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X-Ray Crystal Structures and Chemical Properties of Heterocyclic Azo Compounds Coupled with *m*-Alkoxyphenols

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X-Ray crystal structures have been determined for two compounds obtained by the coupling reaction of 2-pyridinediazonium salt and *m*-methoxyphenol, viz., 3-methoxy-4-(2-pyridylazo)phenol (**1**) and 5-methoxy-2-(2-pyridylazo)phenol (**2**). The 2-pyridylazo and 2-thiazolylazo compounds having *o*-methoxy and *p*-hydroxy groups, such as **1**, have lower pK_a values and lower affinities for or higher selectivities to metal ions than corresponding *o*-hydroxy isomers. The resulting bis complexes with metal ions show molar absorptivities greater than 10^5.

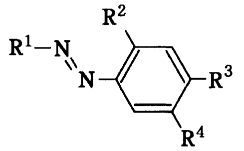
1-(2-Pyridylazo)-2-naphthol reacts with metal ions to form extractable colored complexes (molar absorptivities of 2—5×10^4 $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$). Various structural modifications have been examined in order to improve the sensitivity and selectivity of this reagent.[1,2] Use of thiazole as a heterocyclic ring generally reduces the reactivity to any metal ion. Elimination of an –OH group ortho to the azo group in a coupling component, or even its substitution for –COOH or $-NH_2$ increases the selectivity. The sensitivity, on the other hand, can be increased by the introduction of a substituted amino group at a para position to the azo group or by bromination of a heterocyclic ring.

In a previous paper,[3] we reported the syntheses and properties of new heterocyclic azo compounds obtained by the coupling reaction of 2-pyridinediazonium salt and several *m*-alkoxyphenols. For example, the compound derived from 2-pyridinediazonium salt and *m*-methoxyphenol (**1**, decomposes at 187 °C) forms a nickel complex, which is extractable into chloroform and shows a molar absorptivity as large as 1.1×10^5. We tentatively assigned the compound to 5-methoxy-2-(2-pyridylazo)phenol at that stage.

Further studies on these and related 2-thiazolylazo compounds, however, have shown that two compounds having an identical chemical composition are formed in the coupling reaction. In coupling with *m*-methoxyphenol, compound **2** (mp 158 °C) as well as **1** was obtained. In this work we carried out X-ray crystal structure analyses for **1** and **2** in order to identify these compounds; we have found that **1** is 3-methoxy-4-(2-pyridylazo)phenol and **2** is 5-methoxy-2-(2-pyridylazo)phenol. Compound **1** having *o*-OR and *p*-OH groups will construct a new class of heterocyclic azo compounds in addition to the conventional *o*-NH_2, *o*-COOH and *o*-OH compounds. Chemical properties of **1**, **2**, and 4-methoxy-2-(2-pyridylazo)phenol (**3**) as well as those of the corresponding 2-thiazolylazo compounds (**4**, **5**, and **6**; Chart 1) were studied and compared.

Experimental

Preparation of 2-Pyridylazo Compounds. 2-Pyridinediazonium salt was prepared as described previously.[3] Its coupling reaction with *m*-methoxyphenol in pure ethanol mainly gave **2**, whereas the same in the presence of sodium ethoxide gave **1**. This was confirmed by a reversed-phase HPLC analysis of each product [k'=0.56 for **1**; 2.16 for



Compound	R^1	R^2	R^3	R^4
1	2-Pyridyl	OCH_3	OH	H
2	2-Pyridyl	OH	OCH_3	H
3	2-Pyridyl	OH	H	OCH_3
4	2-Thiazolyl	OCH_3	OH	H
5	2-Thiazolyl	OH	OCH_3	H
6	2-Thiazolyl	OH	H	OCH_3

Chart 1.

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2, CH_3CN/H_2O (60/40) as a mobile phase and octadecyl-bonded silica gel as a stationary phase]. Although carbon dioxide was bubbled through the solution to complete the coupling reaction, the yields, especially that of **2**, were low.

3-Methoxy-4-(2-pyridylazo)phenol (1): Recrystallized from ethanol–water. Mp 187 °C (decomp). IR (KBr) 3420, 2940, 2840, 2600, 1610, 1580, 1495, 1410, 1280, 1250, 1205, 1120, 820, 775, 730 cm^{-1}; ^1HNMR ($CDCl_3$) δ=3.99 (s, 3H), 5.97 (d, 1H), 6.41 (dd, 1H), 7.02—7.10 (m, 1H), 7.20 (d, 1H), 7.54—7.84 (m, 2H), 8.34 (dd, 1H). Found: C, 63.03; H, 4.79; N, 18.21%. Calcd for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33%.

