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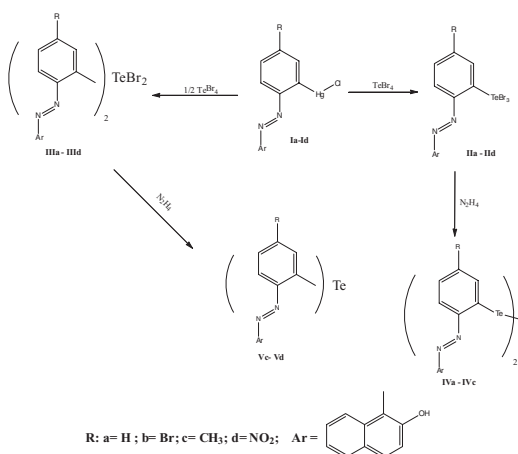
SYNTHESIS OF A NEW SERIES OF 2-(2-HYDROXYNAPHTHYLAZO)ARYLTELLURIUM COMPOUNDS

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GRAPHICAL ABSTRACT



Abstract A new series of 2-(2-hydroxynaphthylazo)arylmercury chlorides (**Ia–Ib**) were prepared by azo coupling of diazonium salts of 2-aminophenyl-, 2-amino-5-bromophenyl-, 2-amino-5-methylphenyl-, and 2-amino-5-nitrophenylmercury chlorides with 2-naphthol. Reactions of compounds **Ia–Ib** with tellurium tetrabromide in 1:1 and 2:1 molar ratios in dry dioxane gave 2-(2-hydroxynaphthylazo)aryltellurium tribromides (**IIa–IIb**) and bis(2-(2-hydroxynaphthylazo)aryl)tellurium dibromides (**IIIa–IIIb**), respectively, in good yields. Reduction of compounds **IIa–IIc** and **IIIc–IIId** by ethanolic hydrazine hydrate gave the corresponding ditellurides (**IVa–IVc**) and tellurides (**Vc–Vd**), respectively, in moderate to good yields. Treatment of compounds **IIIb** and **IIId** with [Pd(PPh₃)₄] in acetonitrile gave new

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symmetrical biaryls containing azo groups. All compounds were characterized by spectroscopic data and elemental analysis.

Keywords Azo compounds; coupling reactions; mercury(II) chloride; organotellurium compounds; palladium(0)

INTRODUCTION

There are few examples of tellurated derivatives of azobenzene in the literature, although the first example was prepared in 1979,¹ by mercuration of azobenzene followed by *trans*-metallation with tellurium tetrachloride. This method provided a satisfactory route to tellurated azobenzene.¹ 2-Phenylazophenyl(C,N')tellurium trichloride was also prepared by a direct reaction of azobenzene with tellurium tetrachloride.² Several new organotellurium compounds derived from 4-aminoazobenzene were prepared by reaction of 3-HgCl-4-NH₂-C₆H₃N=NC₆H₅ with TeBr₄ or *p*-CH₃OC₆H₄TeCl₃.³ Organotellurium containing an azo group, such as 2-phenylazophenyl(C,N') tellurium(II)-halides⁴ and pseudohalides^{5,6} were prepared by metathesis. Sodium benzene- and 4-methoxybenzenetellurolate was added to the C—C triple bond in 4-nitrophenyl- and 3-nitrophenylethyne and concomitantly catalyzed the reduction of the nitro groups to azo groups by sodium borohydride.⁷ Reduction of (3,5-dimethylphenyl)(2-nitrophenyl)tellurium(II) gave the first example of an azo group bridging two tellurium(II) centers.⁸ Reaction of 4-CH₃-2-TeClC₆H₃N=NC₆H₄-4-CH₃ with silver perchlorate gave 4,5-benzo-1,2,3-telluradiazolium perchlorate as a first example of a compound containing a tellurazole ring.⁹

It is worth noting that there is a considerable interest in preparation of organomercury and organotellurium compounds possessing a photoactive substituent such as CH=N.¹⁰ This article describes the synthesis of several new types of organotellurium compounds containing an azo group (Figure 1) by diazo-coupling reaction of halomercury-substituted diazobenzene derivatives and transmetallation from mercury to tellurium. Furthermore, the use of tellurium dibromides derivatives **IIIb** and **IIIc** in organic synthesis using [Pd(PPh₃)₄] is also described.

