxidation of **5a—c** with chromium(VI) oxide[3] or *N*-bromosccinimide[4] (NBS) afforded tetrazolium salts **6a—c**. The salts **6a—c** were isolated as tetra-



Scheme 1.



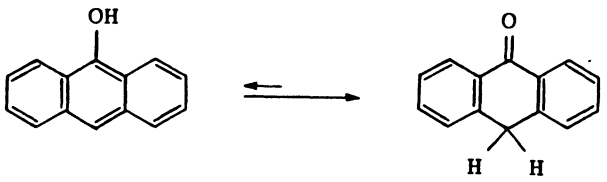
Scheme 2.

fluoroborates after an anion exchange with sodium tetrafluoroborate. Demethylation with boron tribromide furnished phenols **7a**—**c** in good yields. Deprotonation with a base followed by column chromatography on Sephadex 20 afforded quinonoid mesoions **3a**—**c** as hydrated crystals.

2,6-Di-*t*-butyl derivative **4** was synthesized by a similar synthetic scheme (Scheme 2) starting with 3,5-di-*t*-butyl-4-hydroxybenzaldehyde. In this synthesis, the protection of the hydroxyl group was unnessesary. The phenolate **4** was isolated as stable pale blue crystals.

Quinonoid mesoion **16** having three phenolate rings was synthesized according to Scheme 3. The dianion **16** is hygroscopic orange-red crystals. Upon the treatment of **16** with bromine, hexabrominated salt **17** was obtained. Deprotonation of **17** gave the conjugate anion **18** as brownish red crystals.

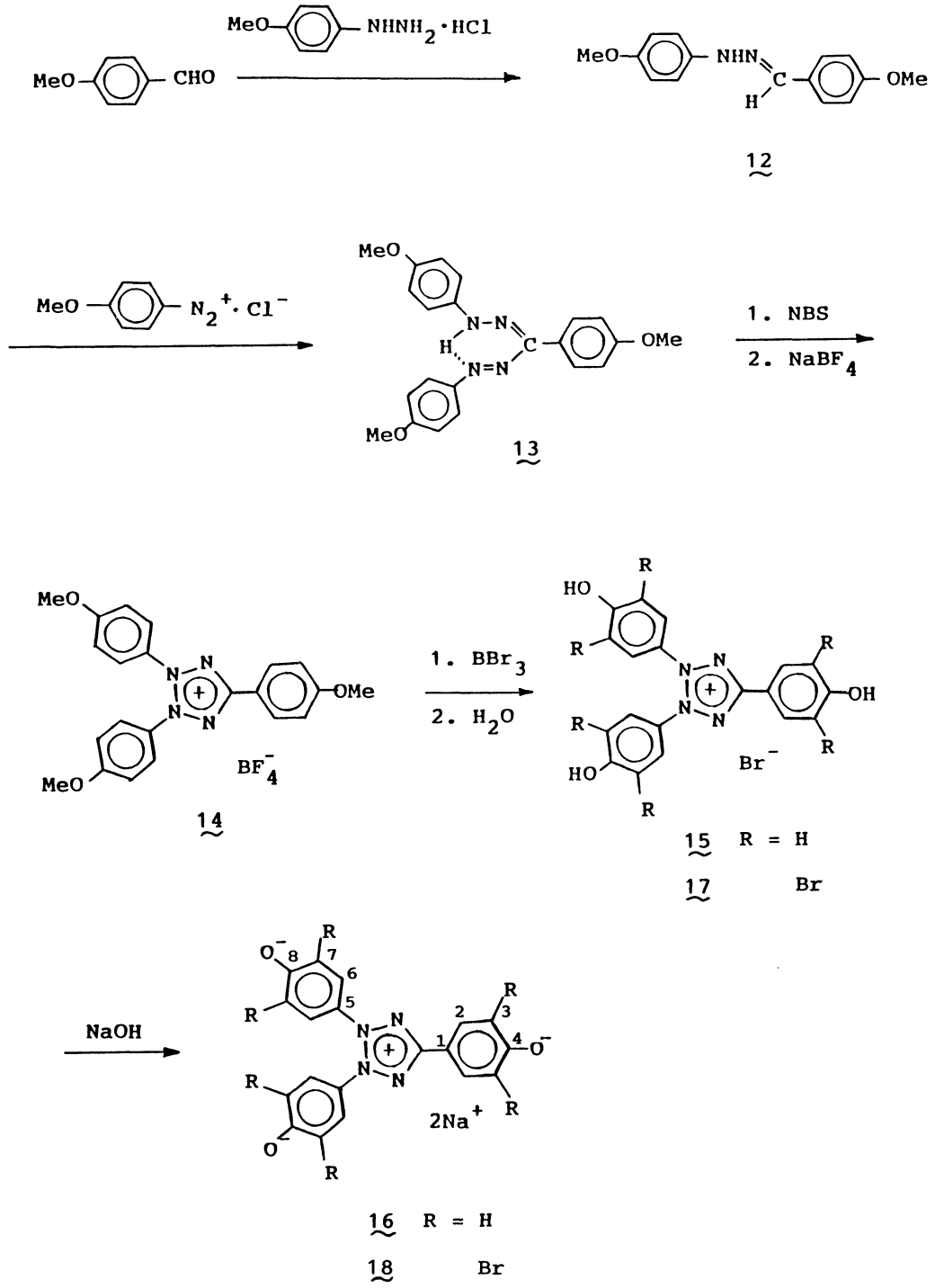
Quinonoid mesoionic compound **23** having an inserted anthracene ring instead of a benzene ring is of particular interest from the viewpoint of the comparison of the effects of the inserted aromatic ring (benzene vs. anthracene ring) upon the electronic structure of the quinonoid mesoions. The compound **23** was synthesized as shown in Scheme 4 and isolated as greenish brown crystals. It is worth noting here that compound **22** was isolated as the anthrol form rather than the anthrone form, despite the equilibrium between 9-anthrol and anthrone which lies to anthrone.[5] All the quinonoid mesoions **3a**—**c**, **4**, **16**, **18**, and **23** gave back to the corresponding conjugate acids



reversively by an acid treatment.

Properties of Quinonoid Mesoions 3a—c. The conjugate acids **7a**—**c** are stable pale yellow crystals. Their pK_a values measured by a UV method are 7.75 (for **7a**), 8.65 (**7b**), and 8.08 (**7c**), which are smaller by 1.3—2.2 than of phenol itself (pK_a=9.96) owing to the substitution of the strongly electron-withdrawing tetrazolium ring. Treatment of the salts **7a**—**c** with a base such as aqueous sodium hydroxide and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dimethyl sulfoxide (DMSO) gave quinonoid mesoions **3a**—**c**.