5-Methoxy-2-(2-pyridylazo)phenol (2): Purified by acid-precipitation and vacuum sublimation. Mp 157—159 °C; IR (KBr) 3430, 2940, 1620, 1495, 1335, 1210, 1110, 1000, 840, 810, 775 cm^{-1}; ^1HNMR ($CDCl_3$) δ=3.88 (s, 3H), 6.34 (d, 1H), 6.57 (dd, 1H), 7.24—7.34 (m, 1H), 7.62 (d, 1H), 7.74—7.92 (m, 2H), 8.62 (dd, 1H). Found: C, 62.88; H, 4.74; N, 18.23%. Calcd for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33%.

The coupling reaction of 2-pyridinediazonium salt with *p*-methoxyphenol gave only one product, which was purified by repeated extraction of chloroform and back-extraction with an 0.1 mol dm^{-3} NaOH solution.

4-Methoxy-2-(2-pyridylazo)phenol (3): Purified by vacuum-sublimation. Mp 100 °C; yield, 20%. Found: C, 62.6; H, 4.92; N, 18.9%. Calcd for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.33%.

Preparation of 2-Thiazolylazo Compounds. To an aqueous solution of *m*-methoxyphenol in 4 mol dm^{-3} HCl, a solution of 2-thiazolediazonium salt was added at temperatures below −10 °C. An acetonitrile solution of the precipitates was separated on octadecyl-bonded silica gel using a 0.01 mol dm^{-3} NH_4SCN solution of CH_3CN/H_2O (70/30) as a mobile phase. Two components (**4**, k'=0.50, decomposes at 177 °C; **5**, k'=1.87, mp 155—156 °C) were obtained in a ratio of 70:30. Based on a comparison of the chromatographic behaviors, melting points and others of **4** and **5** with those of **1** and **2**, **4** was reasonably assigned to 3-methoxy-4-(2-thiazolylazo)phenol and **5** to 5-methoxy-2-(2-thiazolylazo)phenol. The coupling reaction of 2-thiazolediazonium salt with *p*-methoxyphenol gave only one product (**6**, mp 109 °C). The purities of **5** and **6** were 100%, as determined by the reaction with Cu(II).

X-Ray Structure Analysis. The X-ray diffraction data were collected using a Rigaku AFC-5R diffractometer with graphite-monochromatized Cu $K\alpha$ radiation (λ= 1.54178 Å, ω -2θ scans) at room temperature. The crystal data and details concerning data collection are summarized in Table 1. The structures were solved by a direct method and refined by the block-diagonal least-squares method. The weighting scheme, $w=[\sigma^2(F_o)+a|F_o|^2]^{1/2}$ (a=0.00639 for **1** and 0.00097 for **2**), was employed. All the hydrogen atoms were located in a difference density map for both the compounds. The atomic coordinates and thermal parameters of the non-hydrogen atoms are listed in Table 2. The anisotropic thermal parameters of the non-hydrogen atoms, the atomic coordinates and temperature factors of the hydrogen atoms, and the F_o-F_c tables were deposited as Document No. 68039 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results

X-Ray Crystal Structures of 1 and 2. The molecular structures are shown in Fig. 1 for one of two independent molecules of **1** and for **2**. The bond distances and angles are given in Table 3. Compound **1** was identified as 3-methoxy-4-(2-pyridylazo)phenol and compound **2** as 5-methoxy-2-(2-pyridylazo)phenol.

Table 1. Crystallographic Data for **1** and **2**

Compound	**1**	**2**
Formula	$C_{12}H_{11}N_3O_2$	
Formula weight	229.24	
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
a/Å	11.40(1)	9.163(1)
b/Å	13.92(1)	22.86(2)
c/Å	7.50(1)	5.283(6)
α/°	91.5(1)	—
β/°	98.4(1)	—
γ/°	68.1(1)	—
V/Å^3	1091(2)	1106(2)
Z	4	4
D_x/g cm^{-3}	1.396	1.377
μ(Cu $K\alpha$)/cm^{-1}	8.23	8.12
Crystal size/mm	0.3×0.2×0.2	1.0×0.1×0.01
$2\theta_{max}$/°	100	130
No. of unique rflns	2249	1120
No. of obsd rflns, $F_o>3\sigma(F_o)$	2038	866
No. of rflns used	1986	853
$R^{a)}$	0.064	0.045
$R_w{}^{b)}$	0.090	0.054

a) $R=\Sigma|\Delta F|/\Sigma|F_o|$. b) $R_w=(\Sigma w|\Delta F|^2/\Sigma w|F_o|^2)^{1/2}$.