RESULTS AND DISCUSSION

In the present study, 2-aminoarylmercury chlorides were satisfactorily diazotized at 0–5°C by sodium nitrite solution to form the corresponding diazonium salts, and by

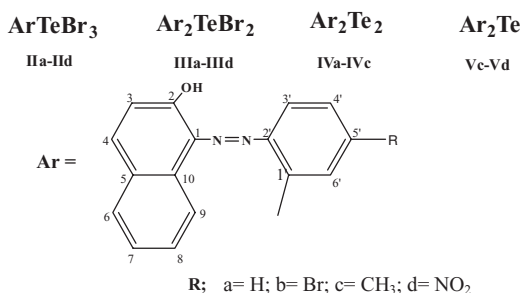


Figure 1 General structure formula.

subsequent coupling with 2-naphthol, the required 2-(2-hydroxy-naphthylazo)arylmercury chlorides [i.e., 2-HOC₁₀H₆N=NC₆H₄-1-HgCl-5-R; where 2-HOC₁₀H₆ = 2-hydroxy-naphthyl, R=H (**Ia**), Br(**Ib**), CH₃(**Ic**), NO₂(**Id**)] were obtained in good yields (Scheme 1). Reaction of tellurium tetrabromide with the corresponding 2-(2-hydroxy naphthylazo)arylmercury chloride in 1:1 and 1:2 molar ratio gave the tribromides (**IIa–IIc**) and the dibromides (**IIIa–IIIc**) derivatives, respectively, as dark brown solids in good yields (Scheme 1). Reduction of compounds **IIa–IIc** and **IIIc–IIIc** using ethanolic hydrazine hydrate gave the ditellurides **IVa–IVc** and the tellurides **Vc–Vd**, respectively in moderate to good yields (Scheme 1).

In general all the prepared compounds are reddish brown to dark brown solids with high melting points, and they are soluble in common organic solvents. The carbon, hydrogen, and nitrogen analyses for these compounds agreed well with the calculated values and are presented in Table 1.

The FT-IR spectra of all mercurated and tellurated azo derivatives show the disappearance of the asymmetric and symmetric stretching bands near 3450–3300 and 1450 cm⁻¹ due to the N–H bonds of NH₂. This supports the conversion of primary amino groups to azo groups. The stretching of –N=N– bonds could not be observed, as they are probably masked by the aromatic vibrations. In general, the IR spectra of compounds **IIa–IIc**, **IIIa–IIIc**, **IVa–IVc**, and **Vc–Vd** are quite similar to those of azo organomercury chloride derivatives (i.e., compounds **Ia–Id**), which confirms that telluration has occurred at the position initially occupied by HgCl. For compounds **Id**, **IIc**, **IIIc**, and **Vd**, the bands at 1363–1330 cm⁻¹ and 1573–1531 cm⁻¹ are assigned to the symmetrical and asymmetrical stretching vibration of the NO₂ group, respectively.^{11,12}

The UV-Vis spectra of all compounds were recorded in absolute ethanol solution at 10⁻⁴ M. Generally, the UV-Vis spectra for all compounds showed three absorption regions. The first region appeared around 208nm ($\epsilon = 9150\text{--}11510 \text{ M}^{-1} \text{ cm}^{-1}$), which may be attributed to $\pi \rightarrow \pi^*$ transition of the benzene ring.^{10–12} The second band was observed around 228 nm ($\epsilon = 9510\text{--}11990 \text{ M}^{-1} \text{ cm}^{-1}$), which is due to $\pi \rightarrow \pi^*$ transition of the naphthyl rings.^{11–13} The third band was observed as a broad shoulder between 473–480 nm ($\epsilon = 2384\text{--}4000 \text{ M}^{-1} \text{ cm}^{-1}$), which is attributed to $\pi \rightarrow \pi^*$ transition of the azo groups.^{11–13}

The ¹H NMR spectra of the synthesized compounds show that the resonance of the aromatic rings were observed in the range 6.94–8.58 ppm. The signal characteristic of the proton of the hydroxyl group was observed in region 8.00–11.23 ppm. The ¹H NMR spectra of all compounds show that in each case a distinct doublet appears between 6.94–7.12 ppm due to H₃ of the naphthyl group (Table 1). The ¹H NMR data for the studied compounds are presented in Table 1. The ¹³C NMR spectra for compounds **IIb** and **Vc** agree well with their structures (Table 1).