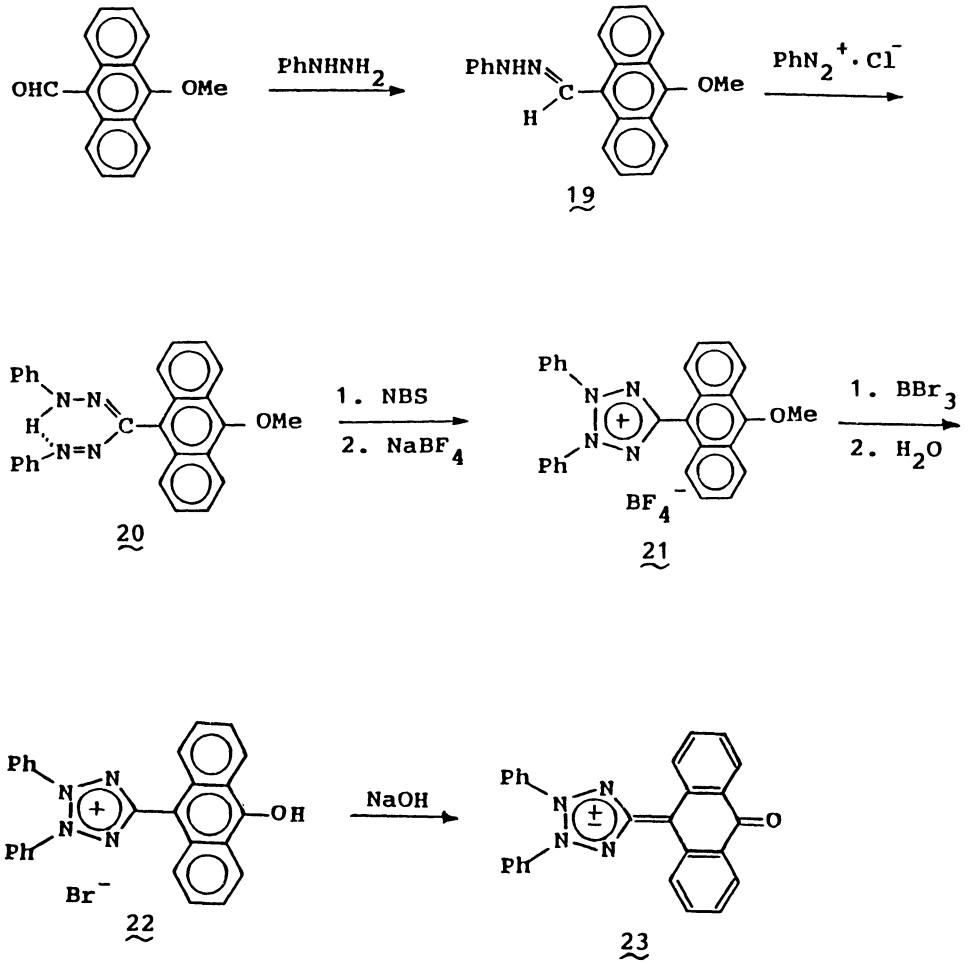
Electronic Spectra: The quinonoid mesoions **3a**—**c** are brown (**3a**) to purple crystals (**3b**, **c**) and soluble in polar solvents such as water, methanol, and DMSO but practically insoluble in nonpolar solvents such as benzene, carbon tetrachloride, and hexane. The mesoions **3a**—**c** showed lowest excitation absorptions at 496—513 nm in the electronic spectra (see Experimental). These bands showed a distinctive negative solvatochromism: by decreasing a solvent polarity, large bathochromic shifts were observed. For example, by changing the solvent from water to less polar chloroform, the absorption maximum of **3c** was shifted by $\Delta\lambda$=152 nm. As shown in Fig. 1, linear



Scheme 3.

relation was observed between the wavenumber ($\tilde{\nu}$) of the longest-wavelength absorption and solvent polarity (E_T parameter[6]). The observed large solvent effect indicates that **3a—c** are polar compounds, mesoionic dipolar character contributing importantly to their ground state structures.[7]

^{1}H and ^{13}C NMR Spectra: The ^{1}H NMR parameters of the compounds **3a—c** are listed in Table 1 together with those of the corresponding conjugate acids **7a—c**. By deprotonation, the chemical shifts of the phenol ring protons of **7a—c** were shifted to higher field. For example, the AA'BB' pattern of the *p*-isomer **7c** at δ 7.08 and 8.15 (J=9 Hz) was shifted to 6.29 and 7.74 (J=9 Hz). On the other hand, the chemical shifts of the phenyl protons of **3a—c** and **7a—c** are almost coincident. This means the negative charge of the



Scheme 4.

Table 1. ^{1}H NMR Data of **7a**—**c** and **3a**—**c**[a)]

Compd	δ
7a	7.00—8.10 (m, 14H, Ph and H-3—H-6), 10.95 (s, 1H, OH)
7b	7.10—8.00 (m, 14H, Ph, H-2, and H-4—H-6), 10.30 (s, 1H, OH)
7c	7.08 (d, J=9 Hz, 2H, H-3 and H-5), 7.65—7.85 (m, 10H, Ph), 8.15 (d, J=9 Hz, 2H, H-2 and H-6), 11.00 (s, 1H, OH)
3a	6.24 (t, J=8 Hz, 1H, H-5), 6.57 (d, J=8 Hz, 1H, H-3), 7.09 (d, J=8 Hz, 1H, H-4), 7.64—7.84(m, 7H, H-6 and Ph), 7.91 (d, J=7 Hz, 4H, Ph)
3b	6.64 (d, J=8 Hz, 1H, H-4), 7.01 (d, J=8 Hz, 1H, H-6), 7.17 (m, 2H, H-2 and H-5), 7.68—7.82 (m, 6H, Ph), 7.89 (d, J=7 Hz, 4H, Ph)
3c	6.29 (d, J=9 Hz, 2H, H-3 and H-5), 7.63—7.81 (m, 6H, Ph), 7.74 (d, J=9 Hz, 2H, H-2 and H-6), 7.87 (d, J=7 Hz, 4H, Ph)

a) Measured in DMSO-d_6.

Table 2. ^{13}C NMR Data of **7a**—**c** and **3a**—**c**[a)]

Compd	C-1	C-2	C-3	C-4	C-5	C-6	C+	Phenyl			
								ipso	ortho	meta	para
7a	109.8	157.1	117.4	130.2[b)]	120.1	134.6[b)]	163.1	133.2	126.6	130.4	134.1
7b	124.0	117.9[c)]	158.5	113.4[c)]	131.4	120.6	164.1	133.0	126.5	130.2	134.0
7c	113.5	129.4	117.0	162.2	117.0	129.4	164.5	133.1	126.5	130.4	134.0
3a	107.1	170.6	123.0	129.4[d)]	108.6	133.2[d)]	166.8	133.5	126.6	130.0	133.4
3b	124.0	123.0[e)]	170.3	115.9[e)]	130.3	107.5	166.4	133.1	126.4	130.2	133.8
3c	99.7	128.9	120.4	176.4	120.4	128.9	166.6	133.3	126.5	130.2	133.5

a) Measured in DMSO-d_6. b—e) These values may be interchanged.