Table 2. Fractional Coordinates and Isotropic Thermal Parameters (Å^2) of Nonhydrogen Atoms

Atom	x	y	z	B_{eq}[a)]
Compound **1**				
C1	−0.1718(2)	0.0411(2)	−0.1907(3)	3.7(1)
N2	−0.2846(2)	0.1090(1)	−0.1548(3)	4.0(1)
C3	−0.3711(2)	0.0709(2)	−0.1234(4)	4.8(1)
C4	−0.3511(2)	−0.0331(2)	−0.1236(4)	4.7(1)
C5	−0.2346(2)	−0.1015(2)	−0.1611(4)	4.8(1)
C6	−0.1444(2)	−0.0649(2)	−0.1962(4)	4.4(1)
N7	−0.0882(2)	0.0893(1)	−0.2295(3)	4.1(1)
N8	0.0210(2)	0.0246(2)	−0.2524(3)	4.0(1)
C9	0.1056(2)	0.0681(2)	−0.2941(3)	3.8(1)
C10	0.2266(2)	0.0001(2)	−0.3332(3)	3.8(1)
C11	0.3130(2)	0.0384(2)	−0.3818(3)	4.2(1)
C12	0.2822(2)	0.1457(2)	−0.3903(3)	4.2(1)
C13	0.1659(2)	0.2138(2)	−0.3430(4)	4.7(1)
C14	0.0809(2)	0.1745(2)	−0.2980(4)	4.6(1)
O15	0.2472(2)	−0.1027(1)	−0.3220(3)	5.0(1)
C16	0.3695(2)	−0.1763(2)	−0.3551(4)	5.7(1)
O17	0.3679(2)	0.1799(1)	−0.4461(3)	5.3(1)
C1′	0.1801(2)	0.4575(2)	0.4015(3)	3.7(1)
N2′	0.2878(2)	0.3908(2)	0.4937(3)	4.4(1)
C3′	0.3733(2)	0.4294(2)	0.5771(4)	4.8(1)
C4′	0.3518(2)	0.5340(2)	0.5714(4)	5.0(1)
C5′	0.2408(3)	0.6013(2)	0.4744(4)	5.1(1)
C6′	0.1526(2)	0.5629(2)	0.3875(3)	4.5(1)
N7′	0.0977(2)	0.4082(1)	0.3180(3)	3.9(1)
N8′	−0.0074(2)	0.4721(1)	0.2438(3)	3.9(1)
C9′	−0.0942(2)	0.4290(2)	0.1592(3)	3.7(1)
C10′	−0.2099(2)	0.4968(2)	0.0638(3)	3.7(1)
C11′	−0.2974(2)	0.4583(2)	−0.0241(3)	4.1(1)
C12′	−0.2704(2)	0.3522(2)	−0.0192(3)	4.0(1)
C13′	−0.1601(2)	0.2849(2)	0.0820(4)	4.7(1)
C14′	−0.0719(2)	0.3229(2)	0.1691(3)	4.3(1)
O15′	−0.2278(2)	0.5991(1)	0.0654(2)	4.8(1)
C16′	−0.3458(2)	0.6713(2)	−0.0224(4)	5.1(1)
O17′	−0.3575(1)	0.3179(1)	−0.1131(3)	5.2(1)
Compound **2**				
C1	1.5127(4)	0.3853(2)	−0.4688(7)	3.8(1)
N2	1.5568(4)	0.3391(1)	−0.5973(6)	4.7(1)
C3	1.6539(5)	0.3494(2)	−0.7871(9)	5.2(1)
C4	1.7067(5)	0.4033(2)	−0.8425(8)	5.0(1)
C5	1.6575(5)	0.4508(2)	−0.7035(9)	5.3(1)
C6	1.5595(5)	0.4422(2)	−0.5090(7)	4.5(1)
N7	1.4114(3)	0.3701(1)	−0.2786(6)	3.9(1)
N8	1.3549(3)	0.4106(1)	−0.1342(6)	3.8(1)
C9	1.2587(4)	0.3924(2)	0.0412(7)	3.6(1)
C10	1.2152(4)	0.3320(2)	0.0815(7)	3.6(1)
C11	1.1156(4)	0.3200(1)	0.2833(8)	4.1(1)
C12	1.0609(4)	0.3649(2)	0.4250(7)	3.8(1)
C13	1.1016(4)	0.4246(2)	0.3844(7)	4.1(1)
C14	1.1987(4)	0.4373(2)	0.1963(7)	4.0(1)
O15	1.2649(3)	0.2912(1)	−0.0558(5)	4.7(1)
O16	0.9654(3)	0.3579(1)	0.6190(5)	4.9(1)
C17	0.9157(5)	0.2994(2)	0.6742(10)	6.0(1)