When tellurium dibromides **IIb** and **IIIc** were reacted with Ph(PPh₃)₄ in acetonitrile,^{14,15} the corresponding biaryls (i.e., 2,2'-bis(2-hydroxynaphthylazo)5,5'-dibromobiphenyl (**VIb**) and 2,2'-bis(2-hydroxynaphthylazo)5,5'-dinitrobiphenyl (**VIc**) were obtained in 75% and 84% yields, respectively, as the only products (Scheme 2). Both compounds gave satisfactory elemental analysis, and their IR and UV-Vis spectra are similar to the spectra of tellurated azo compounds.

In conclusion, we have introduced a new and efficient synthetic route for preparation of a new range of organotellurium compounds containing azo groups. These compounds could be useful for synthesis of organic compounds and as organic dyes.

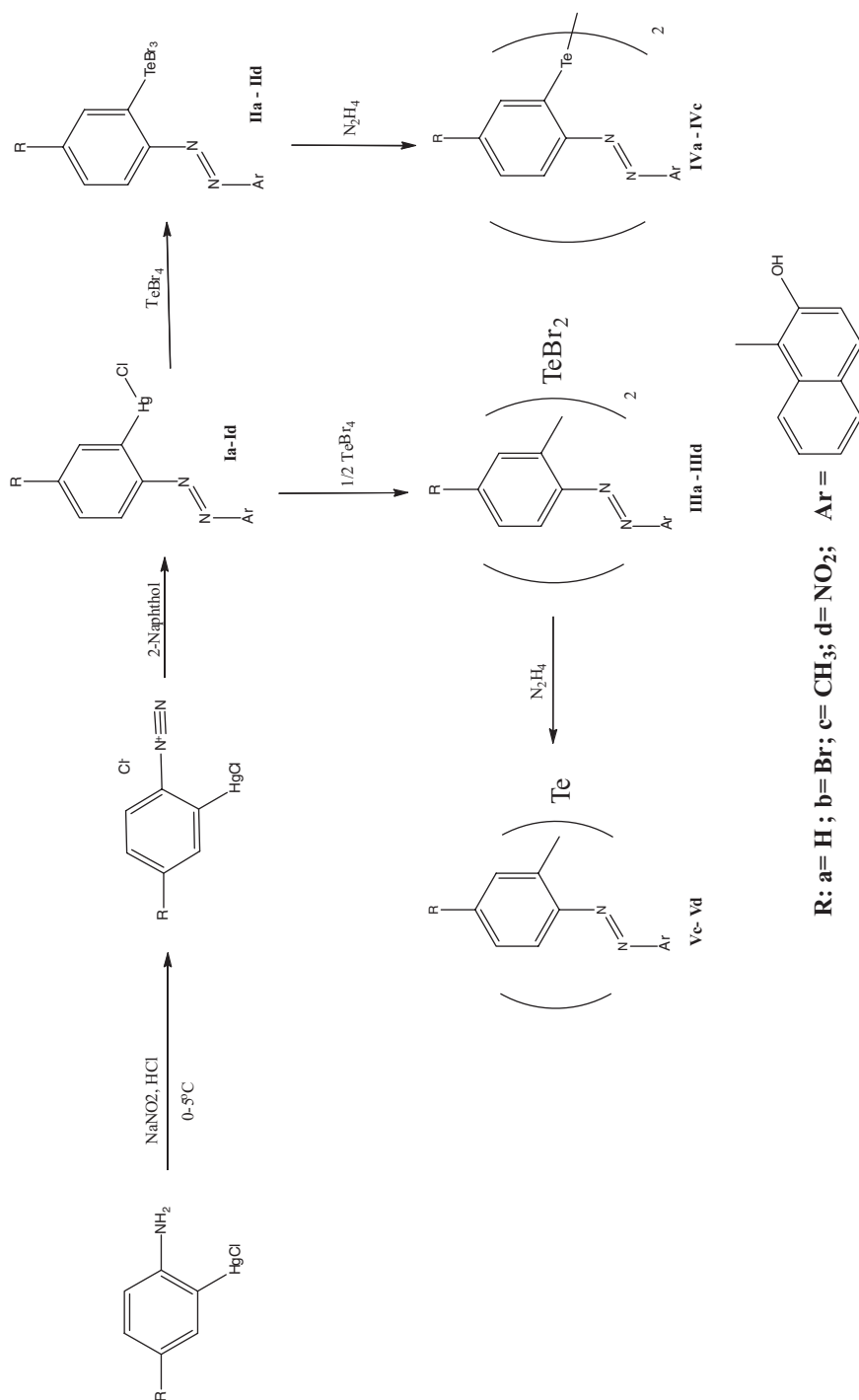
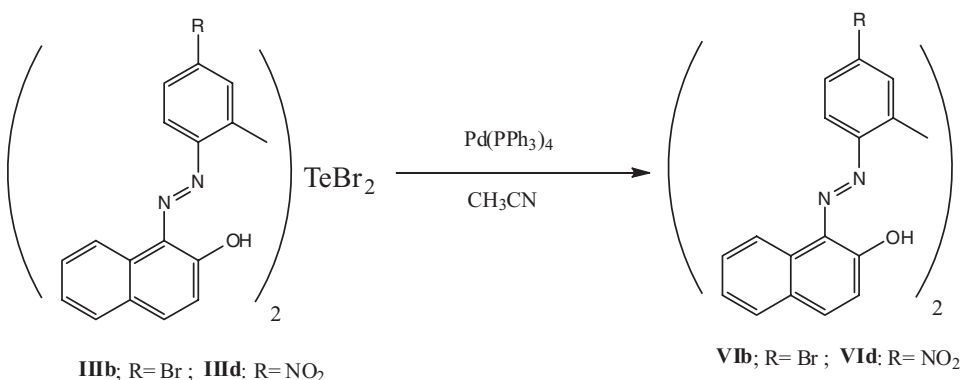
**Scheme 1** Preparative methods for the new azo compounds.

