The Synthesis and Structure of a New Type of Aromatic Heterocyclic Macrocycle. IV. Synthesis of a 1,3,4-Oxadiazole-containing Azomacrocycle

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A novel azomacrocycle containing the 1,3,4-oxadiazole ring has been prepared from 2,5-bis[3-(4-hydroxyphenylazo)phenyl]-1,3,4-oxadiazole **5** and 2,5-bis(2-chloromethlylphenyl)-1,3,4-oxadiazole **8**. The coupling reaction between the diazonium salt **4** and bisphenol A has been reported.

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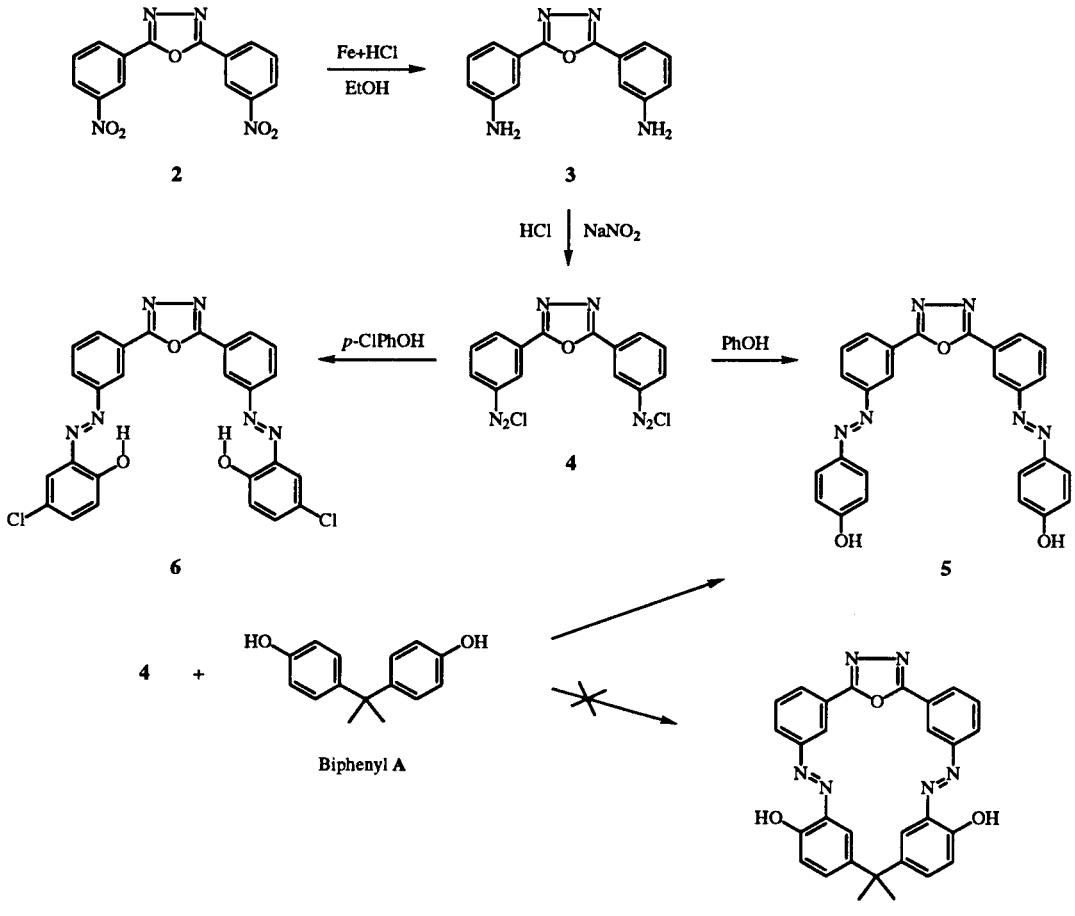
Using azobenzene derivatives it is possible to control chemical functions by an "on-off switch" and also to store information [1-2], the synthesis of new types of azo compounds is of interest [3-5]. Voegtle and coworkers have reported for the first time the preparation of photochemically reversibly switchable azomacrocycles [6].

We have recently prepared a novel azomacrocycle containing 1,3,4-oxadiazole **1** from synthons **5** and **8**.