a) $B_{eq}=(4/3)\sum_i\sum_j\beta_{ij}(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

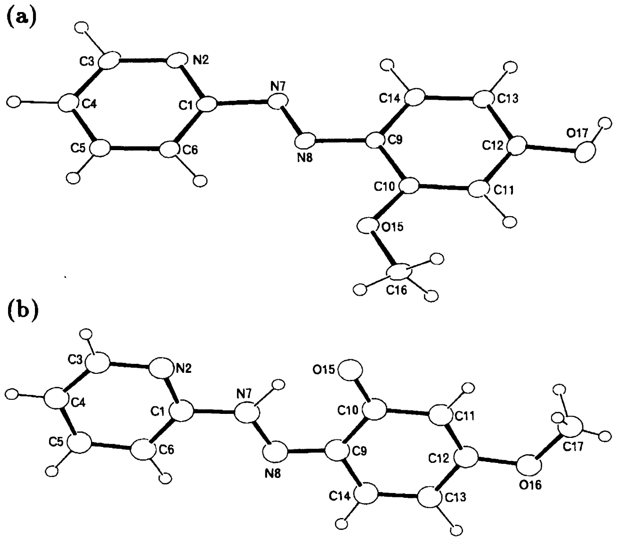

Fig. 1. Molecular structures of 3-methoxy-4-(2-pyridylazo)phenol (a) and 5-methoxy-2-(2-pyridylazo)phenol (b).

In both **1** and **2**, the azo groups adopt a trans configuration and N2 and N8 are in the trans position with respect to C1–N7. A difference in conformation between **1** and **2** is found with respect to N8–C9; N7 in **1** is in the trans position to C10 having a substituent, which is expected to be a more stable conformation. The N7–N8 distance (1.269 Å) is within the range of the normal N–N distance for azo groups. In contrast, C10 of **2** occupies the cis position to N7 because of the intramolecular hydrogen bond, N7–O15=2.538 Å. Such hydrogen bonds have been found for other heterocyclic azo compounds: 2.552 (av) Å for 1-(2-thiazolylazo)-2-naphthol (Htan) and 2.54 Å for its 6-bromo derivative.[4,5] The dissociable proton is found 1.05 Å apart from N7 for **2**, indicating a keto-hydrazone form in a solid. The N7–N8 distance (1.306 Å) is substantially equal to the average N–N distance of the usual azo and hydrazone groups, while the O15–C10 distance (1.266 Å) indicates a double-bond character. Accordingly, N8–C9, C11–C12, and C13–C14 are appreciably shortened. In the case of Htan, hydrogen atoms were found rather on a phenolic oxygen atom.[4,5]

Chemical Properties. The acid dissociation constants of 2-pyridylazo compounds were spectrophotometrically determined in 10% aqueous dioxane, while those of 2-thiazolylazo compounds were determined in 10% aqueous ethanol (Table 4). The p$K_{a,1}$'s of 2-thiazolylazo compounds were outside the usual pH range. As is well known, the p$K_{a,2}$'s of 2-pyridylazo compounds are greater than those of 2-thiazolylazo compounds. The p$K_{a,2}$'s of **2** and **3** are similar to each other and greater than that of **1**. Likewise those of **5** and **6** are similar to each other and greater than that of **4**. These results are explained by the intramolecular hydrogen bond between an azo nitrogen atom and an o-OH group

Table 3. Bond Lengths (Å) and Angles (°)