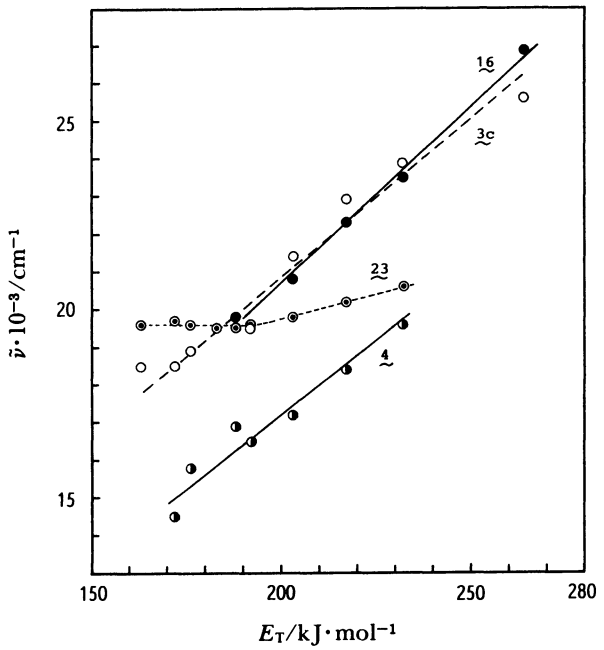
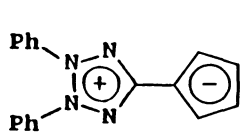


Fig. 1. Solvent dependence of the longest wavelength absorptions of **3c** (○), **4** (◑), **16** (●), and **23** (⊙).

mesoions **3a—c** is locarized in the phenolate ring. By comparison of the ^{13}C chemical shifts (Table 2) of **3a—c** and **7a—c**, it is evident that the oxygen-bearing carbons were shifted to lower field (by 11.8—14.2 ppm) by deprotonation. This corresponds well to the chemical shift difference (12.7 ppm) between the corresponding carbons of phenol (δ 155.6) and phenolate anion (δ 168.3). In contrast, the tetrazolium ring carbon and phenyl carbons were very little affected on going from **7a—c** to **3a—c**. These magnetic properties indicate that the mesoions **3a—c** can be regarded as phenolate anions substituted by a 2,3-diphenyltetrazolium ring.

Mass Spectra: The electron-impact mass spectra of the three quinonoid mesoions **3a—c** were essentially identical; no molecular ion peaks were observed but a characteristic fragment ion appeared at *m/z* 286. This peaks is considered due to mesoionic fulvalene **24** arising from the elimination of carbon monoxide from the quinonoid mesoions **3a—c**. The fulvalene **24** is an isomer of the 1,3-diphenyl derivative **25** which was recently prepared and fully characterized.[8] Attempts to synthesize **24** by flash vacuum thermolysis of **3a—c** are now in progress.



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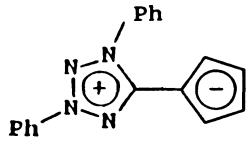

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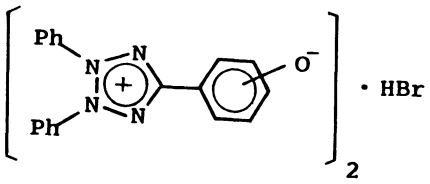
Adducts with Hydrobromic Acid: When an excess of DBU was added into a suspension of phenol **7c** in dichloromethane, the mixture turned to reddish purple and **7c** went into solution. After a few minutes, orange crystals of **8c** were precipitated. They were filtered and purified by recrystallization. Elemental analysis of the compound **8c** revealed that **8c** is the 2:1 adduct of mesoion **3c** and hydrobromic acid. Similar adducts **8a, b** were obtained in the same manner. The electronic spectra of **8a—c** were the sum of the absorptions of both mesoions **3a—c** and phenols **7a—c**. Moreover, the ^1H and ^{13}C NMR chemical shifts (Table 3) of **8a—c** are average of those of **3a—c** and **7a—c**, indicating that **8a—c** exist as the rapid equiliblium between **3a—c** and **7a—c** in the solution.



8a o-
b m-
c p-

Properties of Quinonoid Mesoions 4 and 16. The quinonoid mesoion **4** having two *t*-butyl groups at the ortho positions of the oxygen atom revealed similar spectroscopic properties to the parent compound **3c**. The lowest excitation band in the electronic spectrum showed large bathochromic shift on going from polar to less polar solvent (Fig. 1). The phenol ring protons of **11** at 8.00 ppm shifted to 7.64 by deprotonation, indicating high electron density of the phenolate ring of **4**. The phenolate ring carbons of **4** resonate at higher field than those of the phenol **11** (Table 4),

Table 3. ^{13}C NMR Data of **8a—c**[a]

Compd	C-1	C-2	C-3	C-4	C-5	C-6	C+	Phenyl			
								ipso	ortho	meta	para
8a	111.1	168.6	122.0	129.5[b]	109.0	133.3[b]	166.0	133.5	126.6	130.1	133.4
8b	123.4	122.6[c]	165.6	114.9[c]	130.7	112.2	165.2	133.0	126.6	130.2	133.9
8c	106.7	129.1	118.6	170.3	118.6	129.1	165.6	133.2	126.5	130.2	133.8

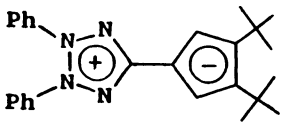
a) Measured in DMSO-d_6. b, c) These values may be interchanged.

Table 4. ^{13}C NMR Data of **4** and **11**[a)]

Compd	*t*-Bu		C-1	C-2	C-3	C-4	C+	Phenyl			
	Me	-C-						ipso	ortho	meta	para
11	30.0	34.7	117.0	124.0	140.4	159.6	162.7	133.0	126.5	130.3	134.0
4	29.8	34.8	95.9	123.0	138.1	175.4	168.2	133.4	126.4	130.1	133.4

a) Measured in DMSO-d_6.

except for the oxygen-bearing carbon whose chemical shift is δ 175.4, 15.8 ppm downfield than that of **11**. In contrast to **3a—c**, the mass spectrum of **4** exhibits the intense molecular ion peak at *m/z* 426 and the daughter ion corresponding to M^+-CO was not observed at all. This is because fulvalene **26**, which is expected to be formed by the loss of carbon monoxide from **4**, is energetically unfavorable owing to the presence of the two adjacent *t*-butyl groups.