Table 1 CHN analysis and ^1H NMR data for the new mercurated and tellurated azo compounds based on 2-(2-hydroxynaphthylazo)aryl

Compounds	Elemental analysis% Found (calcd.)			^1H NMR(DMSO- d_6) TMS = 0 ppm
	C	H	N	
Ia	39.55(39.76)	2.33(2.29)	5.78(5.80)	6.95(d, 1H, Ar- <i>H</i>); 7.48–7.65(m, 5H, Ar- <i>H</i>); 7.78–7.98(m, 4H, Ar- <i>H</i> +OH); 8.58(d, 1H, J = 8.1Hz, Ar- <i>H</i>).
Ic	40.91(41.05)	2.46(2.63)	5.88(5.63)	2.26(s, 3H, CH ₃); 6.94(d, 1H, J = 8.3Hz, Ar- <i>H</i>); 7.27–7.36(m, 4H, Ar- <i>H</i>); 7.63–7.69(m, 4H, Ar- <i>H</i>); 7.75(d, 1H, Ar- <i>H</i>); 7.87(d, 1H, Ar- <i>H</i>); 10.23(s, 1H, OH).
IIa	31.10(31.27)	1.72(1.80)	4.34(4.56)	7.02(d, 1H, J = 7.4Hz), Ar- <i>H</i>); 7.25–7.48(m, 5H, Ar- <i>H</i>); 7.63–7.79(m, 3H, Ar- <i>H</i>); 7.89–8.01(m, 2H, Ar- <i>H</i>); 9.95(s, 1H, OH).
IIb	27.58(27.71)	1.39(1.45)	4.23(4.04)	7.00(d, 1H, J = 7.2Hz, Ar- <i>H</i>); 7.30–7.35(m, 2H, Ar- <i>H</i>); 7.59–7.75(m, 5H, Ar- <i>H</i>); 7.87(d, 1H, J = 7.6Hz, Ar- <i>H</i>); 10.7(s, 1H, OH).
IIc	32.32(32.48)	1.98(2.08)	4.28(4.46)	2.28(s, 3H, CH ₃); 6.94(d, 1H, J = 7.55Hz, Ar- <i>H</i>); 7.58–7.73(m, 2H, Ar- <i>H</i>); 7.80(d, 1H, J = 7.63Hz, Ar- <i>H</i>); 7.91(s, 1H, Ar- <i>H</i>); 8.84(s, 1H, OH).
IIId*	29.08(29.14)	1.67(1.53)	6.31(6.37)	6.85(d, 1H, Ar- <i>H</i>); 6.92–7.74(m, 5H, Ar- <i>H</i>); 7.82–8.45(m, 3H, Ar- <i>H</i>); 9.50(s, 1H, OH).
IIIa	48.98(49.15)	2.80(2.84)	7.19(7.17)	6.94(d, 2H, J = 9.3Hz); 7.26–7.70(m, 10H, Ar- <i>H</i>); 7.30–8.15(m, 6H, Ar- <i>H</i>); 8.21–8.45(m, 2H, Ar- <i>H</i>); 8.92(s, 2H, OH).
IIIb	40.79(40.90)	2.37(2.15)	5.90(5.96)	6.98(d, 2H, J = 7.2Hz, Ar- <i>H</i>); 7.24–7.34(m, 4H, Ar- <i>H</i>); 7.61–7.72(m, 10H, Ar- <i>H</i>); 8.02(d, 2H, J = 6.92, Ar- <i>H</i>); 11.23(s, 2H, OH).