Bond lengths/Å		Bond angles/°	
Compound **1**			
C1–N2	1.342(4)	N2–C1–C6	122.4(3)
C1–C6	1.391(4)	N2–C1–N7	113.0(2)
C1–N7	1.419(4)	C6–C1–N7	124.5(3)
N2–C3	1.332(4)	C1–N2–C3	117.2(2)
C3–C4	1.380(4)	N2–C3–C4	124.1(3)
C4–C5	1.380(4)	C3–C4–C5	117.7(3)
C5–C6	1.366(4)	C4–C5–C6	119.7(3)
N7–N8	1.269(4)	C1–C6–C5	118.9(3)
N8–C9	1.389(4)	C1–N7–N8	112.8(2)
C9–C10	1.420(4)	N7–N8–C9	114.9(3)
C9–C14	1.402(4)	N8–C9–C10	117.9(3)
C10–C11	1.377(4)	N8–C9–C14	124.7(3)
C10–O15	1.365(4)	C10–C9–C14	117.4(3)
C11–C12	1.403(4)	C9–C10–C11	120.7(3)
C12–C13	1.402(4)	C9–C10–O15	115.0(2)
C12–O17	1.355(4)	C11–C10–O15	124.2(3)
C13–C14	1.362(4)	C10–C11–C12	119.8(3)
O15–C16	1.442(4)	C11–C12–C13	120.2(3)
		C11–C12–O17	117.7(2)
		C13–C12–O17	122.1(3)
		C12–C13–C14	119.0(3)
		C9–C14–C13	122.7(3)
		C10–O15–C16	118.0(2)
C1′–N2′	1.335(4)	N2′–C1′–C6′	123.4(3)
C1′–C6′	1.385(4)	N2′–C1′–N7′	112.6(2)
C1′–N7′	1.425(4)	C6′–C1′–N7′	124.0(2)
N2′–C3′	1.351(4)	C1′–N2′–C3′	117.5(3)
C3′–C4′	1.385(4)	N2′–C3′–C4′	122.4(3)
C4′–C5′	1.375(5)	C3′–C4′–C5′	119.2(3)
C5′–C6′	1.383(4)	C4′–C5′–C6′	119.1(3)
N7′–N8′	1.254(3)	C1′–C6′–C5′	118.4(3)
N8′–C9′	1.407(4)	C1′–N7′–N8′	112.2(2)
C9′–C10′	1.404(4)	N7′–N8′–C9′	115.4(2)
C9′–C14′	1.405(4)	N8′–C9′–C10′	117.6(2)
C10′–C11′	1.380(4)	N8′–C9′–C14′	123.4(2)
C10′–O15′	1.362(4)	C10′–C9′–C14′	119.0(3)
C11′–C12′	1.393(4)	C9′–C10′–C11′	119.9(3)
C12′–C13′	1.383(4)	C9′–C10′–O15′	116.1(2)
C12′–O17′	1.357(4)	C11′–C10′–O15′	124.0(3)
C13′–C14′	1.380(4)	C10′–C11′–C12′	120.0(3)
O15′–C16′	1.421(4)	C11′–C12′–C13′	120.9(3)
		C11′–C12′–O17′	117.7(2)
		C13′–C12′–O17′	121.4(3)
		C12′–C13′–C14′	119.3(3)
		C9′–C14′–C13′	120.8(3)
		C10′–O15′–C16′	118.2(2)
Compound **2**			
C1–N2	1.319(6)	N2–C1–C6	125.3(4)
C1–C6	1.386(6)	N2–C1–N7	111.8(4)
C1–N7	1.411(6)	C6–C1–N7	122.9(4)
N2–C3	1.361(6)	C1–N2–C3	116.2(4)
C3–C4	1.355(7)	N2–C3–C4	123.3(4)
C4–C5	1.386(7)	C3–C4–C5	118.8(4)
C5–C6	1.379(7)	C4–C5–C6	119.7(4)
N7–N8	1.306(4)	C1–C6–C5	116.7(4)
N8–C9	1.345(6)	C1–N7–N8	120.1(3)
C9–C10	1.453(6)	N7–N8–C9	116.3(3)
C9–C14	1.424(6)	N8–C9–C10	125.1(4)
C10–C11	1.430(6)	N8–C9–C14	115.3(4)
C10–O15	1.266(5)	C10–C9–C14	119.7(4)
C11–C12	1.366(6)	C9–C10–C11	117.8(4)
C12–C13	1.431(6)	C9–C10–O15	121.1(4)
C12–O16	1.357(5)	C11–C10–O15	121.0(4)
C13–C14	1.365(6)	C10–C11–C12	119.9(4)
O16–C17	1.442(6)	C11–C12–C13	122.6(4)
		C11–C12–O16	124.2(4)
		C13–C12–O16	113.2(4)
		C12–C13–C14	118.8(4)
		C9–C14–C13	121.2(4)
		C12–O16–C17	117.7(3)

for **2**, **3**, **5**, and **6**, as demonstrated by the X-ray crystallographic structure of **2**.