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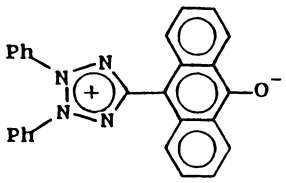
The triphenolate **16** prepared by the base treatment of the triphenol **15** was isolated as a disodium salt. It showed similar solvatochromism and magnetic properties to the quinonoid mesoions **3a—c** and **4**, as shown in Fig. 1. The three negative charges are located in the three phenolate rings, and this compound is rationalized as a tetrazolium cation having three phenolate rings in the 2, 3, and 5 positions. Attempts to oxidize **16** to its anion radical or other oxidized species with various oxidants (potassium hexacyanoferrate(III), silver(I) oxide, lead tetracetate, etc.) were unsuccessful. Only with bromine, hexabrominated compound **17** was isolated. The conjugate anion **18** of the acid **17** is an another example of quinonoid mesoions.

Properties of Anthracene-Inserted Mesoion 23. The compound **23** having an inserted anthracene ring shows marked differences in its electronic structure from those of the benzene-ring-inserted mesoions **3a—c**, **4**, **16**, and **18**. The longest wavelength absorption of **23** in its visible spectrum exhibits very smaller solvent effect than **3c**, **4**, and **16** do as shown in Fig. 1. The carbonyl carbon of **23** resonates at δ 185.9, more than 17 ppm downfield than that of phenolate anion (δ 168.3). The chemical shift of the tetrazolium ring carbon is δ 175.7 and this value is also shifted downfield by 7.5—13.4 ppm compared with those of **3a—c**, **4**, **16**, and **18**. These spectroscopic properties clearly indicate that the compound **23** has a different type of electronic structures from the mesoions with an inserted benzene ring; the dipolar 10-(5-tetrazolylio)-anthrolate structure **27** is not important but the mesoionic betain **28** and/or bis(phenylazo)methylene structure **29** make(s) a significant contribution to the ground state of the compound **23**. This large difference in the ground state electronic structure between the benzene-inserted mesoions **3a—c**, **4**, **16**, and **18** and the anthracene-inserted mesoion **23** can be explained in terms of little stabilization of **27** compared to **28** or **29**, whereas **30** has a larger aromatic resonance energy compared to **31** or **32**.



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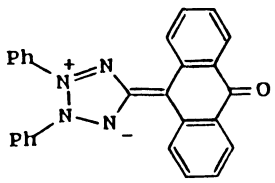

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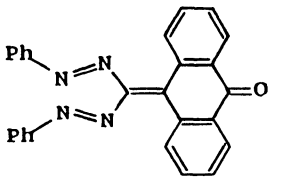

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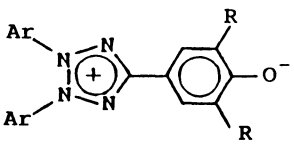

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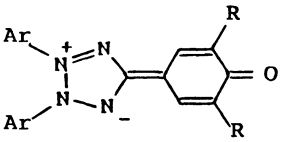

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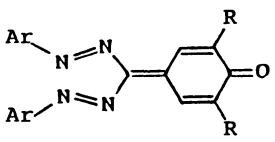

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Experimental

General. Melting points were determined with a hot-stage apparatus and uncorrected. IR spectra were taken for KBr discs with a JASCO A-102 instrument. Electronic spectra were measured on a Hitachi 124 spectrophotometer. Mass spectra were recorded with a Hitachi M-52 instrument at 20 eV using a direct inlet system. ^1H NMR spectra were run with Hitachi R-24A (60 MHz) and Varian XL-200 (200 MHz) spectrometers. ^{13}C NMR spectra were recorded with a Varian XL-200 (50.3 MHz) spectrometer. Elemental

analysis were performed at Elemental Analysis Center in Kyoto University.

1,5-Diphenyl-3-(*o*-methoxyphenyl)formazane (5a). *o*-Anisaldehyde phenylhydrazone (9.09 g, 40.2 mmol) in pyridine (60 cm³) was slowly added below 5 °C to a solution of benzenediazonium chloride prepared from aniline (3.7 cm³, 40.8 mmol) and sodium nitrite (2.82 g, 40.9 mmol) in a mixture of acetic acid (5 cm³) and concd hydrochloric acid (15 cm³). After stirring for 2 h, the mixture was poured into water (300 cm³). The precipitate was filtered, washed with warm water and a small amount of ethanol and then dried giving formazane **5a** (10.2 g, 77%), a reddish orange powder. The corresponding *m*- (**5b**) and *p*-isomers (**5c**) were synthesized in the same manner in 55 and 89% yields, respectively.

5a: Mp 147—149 °C; IR: 3250, 3050, 2850, 1602, 1564, 1508, 1490, 1460, 1438, 1410, 1290, 1168, 1136, 1090, 1070, 1044, 1020, 760, 750, 690 cm⁻¹; MS: *m/z* 330 (M^+).

1,5-Diphenyl-3-(*m*-methoxyphenyl)formazane (5b): Mp 126 °C; IR: 3050, 2950, 2850, 1598, 1580, 1514, 1488, 1452, 1432, 1356, 1318, 1242, 1220, 1078, 1060, 1038, 920, 884, 860, 770, 750, 690, 684 cm⁻¹; MS: *m/z* 330 (M^+).

1,5-Diphenyl-3-(*p*-methoxyphenyl)formazane (5c): Mp 155 °C (lit,[8] mp 156—158 °C); IR: 3050, 2950, 2850, 1610, 1600, 1520, 1500, 1456, 1360, 1318, 1300, 1252, 1230, 1180, 1080, 1048, 1030, 1010, 844, 822, 776, 760, 740, 690, 660 cm⁻¹; MS: *m/z* 330 (M^+).

2,3-Diphenyl-5-(*o*-methoxyphenyl)tetrazolium Tetrafluoroborate (6a). A mixture of formazane **5a** (2.20 g, 6.7 mmol) and chromium(VI) oxide (2.16 g, 21.6 mmol) in acetic acid (50 cm³) and 5—6 drops of water was refluxed for 15 min. When the mixture turned to green, it was cooled and poured into water (200 cm³). The yellow precipitate deposited was collected by filtration. The precipitate was dissolved in dichloromethane and shaked with aqueous sodium tetrafluoroborate. The dichloromethane layer was separated and dried over anhydrous sodium sulfate. After evaporation, the residue was recrystallized from dichloromethane–ether giving **6a** (723 mg, 26%), a pale yellow powder. Oxidation with NBS (vide infra) gave a much better yield (79%).

6a: Mp 200 °C; IR: 3090, 2950, 2850, 1610, 1586, 1520, 1490, 1440, 1280, 1260, 1164, 1140—1000, 776, 760, 690 cm⁻¹; ¹H NMR (DMSO-d_6): δ=4.00 (s, 3H, OMe), 7.20—8.20 (m, 14H, Ph); Found: C, 57.70; H, 4.08; N, 13.18%. Calcd for $C_{20}H_{17}BF_4N_4O$: C, 57.72; H, 4.12; N, 13.46%.