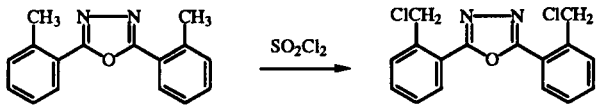
Compound **2** was prepared by Saegusa *et. al.* from *m*-nitrobenzoic acid and 100% hydrazine hydrate with polyphosphoric acid heated at 130° for 24 hours and obtained **2** in 78% yield [7]. We found that when *m*-nitrobenzoic acid and 85% hydrazine hydrate with polyphosporic acid reacted at 100-110° for 36 hours, the yield increased to 80-90%.

Catalytic hydrogenation of **2** provides **3** in low yield [lit 38%] [7]. When **2** is reduced with iron powder and hydrochloric acid in ethanol, the yield may be increased to 60%. Acetic acid is not suitable because many byproducts are produced.

Scheme 1



Scheme 2



7 8

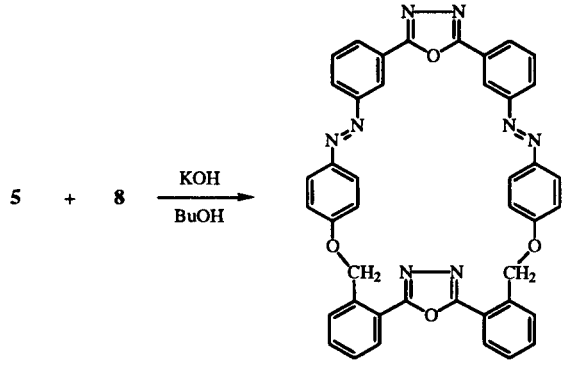
Diamine **3** is insoluble even in hot hydrochloric acid. Attempts to use concentrated sulfuric acid and sodium nitrite as the diazotizing agent were unsuccessful because the diazonium salt may be decomposed on under these conditions. When **3** was suspended in hot hydrochloric acid, then ice-cooled, addition of a sodium nitrite solution dropwise with stirring, produced a clear yellow diazonium solution containing **4**.

The coupling reaction was carried out at *p*H 8-9 using sodium acetate as the *p*H regulator. Compunds **5** and **6** were obtained in yields of 78% and 66%, respectively.

While the diazonium solution **4** coupled with bisphenol **A**, which has two coupling positions, attempts to obtain a macrocycle by this one-step coupling failed. After column chromatographic separation, a pure compound was obtained which was identified by ir, ms and nmr as the non-cyclized product **5**. The mechanism of formation is under investigation.

The cyclocondensation of **5** with an equimolar amount of **8** was carried out by heating a moderately dilute solution at reflux in 1-butanol in the presence of sodium hydroxide. Macrocycle **1** was obtained as an orange powder. It does not melt under 360° and is insoluble in all common organic solvents. It is difficult to characterize. The synthesis of more soluble azomacrocycles is in progress.

Scheme 3



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EXPERIMENTAL

Melting points were determined on a micromelting-point appratus and uncorrected. The nmr spectra observed on a ARX-400 (Bruker) spectrometer with tetramethylsilane as the internal standard. The ir spectra were measured with a Nicolet MX-5 spectrophotometer as pottasium bromide pellets. The mass spectra were obtained on a ZAB-HS (VG) spectrometor. The reactions were monitored by tlc using silica-gel plates. Microanalyses were performed by the Institute of Chemistry, Academia Sinica.

Compounds **2** [7], 7 [8], and **8** [9] were prepared as reported.

2,5-bis(*m*-Aminophenyl)-1,3,4-oxadiazole **3**.

A mixture of 6.24 g (20 mmoles) of **2** , 6.72 g (120 mmoles) of iron powder and 300 ml ethanol was heated to 70°, while 15 ml of concentrated hydrochloric acid was added slowly, then stirred and refluxed for 2 hours. The mixture was filtered while still hot. The residue was washed twice with dimethyformamide (10 ml each). The filtrate was neutralized with sodium acetate to *p*H 5-6. The product, a yellow solid that precipitated was collected by filtration. A pure product was obtained after recrystallization from dimethylformamide-water (2:1) to yield 3.1 g of **3** (60%), mp 250-252° (lit [7] 255°); ir (potassium bromide): ν 3380, 3200 (NH_2), 1600 (C=N) cm^{-1}.

General Procedure for the Preparation of Bisazo Compounds **5** and **6**.