The reactions of metal ions with **2**—**6** were studied for the first time, while those with **1** were fully described elsewhere.[3] The reactivity of **2** is much higher than that of **1**. Nickel(II) is completely extracted with **2** into chloroform at pH$>$4, while being extractable with **1** only at pH$>$8. Zinc(II) is completely extracted with **2**, but not with **1**. Among 2-thiazolylazo compounds, although both **5** and **6** react quantitatively with Cu(II) at pH 5 in 10% aqueous ethanol, **4** does not. The OH group ortho to an azo group can deprotonate and strongly coordinate to a metal ion, while the OR group only weakly interacts with the metal ion.

The absorption maxima and molar absorptivities of neutral and anionic forms of six reagents and their metal complexes are summarized in Table 4. The anionic forms of **1** and **4** have molar absorptivities that are almost two-times greater than those of **2**, **3**, **5**, and **6**. This is also reflected in the metal complexes. The spectra of ML$_2$ extracted in chloroform were recorded for **1**—**3**, while those of complexes formed at pH 5 in 10% aqueous ethanol were measured for **5**—**6**. In the latter case, a 1 : 1 complex may be formed for Cu(II) and a 1 : 2 complex for Ni(II) in solutions. The absorption spectra of metal complexes with **4** could not be measured because of the low stability.

Discussion

The reaction of 2-pyridinediazonium salt with the OH form of *m*-methoxyphenol in ethanol is slow and favors coupling at the *o*-position. The ONa form accelerates the coupling reaction at the *p*-position to give fairly pure **1**. The reaction of 2-thiazolediazonium salt in an aqueous HCl solution gives a mixture including a larger portion of **4**. Although the synthesis of **5** has been claimed previously,[6] the compound obtained is expected to have been **4** based on a comparison of the acid-base and spectroscopic properties (pK_a=6.70; molar absorptivity (wavelength): 16700 (418) for HL; 27400 (505) for L$^-$).

Table 4. Acid-Base and Spectroscopic Properties of **1**—**6**

Compound	$\mathrm{p}K_{\mathrm{a},1}$ [a]	$\mathrm{p}K_{\mathrm{a},2}$ [a]	Molar absorptivity (wavelength)			
			HL [a]	L^- [a]	Ni complex [b]	Cu complex [b]
1	3.15	7.80	21400 (402)	27500 (460)	113000 (520)	113000 (530)
2	2.98	8.98	22000 (377)	15500 (473)	60000 (566)	45000 (540)
3	2.50	8.73	5600 (425)	11000 (518)	27000 (600)	25000 (600)
4	—	6.79	16600 (415)	33000 (500)	—	—
5	—	7.83	20000 (410)	21300 (510)	42200 (545)	20900 (560)
6	—	8.05	8560 (462)	15800 (555)	28400 (613)	15100 (628)

a) Solvent: 10% dioxane for **1**—**3** and 10% ethanol for **4**—**6**. b) Chloroform extracts for **1**—**3** and complexes formed at pH 5 in 10% ethanol for **5** and **6**.

The molar absorptivities of metal complexes with **1** exceed $10^5\ \mathrm{mol^{-1}\,dm^3\,cm^{-1}}$; this is ascribed to the charged quinonoid resonance structure of metal complexes, due to deprotonation of the OH group at the para position to an azo group. The same mechanism of color-intensification has also been found for 4-(2-pyridylazo)resorcinol (PAR; $\mathrm{H_2par}$). For example, the deprotonation of the Ni–PAR complex at the para position doubles the molar absorptivity: 37200 for $\mathrm{Ni(Hpar)_2}$ and 79400 for $\mathrm{Ni(par)_2{}^{2-}}$ in an aqueous solution.[7)]

The stabilities of PAR complexes are sufficiently high for simultaneous determination of multi-metal ions by HPLC-spectrophotometry.[8)] On the other hand, compound **1** has a higher selectivity as an extraction-spectrophotometric reagent. Since the alkoxy group of low coordinating ability is appropriately located to form a chelate ring, residual water molecules are expelled to form coordination-saturated extractable complexes only with metal ions of high reactivity, such as Cu(II) and Ni(II). This constructs a new group of heterocyclic azo compounds.

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