2,3-Diphenyl-5-(*m*-methoxyphenyl)tetrazolium Tetrafluoroborate (6b). Into a solution of formazane **5b** (1.70 g, 5.2 mmol) in ethyl acetate (16 cm³) was added a solution of NBS (1.86 g, 10.5 mmol) in ethyl acetate (12 cm³) at 50 °C and the mixture was stirred at 50 °C for 2 h. After evaporation, the residue was dissolved in dichloromethane and shaked with aqueous sodium tetrafluoroborate. The dichloromethane layer was separated and dried (Na_2SO_4). After evaporation, the residue was recrystallized from dichloromethane–ether giving **6b** (0.77 g, 36%), pale yellow needles. The *p*-isomer **6c** was similarly prepared as pale yellow crystals.

6b: Mp 201 °C; IR: 3090, 2970, 2850, 1620, 1588, 1534, 1490, 1440, 1286, 1250, 1230, 1170, 1126, 1110—1000, 880, 856, 800, 776, 770, 750, 690 cm⁻¹; ¹H NMR (DMSO-d_6): δ=3.90 (s, 3H, OMe), 7.30—7.95 (m, 14H, Ph); Found: C, 57.95; H, 3.99; N, 13.41%. Calcd for $C_{20}H_{17}BF_4N_4O$: C, 57.72; H, 4.12; N, 13.46%.

6c: Mp 230 °C; IR: 3100, 2980, 2850, 1612, 1490, 1468, 1440, 1310, 1280, 1266, 1180, 1162, 1130—1030, 1000, 930, 856, 770, 750, 688 cm⁻¹; ¹H NMR (DMSO-d_6): δ=3.90 (s, 3H, OMe), 7.25 (d, *J*=9.0 Hz, 2H, Ar), 7.65—7.75 (m, 10H, Ph), 8.20 (d, *J*=9.0 Hz, 2H, Ar); Found: C, 57.96; H, 4.03; N, 13.38%. Calcd for $C_{20}H_{17}BF_4N_4O$: C, 57.72; H, 4.12; N, 13.46%.

2,3-Diphenyl-5-(*o*-hydroxyphenyl)tetrazolium Bromide (7a). To a solution of tetrazolium salt **6a** (1.49 g, 3.58 mmol) in dichloromethane (10 cm³) was added boron tribromide (0.60 cm³, 6.3 mmol) at −78 °C under argon. The reddish brown mixture was gradually warmed to room temperature and poured into water. The precipitate was filtered, dried, and recrystallized from ethanol giving pale yellow needles of **7a** as the 1 : 1 complex with ethanol (1.19 g, 84%). Phenols **7b** and **7c** were similarly synthesized and obtained as pale yellow crystals.

7a: Mp 259 °C (decomp); IR: 3600—3300, 3050, 1616, 1600, 1522, 1484, 1456, 1410, 1370, 1294, 1260, 1162, 1110, 1070, 1068, 1022, 1000, 938, 880, 840, 778, 760, 690 cm⁻¹; UV (MeCN): λ_{max} (log ε) 216 nm (4.42), 248 (4.28), 300 (4.01); Found: C, 57.24; H, 4.70; N, 12.82%. Calcd for $C_{19}H_{15}BrN_4O \cdot C_2H_5OH$: C, 57.15; H, 4.80; N, 12.70%.

7b: Mp 258 °C (decomp); IR: 3550—3350, 3150, 1620, 1590, 1530, 1486, 1440, 1346, 1290, 1216, 1160, 1126, 1076, 1042, 1000, 920, 888, 870, 794, 766, 740, 682 cm⁻¹; UV (MeCN): λ_{max} (log ε) 218 nm (4.56), 252 (4.37), 297 (3.96); Found: C, 57.71; H, 3.71; N, 14.19%. Calcd for $C_{19}H_{15}BrN_4O$: C, 57.74; H, 3.82; N, 14.17%.

7c: Mp 280 °C (decomp); IR: 3550—3350, 3100—2950, 1610, 1588, 1486, 1460, 1448, 1278, 1224, 1170, 1160, 1000, 856, 770, 750, 690, 680 cm⁻¹; UV (MeCN): λ_{max} (log ε) 213 nm (4.21), 271 (4.40); Found: C, 57.79; H, 3.63; N, 14.01%. Calcd for $C_{19}H_{15}BrN_4O$: C, 57.74; H, 3.82; N, 14.17%.

2-(2,3-Diphenyl-5-tetrazolylio)phenolate (3a). Phenol **7a** (246 mg, 0.62 mmol) was dissolved in an aqueous sodium hydroxide solution (1 M, 1.5 cm³; 1 M=1 mol dm⁻³) at room temperature. Water was removed under reduced pressure and the residue was purified by column chromatography on Sephadex LH-20 using dichloromethane as an eluent. Mesoion **3a** was obtained as a brown powder (186 mg, 95%). By the same method, **3b** and **3c** were isolated in 84 and 68% yields, respectively, purple crystals.

3a: Mp 140 °C (decomp); IR: 3060, 1602, 1504, 1478, 1434, 1318, 1240, 1152, 1000, 846, 760, 686 cm⁻¹; UV (MeCN): λ_{max} (log ε) 220 nm (4.18), 258 (sh, 4.00), 381 (4.03), 496 (2.59); solvent dependence of the longest wavelength band: 398 nm (sh) (H_2O), 412 (MeOH), 425 (EtOH), 460 (*i*-PrOH), 491 (DMSO), 499 (Me_2C=O), 496 (CH_2Cl_2), 525 ($CHCl_3$); MS: *m/z* (rel intensity) 286 (M−CO, 15), 238 (23), 211 (50), 169 (14), 167 (14), 119 (14), 91 (100); Found: C, 70.44; H, 4.37; N, 17.18%. Calcd for $C_{19}H_{14}N_4O \cdot 0.5H_2O$: C, 70.57; H, 4.68; N, 17.33%.

3b: Mp 141 °C (decomp); IR: 3060, 1588, 1570, 1504, 1486, 1460, 1316, 1282, 1160, 1000, 982, 892, 764, 746, 688 cm⁻¹; UV (MeCN): λ_{max} (log ε) 250 nm (4.42), 320 (sh, 3.64), 535 (2.61); solvent dependence of the longest wavelength band: 396 nm (sh) (H_2O), 428 (MeOH), 443 (EtOH), 484 (*i*-PrOH), 536 (DMSO), 477 (Me_2C=O), 537 (CH_2Cl_2), 538 ($CHCl_3$); MS: *m/z* (rel intensity) 286 (M−CO, 19), 211 (92), 91 (100); Found: C, 68.12; H, 4.57; N, 16.17%. Calcd for $C_{19}H_{14}N_4O \cdot H_2O$: C, 68.66; H, 4.85; N, 16.86%.