IIIc	50.52(50.42)	3.18(3.24)	6.90(6.92)	2.31(s, 6H, CH ₃); 6.94(d, 2H, J = 7.52Hz, Ar- <i>H</i>); 7.21–7.38(m, 8H, Ar- <i>H</i>); 7.58–7.74(m, 4H, Ar- <i>H</i>); 7.80(d, 2H, J = 8.40Hz); 7.91(s, 2H, Ar- <i>H</i>); 9.24(s, 2H, OH).
IIId	43.81(44.08)	2.09(2.31)	9.57(9.64)	7.01(d, 2H, J = 7.2Hz, Ar- <i>H</i>); 7.30–7.79(m, 14H, Ar- <i>H</i>); 8.13(d, 2H, J = 7.2); 9.98(s, 2H, OH).
Iva	51.63(51.26)	2.90(2.96)	7.28(7.47)	6.92 (d, 2H, J = 7.1Hz, Ar- <i>H</i>). 7.18–8.30 (m, 16H, Ar- <i>H</i>); 9.95 (s, 2H, 2OH);
IVc	52.48(52.50)	3.16(3.37)	7.06(7.20)	2.23(s, 6H, CH ₃); 6.96(d, 2H, J = 7.0Hz); 7.28–7.35(m, 8H, Ar- <i>H</i>); 7.62–7.99(m, 8H, Ar- <i>H</i>); 11.53(s, 2H, OH).
IVd	45.52(45.77)	2.38(2.40)	9.85(10.01)	7.01(d, 2H, J = 7.70Hz, Ar- <i>H</i>); 7.31–7.48(m, 4H, Ar- <i>H</i>); 7.79(s, 2H, Ar- <i>H</i>); 8.01–8.23(m, 6H, Ar- <i>H</i>); 10.83(s, 2H, OH).
Vc*	62.56(62.81)	3.92(4.03)	8.86(8.62)	2.30 (s, 6H, 2CH ₃); 6.90 (d, 2H, J = 6.95Hz, Ar- <i>H</i>); 7.32–8.12(m, 16H, Ar- <i>H</i>); 9.35(s, 2H, OH).
Vd	53.92(53.97)	2.79(2.83)	11.55(11.80)	6.94(d, 2H, J = 6.96Hz, Ar- <i>H</i>); 7.22–7.42(m, 4H, Ar- <i>H</i>); 7.62–7.80(m, 6H, Ar- <i>H</i>); 8.01–8.25(m, 2H, OH).
VIb	58.60(58.92)	2.92(3.09)	8.50(8.59)	
VIId	66.01(65.75)	3.52(3.45)	14.12(14.38)	

 ^{13}C NMR(DMSO- d_6) δ : Carbon numbers as shown in Fig. 1.***IIId**: 153.2 (C2'), 152.9 (C2), 152.1 (C5'), 144.0 (C4), 135.0 (C5), 134.1 (C5), 130.8 (C10), 129.3 (C6), 128.5 (C9), 128.13(C8), 126.75(C6'), 126.01(C4'), 125.19(C3'), 124.90(C7), 118.84(C3), 110.06(C1').**Vc**: 151.98(C2), 149.44(C2'), 146.95(C1), 136.77(5'), 136.34(C4), 129.83(C6'), 128.94(C4'), 127.75(C5), 126.51(C10), 126.34(C6), 125.32(C9), 124.14(C8), 123.60(C7), 117.71(C3), 117.15(C3'), 109.47(C1'), 22.68(CH₃).