Compound **3** (0.5 g, 2 mmoles) in 10 ml of concentrated hydrochloric acid was diazotized by treating with 0.3 g of sodium nitrite (4.3 mmoles) at 0° while stirring for 10 minutes. The yellow solution contained **4**. The above diazonium salt solution containiing **4** was added dropwise to 0.4 g of phenol dissolved in 1*M* sodium hydroxide (20 ml) with vigorous stirring at 0-5°. The color of the solution changed to orange then to yellow. To this mixture was added 1*M* sodium hydroxide until the color turned again to orange and the mixture was alolowed to stand overnight. Acidification of this solution with 1*M* hydrochloric acid gave an orange precipitate which was filtered and recrystallized from dimethylformamide-water (2:1) to yield 0.72 g **5** (78%), mp 286-288°; ir (potassium bromide): ν 3100-3500 (OH), 1600 (C=N), 1550 (N=N) cm^{-1}; ^1H nmr (dimethyl-d_6 sulfoxide): δ 6.97-6.99 (m, 2H), 7.80-7.90 (m, 3H), 8.06-8.08 (t, 1H), 8.26-8.28 (d, 1H), 8.49-8.50 (t, 1H), 10.47 (s, 1H); ms: m/z 462 (M^+).

Anal. Calcd. for $C_{26}H_{18}N_6O_3$: C, 67.53; H, 3.92; N, 18.17. Found: C, 67.29; H, 4.25; N, 17.95.

Compound **6** was obtained by following a similar procedure to that above by using *p*-chlorophenol to give a 66% yield of **6**, mp 256-259°; ir (potassium bromide): ν 3240-3540 (OH), 1600 (C=N), 1550 (N=N) cm^{-1}; ^1H nmr (dimethyl-d_6 sulfoxide): δ 7.14-7.16 (d, 1H), 7.49-7.51 (m, 1H), 7.72-7.73 (d, 1H), 7.86-7.89 (t, 1H), 8.27-8.36 (m, 2H), 8.75 (s, 1H), 10.96 (s, 1H); ms: m/z 530 (M^+).

Anal. Calcd. for $C_{26}H_{16}C_{12}N_6O_3$: C, 58.77; H, 3.04; N, 15.82. Found: C, 58.68; H, 3.17; N, 15.70.

The Coupling Reaction of Bisphenol A with Compound **3**.

Compound **3** (0.5 g, 2 mmoles) was diazotized as above and diluted with ice water to give 50 ml of a yellow solution. A second solution containing 0.46 g of bisphenol **A** (2 mmoles) and 5 g of sodium hydroxide in 50 ml cold water was prepared.The two solutions were added simultaneously to 100 ml of ice water, and stirred at 0-5° for 10 hours. Acidification of the solution precipitated the product which was purified by column chromatography on silica gel with ethyl acetate and petroleum ether (1:2) as eluants to give 210 mg (23%) of **5**, mp 285-288°; ir (potassium bromide): ν 3100-3500 (OH), 1600 (C=N), 1550 (N=N) cm^{-1}; ^1H

nmr (dimethyl-d_6 sulfoxide): δ 6.99-7.00 (m, 2H), 7.80-7.90 (m, 3H), 8.05-8.07 (t, 1H), 8.24-8.27 (d, 1H), 8.50-8.51 (t, 1H), 10.49 (s, 1H). ms: m/z 462 (M^+).

Preparation of Macrocycle 1.

Compound **5** (0.462 g 1 mmoles) and 0.08 g of sodium hydroxide was dissolved in 50 ml of 1-butanol. Another solution containing 0.308 g (1 mmole) of **8** in 50 ml of 1-butanol was prepared. The two solutions were simultaneously added dropwise to 200 ml of 1-butanol. After the addition was complete, the reaction mixture was refluxed for 20 hours. The precipitate which formed was filtered, washed successively with water (50 ml), acetone (50 ml), chloroform (50 ml) and dimethylformamide (50 ml), gave 520 mg (73%) of 1 mp >360°; ir (potassium bromide): ν 3240-3360 (H_2O), 1600 (C=N), 1550 (N=N) cm^{-1}; ^1H nmr (deuteriotrifluroacetic acid): δ 5.93-6.02 (s, 2H), 7.51-7.53 (d, 2H), 7.73-7.77 (t, 1H), 7.85-7.90 (m, 1H), 7.96-8.05 (m, 2H), 8.20-8.23 (d, 1H), 8.35-8.65 (m, 4H), 8.98 (s, 1 H); ms: m/z 708 (M^+)

Anal. Calcd. for $C_{42}H_{28}N_8O_4 \cdot H_2O$: C, 69.41; H, 4.16; N, 15.41. Found: C, 68.91; H, 3.71; N, 15.60.

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