3c: Mp 154 °C (decomp); IR: 3060, 1590, 1442, 1336, 1162, 1000, 980, 844, 762, 690 cm^{-1}; UV (MeCN): λ_{max} (log ε) 213 nm (4.06), 228 (3.97), 300 (sh, 4.05), 347 (4.54), 513 (2.68); solvent dependence of the longest wavelength band: 390 nm (H_2O), 419 (MeOH), 437 (EtOH), 467 (*i*-PrOH), 512 (DMSO), 530 (Me_2C=O), 542 (CH_2Cl_2), 542 ($CHCl_3$); MS: *m/z* (rel intensity) 286 (M−CO, 47), 211 (60), 169 (17), 167 (17), 91 (100); Found: C, 65.14; H, 4.91; N, 16.14%. Calcd for $C_{19}H_{14}N_4O \cdot 2H_2O$: C, 65.13; H, 5.13; N, 15.99%.

Adducts 8a—c of Mesoions 3a—c and Hydrobromic Acid. The following preparation of **8c** represents the general procedure. Phenol **7c** (143 mg, 0.36 mmol) was suspended in dichloromethane (15 cm^3) and DBU (0.1 cm^3, 0.67 mmol) was added at room temperature. Phenol **7c** went into solution and the mixture turned to reddish purple. After a few minutes, orange crystals deposited which were filtered off and dried giving **8c** (113 mg, 89%).

8c: Mp 179 °C (decomp); IR: 1610, 1486, 1460, 1174, 1000, 842, 770, 750, 692, 682 cm^{-1}; ^1H NMR (DMSO-d_6): δ=6.72 (d, 2H, *J*=9 Hz, H-3), 7.57—7.80 (m, 10H, Ph), 7.91 (d, 2H, *J*=9 Hz, H-2); Found: C, 63.55; H, 4.27; N, 16.26; Br, 11.29%. Calcd for $C_{38}H_{29}BrN_8O_2$: C, 64.37; H, 4.09; N, 15.80; Br, 11.28%.

Adducts **8a** and **8b** were similarly synthesized in almost quantitative yields.

8a: Mp 143 °C (decomp); IR: 1642, 1608, 1584, 1440, 1370, 1322, 1296, 1160, 1104, 1000, 836, 768, 752, 686 cm^{-1}. ^1H NMR (DMSO-d_6): δ=6.38—6.50 (m, 1H, Ar), 6.69—6.74 (m, 1H, Ar), 7.14—7.24 (m, 1H, Ar), 7.66—8.00 (m, 11H, Ar and Ph).

8b: Mp 180 °C (decomp); IR: 1500, 1490, 1422, 1260, 1160, 1074, 1016, 1000, 992, 894, 880, 870, 790, 762, 740, 680 cm^{-1}; ^1H NMR (DMSO-d_6): δ=6.93—7.02 (m, 1H, Ar), 7.36—7.40 (m, 2H, Ar), 7.52 (s, 1H, Ar), 7.70—7.97 (m, 10H, Ph).

1,5-Diphenyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)formazane (10). This compound was synthesized in 94% yield as a dark purple powder by a similar synthetic method to **5a—c** from 3,5-di-*t*-butyl-4-hydroxybenzaldehyde phenylhydrazone (**9**). Mp 122 °C; IR: 3650—3370, 2960, 2910, 2870, 1600, 1510, 1500, 1438, 1360, 1314, 1254, 1236, 1150, 1118, 1080, 1068, 996, 920, 898, 884, 796, 770, 744, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ=1.44 (s, 18H, *t*-Bu), 5.25 (s, 1H, OH), 7.02—7.71 (m, 10H, Ph), 7.90 (s, 2H, Ar), 8.58 (s, 1H, NH).

2,3-Diphenyl-5-(3,5-di-*t*-butyl-4-hydroxyphenyl)tetrazolium Tetrafluoroborate (11). Formazane **10** was oxidized with NBS as described above and tetrafluoroborate **11** was obtained in 28% yield, colorless crystals, after an anion exchange with sodium tetrafluoroborate. Mp 246 °C (decomp). IR: 3630—3330, 3080, 2960, 1604, 1516, 1488, 1410, 1120—1030, 762, 690 cm^{-1}; ^1H NMR (DMSO-d_6): δ=1.46 (s, 18H, *t*-Bu), 5.73 (s, 1H, OH), 7.65—7.84 (m, 6H, Ph), 7.89—7.96 (m, 4H, Ph), 8.00 (s, 2H, Ar); UV (MeCN): λ_{max} (log ε) 217 nm (4.56), 272 (4.46); Found: C, 62.34; H, 6.11; N, 10.89%. Calcd for $C_{27}H_{31}BF_4N_4O \cdot 0.25H_2O$: C, 62.50; H, 6.12; N, 10.80%.

2,6-Di-*t*-butyl-4-(2,3-diphenyl-5-tetrazolylio)phenolate (4). Into a solution of **11** (630 mg, 1.23 mmol) in methanol (5 cm^3) was added aqueous sodium hydroxide (1 M, 2 cm^3). The mixture turned to purple and a precipitate deposited. Water was evaporated under reduced pressure and the residue was chromatographed on Sephadex LH-20 (dichloromethane–acetone) giving **4** quantitatively, pale blue crystals. Mp 209 °C; IR: 3060, 2950, 2910, 1586, 1478, 1440, 1350, 1334, 992, 900, 808, 760, 684 cm^{-1}; ^1H NMR (DMSO-d_6): δ=1.38 (s, 18H, *t*-Bu), 7.64 (s, 2H, Ar), 7.64—7.78 (m, 6H, Ph), 7.82—7.88 (m, 4H, Ph); UV (MeCN): λ_{max} (log ε) 249 nm (sh, 3.97), 282 (4.08), 373 (4.48), 605 (2.50); solvent dependence of the longest wavelength band: 510 nm (MeOH), 543 (EtOH), 583 (*i*-PrOH), 591 (DMSO), 631 (Me_2C=O), 690 (CH_2Cl_2); MS: *m/z* (rel intensity) 426 (M^+, 100), 411 (77), 384 (73), 342 (47), 322 (67), 105 (40), 77 (40). Found: C, 75.04; H, 7.11; N, 12.83%. Calcd for $C_{27}H_{30}N_4O \cdot 0.25H_2O$: C, 75.24; H, 7.12; N, 12.99%.

1,3,5-Tris(*p*-methoxyphenyl)formazane (13). This compound was prepared in 81% yield from *p*-anisaldehyde *p*-methoxyphenylhydrazone[9] (**12**) (7.05 g, 27.5 mmol) and *p*-methoxybenzenediazonium chloride (35.1 mmol) in a similar manner as **5a—c**. Mp 136—138 °C (lit,[9] mp 140 °C); IR: 3020, 2950, 2850, 1600, 1580, 1510, 1460, 1440, 1422, 1306, 1256, 1230, 1182, 1166, 1142, 1102, 1022, 836, 824, 796, 740, 702 cm^{-1}; ^1H NMR (DMSO-d_6): δ=3.75 (s, 9H, OMe), 6.80 (d, 4H, *J*=9 Hz, Ar), 6.84 (d, 2H, *J*=9 Hz, Ar), 7.55 (d, 4H, *J*=9 Hz, Ar), 7.68 (d, 2H, *J*=9 Hz, Ar), 14.35 (s, 1H, NH); MS: 390 (M^+).