Scheme 2

EXPERIMENTAL

Synthesis

2-Aminophenylmercury chloride,¹⁶ 2-amino-5-bromophenylmercury chloride,¹⁷ 2-amino-5-methylphenylmercury chloride,¹⁷ and 2-amino-5-nitrophenylmercury chloride¹⁷ were prepared by methods in the literature.

2-(2-Hydroxynaphthylazo)phenylmercury Chloride (Ia)

A solution of sodium nitrite (0.55 g, 8 mmol) in distilled water (25 mL) was added slowly to a cold solution of 2-aminophenylmercury chloride (2.62 g, 8 mmol) in 1.0 M hydrochloric acid (25 mL). To this clear solution, a cold solution of 2-naphthol (1.15 g, 8 mmol) in 10% NaOH was added portionwise with stirring over a period of 30 min. The reaction mixture was stirred for 2 h at 0–5°C. The reaction mixture was neutralized with 10% HCl. A yellowish brown solid was formed, collected, washed several times with distilled water, and dried over P₂O₅. Yield: 71%, mp 188–190°C. IR (KBr) cm⁻¹: 3420s,br, 3056w, 1610s, 1488s, 1262s, 1144s, 856s, 837s, 752s. UV-Vis (λ_{max}, nm (ε M⁻¹.cm⁻¹), EtOH): 208(10950), 228(11200) and 478(3350).

The following compounds were prepared by the same above method using the appropriate 2-aminoarylmercury chloride.

2-(2-Hydroxynaphthylazo)-5-bromophenylmercury Chloride (Ib)

A dark brown solid was obtained in 75% yield, mp 230–232°C. IR (KBr) cm⁻¹: 3430br, 3057w, 1612s, 1465s, 1271s, 1141s, 851s, 830s, 750s. UV-Vis (λ_{max}, nm (ε M⁻¹.cm⁻¹), EtOH): 280(10000), 227(10505) and 473(3110).

2-(2-Hydroxynaphthylazo)-5-methylphenylmercury Chloride (Ic)

A dark brown solid, 80% yield, mp 198–200°C. IR (KBr) cm⁻¹: 3449s,br, 3070w, 1626s, 1521s, 1401s, 1336s, 1212s, 855s, 845s, 757s. UV-Vis (λ_{max}, nm (ε M⁻¹.cm⁻¹), EtOH): 209 (10850), 228(11330) and 480(3500).

2-(2-Hydroxynaphthylazo)-5-nitrophenylmercury Chloride (Id)

A dark brown solid was obtained in 73% yield, mp 241–243°C. IR (KBr) cm^{-1} : 3420s,br, 3056w, 2865w, 2917w,1610s, 1488s, 1350 m, 1262s, 1144s, 856s, 837s, 752s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1}.\text{cm}^{-1}$), EtOH): 208(10990), 227(11750) and 476(3560).

2-(2-Hydroxynaphthylazo)phenyltellurium Tribromide (IIa)

2-(2-hydroxynaphthylazo)phenylmercury chloride (1.44 g; 3 mmol) and tellurium tetrabromide (1.34 g, 3 mmol) were mixed in dry dioxane (60 mL). The mixture was stirred under reflux for 6 h. Cooling the mixture gave crystals of a mercury(II) halide.2dioxane complex, which was removed by filtration. The filtrate was poured into ice-water, and a brown precipitate was formed. The product was recrystallized from a methanol and dichloromethane (4:1) to give a brown solid of mp 209–211°C in 79% yield. IR (KBr) cm^{-1} : 3441br, 3059w, 1602s, 1446s, 1272s, 1138s, 868s, 838s, 749s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1}.\text{cm}^{-1}$), EtOH): 208 (11259), 226(11400) and 478(3750).

The following compounds were prepared by the same above method using the appropriate azo mercurated compound.

2-(2-Hydroxynaphthylazo)-5-bromophenyltellurium Tribromide (IIb)

A brown solid was obtained in 68%, mp 197–199°C. IR (KBr) cm^{-1} : 3425br, 3061w, 1611s, 1464s, 1275s, 1147s,1147m, 871s, 811s, 745s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1}.\text{cm}^{-1}$), EtOH): 207 (9153), 228(9880) and 475(2384).