2,3,5-Tris(*p*-methoxyphenyl)tetrazolium Tetrafluoroborate (14). This salt was obtained by the oxidation of **13** (1.98 g, 5.07 mmol) with NBS (3.60 g, 20.2 mmol) in 65% yield. Mp 176 °C; IR: 3100, 2970, 2850, 1616, 1600, 1588, 1510, 1460, 1438, 1310, 1260, 1178, 1160, 1130—1020, 990, 840, 750, 660 cm^{-1}; ^1H NMR (DMSO-d_6): δ=3.82 (s, 6H, 2 OMe), 3.86 (s, 3H, OMe), 7.16 (d, 4H, *J*=9 Hz, H-7), 7.23 (d, 2H, *J*=9 Hz, H-3), 7.72 (d, 4H, *J*=9 Hz, H-6), 8.20 (d, 2H, *J*=9 Hz, H-2); ^{13}C NMR (DMSO-d_6): δ=55.7 (OMe), 56.1 (2 OMe), 115.2 (C-1), 115.4 (C-7), 115.6 (C-3), 125.4 (C-5), 128.1 (C-6), 129.1 (C-2), 162.8 (C-8), 163.1 (C-4), 163.7 (C^+); Found: C, 55.71; H, 4.33; N, 11.79%. Calcd for $C_{22}H_{21}BF_4N_4O_3$: C, 55.49; H, 4.44; N, 11.76%.

2,3,5-Tris(*p*-hydroxyphenyl)tetrazolium Bromide (15). The compound **14** (1.28 g, 2.69 mmol) was demethylated by the action of boron tribromide (0.85 cm^3, 8.95 mmol) in the same manner as **7a—c** giving yellow needles of **15** in 94% yield. Mp 279 °C (decomp); IR: 3450—3050, 1616, 1594, 1512, 1462, 1452, 1350, 1290, 1260, 1220, 1172, 1160, 1104, 1028, 1000, 840, 748, 710, 684 cm^{-1}; ^1H NMR (DMSO-d_6); δ=6.98 (d, 4H, *J*=9 Hz, H-7), 7.07 (d, 2H, *J*=9 Hz, H-3), 7.62 (d, 4H, *J*=9 Hz, H-6), 8.10 (d, 2H, *J*=9 Hz, H-2), 10.58 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ=113.9 (C-1), 116.4 (C-7), 116.9 (C-3), 124.1 (C-5), 128.2 (C-6), 129.2 (C-2), 161.7 (C-8), 161.9 (C-4), 163.8 (C^+); UV (MeCN): λ_{max} (log ε) 217 nm (4.52), 262 (4.45), 272 (sh, 4.42), 308 (sh, 4.07), 352 (sh, 3.80); Found: C, 53.16; H, 3.43; N, 12.88%. Calcd for $C_{19}H_{15}BrN_4O_3$: C, 53.42; H, 3.54; N, 13.11%.

Disodium 4,4′,4″-(Tetrazole-2,3,5-triylio)tris[phenolate] (16). Bromide **15** (160 mg, 0.38 mmol) was dissolved in a sodium hydroxide solution (1 M, 2 cm^3) at room temperature. Water was pumped off and the residue was recrystallized twice from methanol–ether giving reddish orange crystals of **16** quantitatively. Mp 190 °C (decomp); IR: 1580, 1496, 1446, 1332, 1320, 1164, 1140, 842 cm^{-1}; ^1H NMR (DMSO-d_6): δ=6.36 (d, 4H, *J*=9 Hz, H-7), 6.69 (d, 2H, *J*=9 Hz, H-3), 7.23 (d, 4H, *J*=9 Hz, H-6), 7.82 (d, 2H, *J*=9 Hz, H-2); ^{13}C NMR (D_2O): δ=111.7 (C-1), 121.7 (C-5), 121.9 (C-7), 122.7 (C-3), 129.2 (C-6), 131.9 (C-2), 173.3 (C-4), 174.3 (C-8), 167.2

(C^+); UV (MeOH): λ_{max} (log ε) 260 nm (4.29), 274 (sh, 4.24), 320 (sh, 3.93), 425 (3.79); solvent dependence of the longest wavelength band: 372, 413 nm (sh) (H_2O), 425 (MeOH), 448 (EtOH), 480 (*i*-PrOH), 506 (DMSO); Found: C, 48.51; H, 4.62; N, 11.49%. Calcd for $C_{19}H_{12}N_4Na_2O_3 \cdot 4.5H_2O$: C, 48.41; H, 4.49; N, 11.89%.

2,3,5-Tris(3,5-dibromo-4-hydroxyphenyl)tetrazolium Bromide (17). 2,3,5-Tris(*p*-hydroxyphenyl)tetrazolium bromide (**15**) (222 mg, 0.52 mmol) was dissolved in aqueous sodium hydroxide (1 M, 20 cm^3) and bromine (0.16 cm^3, 3.2 mmol) was added at room temperature. The reaction mixture was stirred at room temperature for 3 h. The mixture was acidified with hydrochloric acid (2 M) and the resulting solid was filtered. Recrystallization from methanol–ether gave a yellow powder of **17** (403 mg, 86%). Mp ca. 200 °C; IR: 3630—3310, 3090, 1600, 1560, 1470, 1436, 1312, 1240, 1170—1000, 880, 750, 736 cm^{-1}; ^1H NMR (DMSO-d_6): δ=4.80 (s, 3H, OH), 8.12 (s, 4H, H-6), 8.33 (s, 2H, H-2); ^{13}C NMR (DMSO-d_6): δ=111.7 (C-7), 113.0 (C-3), 116.3 (C-1), 124.0 (C-5), 130.3 (C-6), 131.3 (C-2), 155.6 (C-4), 156.6 (C-8), 161.8 (C^+); UV (MeCN): λ_{max} (log ε) 218 nm (4.46), 266 (4.08), 315 (3.78), 520 (3.62); Found: C, 25.38; H, 0.97; N, 5.85%. Calcd for $C_{19}H_9Br_7N_4O_3$: C, 25.34; H, 1.01; N, 6.22%.

Disodium 4,4′,4″-(Tetrazole-2,3,5-triylio)tris[2,6-dibromophenolate] (18). The acid **17** (400 mg, 0.44 mmol) was dissolved in methanol (2 cm^3) and an aqueous solution of sodium hydroxide (1 M, 1.5 cm^3) was added. Water was pumped off and the residue was purified by recrystallization from methanol–ether and then column chromatography on Sephadex LH-20 giving brownish red plates of **18** (333 mg, 88%). Mp 235 °C (decomp); IR: 1578, 1560, 1410—1320, 1358, 1168, 1140, 880, 758, 742, 730 cm^{-1}; ^1H NMR (DMSO-d_6): δ=7.41 (s, 4H, H-6), 7.76 (s, 2H, H-2); ^{13}C NMR (DMSO-d_6): δ=102.1 (C-1), 112.1 (C-3), 113.1 (C-7), 115.4 (C-5), 128.1 (C-6), 129.5 (C-2), 162.3 (C^+), 162.5 (C-4), 164.2 (C-8); UV (MeOH) λ_{max} (log ε) 217 nm (4.77), 314 (4.55), 399 (4.17), 448 (sh, 4.02); Found: C, 25.67; H, 1.46; N, 6.14%. Calcd for $C_{19}H_6Br_6N_4Na_2O_3 \cdot 2H_2O$: C, 25.36; H, 1.12; N, 6.23%.

1,5-Diphenyl-3-(10-methoxy-9-anthryl)formazane (20). From 10-methoxy-9-anthraldehyde phenylhydrazone (**19**) (1.05 g, 3.20 mmol) and benzenediazonium chloride (3.2 mmol), **20** was obtained as an orange powder (1.32 g, 96%). Mp 174—175 °C (decomp); IR: 1600, 1562, 1558, 1500, 1438, 1360, 1286, 1260, 1216, 1200, 1160, 1092, 982, 962, 780, 750, 726, 700, 680 cm^{-1}; ^1H NMR ($CDCl_3$): δ=4.24 (s, 3H, OMe), 7.12—7.56 (m, 12H, Ar), 7.63—7.76 (m, 4H, Ar), 8.40—8.48 (m, 2H, Ar).

2,3-Diphenyl-5-(10-methoxy-9-anthryl)tetrazolium Tetrafluoroborate (21). Formazane **20** (680 mg, 1.58 mmol) was oxidized with NBS (1.12 g, 6.29 mmol) as the same manner to **5a**—**c**. The crude product was purified by column chromatography on silica gel with dichloromethane–acetone (1:1) as the eluent. Pure **21** was obtained as pale yellow crystals. Mp 150—153 °C; IR: 1664, 1600, 1488, 1458, 1324, 1266, 1122, 1100—1020, 760, 720, 704, 682 cm^{-1}; ^1H NMR (DMSO-d_6): δ=4.06 (s, 3H, OMe), 7.24—7.94 (m, 14H, Ar), 8.06—8.44 (m, 4H, Ar); ^{13}C NMR (DMSO-d_6): δ=64.2 (OMe), 111.7 (=C–), 122.8 (=C–), 123.8 (=CH–), 125.2 (=CH–), 126.4 (=CH–), 126.4 (ortho), 128.9 (=CH–), 130.6 (meta), 132.0 (=C–), 133.3 (ipso), 134.3 (para), 158.2 (C–O), 163.9 (C^+).

2,3-Diphenyl-5-(10-hydroxy-9-anthryl)tetrazolium Bromide (22). The compound **21** (335 mg, 0.65 mmol) was demethylated with boron tribomide (0.20 cm^3, 2.1 mmol) as the cases of **6a**—**c** yielding **22** (239 mg, 74%), orange powder. Mp 215 °C (decomp); IR: 3600—3350, 1558, 1500, 1486, 1422, 1348, 1312, 1176, 1162, 1140, 998, 924, 770, 686 cm^{-1}; ^1H NMR (DMSO-d_6): δ=7.61—7.95 (m, 10H, Ar), 8.03—8.09 (m, 4H, Ar), 8.49 (d, 2H, J=9 Hz, Ar), 8.70 (d, 2H, J=9 Hz, Ar), 11.56 (s, 1H, OH); ^{13}C NMR (DMSO-d_6): δ=103.8 (=C–), 119.4 (=C–), 123.3 (=CH–), 124.5 (=CH–), 124.6 (=CH–), 126.4 (ortho), 128.7 (=CH–), 130.4 (meta), 132.0 (=C–), 133.3 (ipso), 134.1 (para), 154.5 (C–O), 163.2 (C^+); UV (MeCN): λ_{max} (log ε) 214 nm (4.40), 259 (4.69), 275 (sh, 4.18), 386 (sh, 3.60), 400 (3.63): Found: C, 64.14; H, 3.95; N, 10.97%. Calcd for $C_{27}H_{19}BrN_4O \cdot 0.5H_2O$: C, 64.29; H, 4.00; N, 11.11%.

Synthesis of 23 by the Deprotonation of 22. Into a solution of **22** (60 mg, 0.12 mmol) in methanol (10 cm^3) was added an aqueous solution of NaOH (1 M, 0.5 cm^3) at room temperature. The solvent was removed under reduced pressure and the residue was chromatographed on Sephadex LH-20. Recrystallization from acetonitrile–ether gave pure **23** as greenish brown crystals in a quantitative yield. Mp 125 °C (decomp); IR: 3060, 1602, 1558, 1480, 1440, 1424, 1334, 1260, 1180, 1120, 1030, 1016, 996, 772, 768, 732, 690, 674 cm^{-1}; ^1H NMR (DMSO-d_6): δ=7.01—7.13 (m, 2H, Ar), 7.37—7.49 (m, 2H, Ar), 7.53—7.85 (m, 6H, Ph), 7.93—8.01 (m, 4H, Ph), 8.44—8.60 (m, 4H, Ar); ^{13}C NMR (DMSO-d_6): δ=118.4 (=C–), 118.4 (=CH–), 122.0 (=C–), 123.9 (=CH–), 126.5 (ortho), 126.7 (=CH–), 128.6 (=CH–), 130.4 (meta), 133.4 (para), 133.5 (ipso), 135.6 (=C–), 175.7 (C^+), 185.9 (C=O); UV (MeCN): λ_{max} (log ε) 257 nm (4.67), 275 (4.82), 343 (sh, 4.27), 366 (4.37), 425 (sh, 3.75), 450 (3.98), 478 (4.19), 509 (4.19); solvent dependence of the longest wavelength band; 486 nm (sh) (MeOH), 495 (EtOH), 504 (*i*-PrOH), 513 (DMSO), 510 (Me_2C=O), 508 (CH_2Cl_2), 509 ($CHCl_3$), 513 (DMF); MS: *m/z* (rel intensity) 414 (M^+, 45), 413 (100), 325 (41), 324 (59), 308 (34), 237 (32), 232 (54), 93 (59), 92 (43), 77 (64); Found: C, 72.33; H, 5.30%. Calcd for $C_{27}H_{18}N_4O \cdot 2H_2O$: C, 71.99; H, 4.92%.

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