2-(2-Hydroxynaphthylazo)-5-methylphenyltellurium Tribromide (IIc)

A brown solid was obtained in 61%, mp 220–222°C. IR (KBr) cm^{-1} : 3428br, 3065w, 2923w, 2858w,1599s, 1480s, 1350m, 1270s, 1139s, 861s, 839s, 749s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1}.\text{cm}^{-1}$), EtOH): 208 (9250), 228(9510) and 478(3840).

2-(2-Hydroxynaphthylazo)-5-nitrophenyltellurium Tribromide (IId)

A brown solid was obtained in 75%, mp 233–235°C. IR (KBr) cm^{-1} : 3425br, 3061w, 1601s, 1525s, 1484s, 1339s, 851s, 843s, 749s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1}.\text{cm}^{-1}$), EtOH): 208 (10000), 227(10200) and 477(3700).

Bis(2-(2-hydroxynaphthylazo)phenyl)tellurium Dibromide (IIIa)

2-(2-Hydroxynaphthylazo)phenylmercury chloride (3.86 g, 8 mmol) and tellurium tetrabromide (1.78 g, 4 mmol) were refluxed in dry dioxane (60 mL) for 6h. The reaction mixture was treated as described for the preparation of compound **IIa** to give a brown solid in 72% yield, mp 171–172°C. IR (KBr) cm^{-1} : 3480br, 3058w, 1612s, 1449s, 1264s, 1140s, 850w, 837w, 751w. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1}.\text{cm}^{-1}$), EtOH): 206 (10700), 228(11100) and 478(3550).

The following compounds were prepared by the same above method using the appropriate 2-(2-Hydroxynaphthylazo)arylmercury chloride.

Bis(2-(2-hydroxynaphthylazo)-5-bromophenyl)tellurium Dibromide (IIIb)

Brown solid. Yield: 70%, mp 202–204°C. IR (KBr) cm^{-1} : 3450br, 3042w, 1605s, 1456s, 1275s, 1174s, 1145s, 1080m, 846s, 837s, 759s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1} \cdot \text{cm}^{-1}$), EtOH): 210 (11510), 227(11990) and 478(3012).

Bis(2-(2-hydroxynaphthylazo)-5-methylphenyl)tellurium Dibromide (IIIc)

Brown solid. Yield: 81%, mp 177–179°C. IR (KBr) cm^{-1} : 3430br, 3047w, 2920w, 2870w, 1597s, 1480s, 1354m, 1275s, 1148s, 830s, 812s, 756s. UV-Vis [λ_{max} , nm ($\epsilon \text{ M}^{-1} \cdot \text{cm}^{-1}$), EtOH]: 208 (10350), 228(10800) and 476(4000).

Bis(2-(2-hydroxynaphthylazo)-5-nitrophenyl)tellurium Dibromide (IIId)

Brown solid. Yield: 77%, mp 215–217°C. IR (KBr) cm^{-1} : 3435br, 3056w, 1595w, 1570s, 1456m, 1328s, 1258m, 1147s, 854s, 842s, 747s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1} \cdot \text{cm}^{-1}$), EtOH): 207 (10350), 228(10800) and 476(3952).

Bis(2-(2-hydroxynaphthylazo)phenyl)ditelluride (IVa)

To a suspension of compounds **IIa** (1.19 g, 2 mmol) in hot ethanol (25 mL), a solution of hydrazine hydrate (0.26 g, 8 mmol) in ethanol (25 mL) was added dropwise. The mixture was warmed gently until all the solid had dissolved, and was then poured into water (300 mL). After extraction with ether ($3 \times 50 \text{ mL}$), the ethereal layer was separated and dried over anhydrous calcium chloride, and the solvent was removed on a rotary evaporator. The reddish brown solid was recrystallized from ethanol to give reddish brown crystals in 60% yield, mp 135–137°C.

IR (KBr) cm^{-1} : 3421br, 3049w, 1600w, 1462s, 1269s, 1141s, 8595s, 836s, 750s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1} \cdot \text{cm}^{-1}$), EtOH): 208 (10488), 227(10550), and 476(3528).

The following compounds were prepared by the same method described for the preparation of compound **IVa** and by reduction of compounds **IIb** and **IIc** with hydrazine hydrate.

Bis(2-(2-hydroxynaphthylazo)-5-bromophenyl)ditelluride (IVb)

Reddish brown crystals in 61% yield, mp 169–171°C. IR (KBr) cm^{-1} : 3414br, 3028w, 11597s, 1466s, 1278s, 1130s, 1082m, 845s, 813s, 748s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1} \cdot \text{cm}^{-1}$), EtOH): 208 (10890), 228(11220) and 478(2900).

Bis(2-(2-hydroxynaphthylazo)-5-methylphenyl)ditelluride (IVc)

Reddish brown crystals in 58% yield, mp 141–143°C. IR (KBr) cm^{-1} : 3422br, 3030w, 2936w, 2886w, 1597s, 1460s, 1353m, 1265s, 1142s, 852s, 819s, 749s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1} \cdot \text{cm}^{-1}$), EtOH): 206 (10750), 226(11250) and 478(3760).

Bis(2-(2-hydroxynaphthylazo)-5-methylphenyl)telluride (Vc)

Bis(2-(2-hydroxynaphthylazo)-5-methylphenyl)tellurium dibromide (**IIIa**) (4.05 g, 5 mmol) was treated with hydrazine hydrate as described for compound **IVa**. Recrystallization of the brown solid with a mixture of ethanol and chloroform gave a brown solid in 62% yield, mp 122–124°C. IR (KBr) cm^{-1} : 3402br, 3049w, 2931w, 2884w, 1600s, 1458s, 1350m, 1273s, 851s, 817s, 758s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1}\text{cm}^{-1}$), EtOH): 208 (10650), 227(10800) and 477(3500).

Compound **Vd** was prepared by the same above method.

Bis(2-(2-hydroxynaphthylazo)-5-nitrophenyl)telluride (Vd)

Brown solid was obtained in 66% yield, mp 167–168°C. IR (KBr) cm^{-1} : 3416br, 3046w, 1607s, 1523s, 1461s, 1334s, 1275s, 1148s, 854s, 819s, 751s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1}\text{cm}^{-1}$), EtOH): 208 (9900), 228(10800) and 477(3310).

Coupling Reaction of **IIIb and **IIId** with $\text{Pd}(\text{PPh}_3)_4$**

2,2'-Bis(2-hydroxynaphthylazo)-5,5'-dibromobiphenyl (**VIb**) and 2,2'-bis(2-hydroxynaphthylazo)-5,5'-dinitrobiphenyl (**VIId**) were prepared by the same general coupling procedure and as follows:

To a solution of tetrakis(triphenylphosphane)palladium(0) (0.346 g, 0.30 mmol) in acetonitrile (10 mL) was added a solution of compound **IIIb** or **IIId** (0.30 mmol) in of acetonitrile (10 mL) dropwise with stirring. The mixture was stirred for 8 h at room temperature under an argon atmosphere and filtered. The filtrate was evaporated on a rotary evaporator to dryness. The crude solids of compounds **VIId** and **VIId** were recrystallized from a mixture of ethanol and diethyl ether. The corresponding biaryls (**VIb** and **VIId**) were obtained as brown solids.

2,2'-Bis(2-hydroxynaphthylazo)5,5'-dibromobiphenyl (VIb)

Brown solid, mp 149–151°C. Yield: 75%. IR (KBr) cm^{-1} : 3411br, 1483s, 1433s, 1166s, 1118s, 1012m, 754s, 723s, 692s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1}\text{cm}^{-1}$), EtOH): 242 (10576), 266(8820) and 507(280).

2,2'-Bis(2-hydroxynaphthylazo) 5,5'-dinitrobiphenyl (VIId)

Brown solid, mp 161–163°C. Yield: 84%. IR (KBr) cm^{-1} : 3410br, 1501s, 1480m, 1435s, 1330s, 1176s, 1118s, 754s, 726s, 696s. UV-Vis (λ_{max} , nm ($\epsilon \text{ M}^{-1}\text{cm}^{-1}$), EtOH): 242 (10250), 266(9677) and 510(550).

Physical Measurements

Analysis for C, H, and N was done by the Analytical Service Unit, Al al-Bayt University, Jordan. FT-IR spectra were recorded for KBr discs with a FT-IR-8400 Shimadzu instrument. NMR spectra were recorded with a Bruker DPX-300 (300 MHz) and Bruker LA-250 (250 MHz) using TMS as internal standard. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. The electronic absorption spectra

in the 800–200 nm range were recorded on a Sean-80D UV-Vis spectrophotometer, using 1 cm quartz cells.

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