

## A Simple Synthesis of 2,2'-Azobis[(15-crown-5)-eno[g]quinoxaline]

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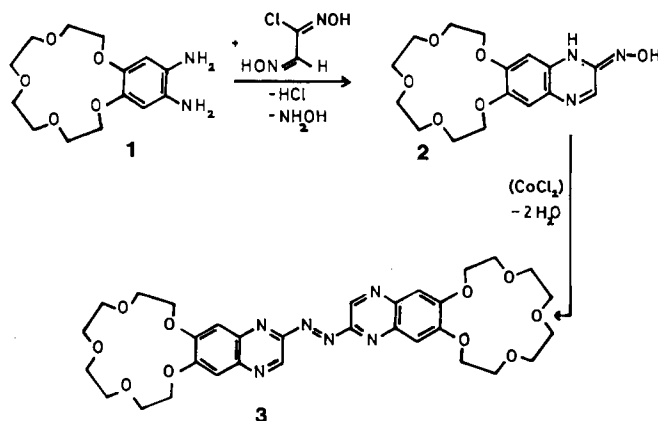
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### Einfache Synthese von 2,2'-Azobis[(15-krone-5)eno[g]chinoxalin]

Die Umsetzung von 2,3-Diaminobenzo-15-krone-5 (1) mit *s-trans*-Chlorethandial-dioxim in Ethanol liefert das 2(1*H*)-(15-Krone-5)eno[g]chinoxalinon-oxim (2), das durch Templat-Effekt von  $\text{Co}^{2+}$  in das 2,2'-Azobis[(15-krone-5)eno[g]chinoxalin] (3) übergeführt wird.

Bis(crown ethers) are proven to be extremely powerful extracting agents for alkali metal salts. In this regard, the photoresponsive bis(crown ethers) which contain an azo group as a photoantenna to capture photons have been investigated recently for the photocontrol of their complexation with alkali metal ions<sup>1,2</sup>. On the other hand, we have reported the conversion of 2(1*H*)-quinoxalinone oxime into 2,2'-azobis(quinoxaline) by the template effect of cobalt and nickel ions<sup>3,4</sup>.

The object of the present study is to synthesize a new compound which simultaneously contains both azobis(quinoxaline) and crown ether groups by making use of the template effect of cobalt(II) ions (scheme).



2(1*H*)-(15-Crown-5)eno[g]quinoxalinone oxime (2) was synthesized from *s-trans*-chloroethanedial dioxime and 2,3-diaminobenzo-15-crown-5 (1) which was obtained from benzo-

15-crown-5 via nitro-, amino-, (acetylamino)-, (acetylamino)nitro-, aminonitrobenzo-15-crown-5 as previously reported<sup>5-7</sup>). The formation of a quinoxaline ring probably directed this cyclization reaction.

When a solution of **2** and cobalt(II) chloride in absolute ethanol was heated at 60°C for 4 h, 2,2'-azobis[(15-crown-5)eno[g]quinoxaline (**3**) was isolated as a reddish brown precipitate. Though the absolute mechanism of this reaction is not known, we might expect the formation of a complex with a deprotonated **2** and cobalt ion in the first step, since we have isolated a dark purple insoluble product corresponding to  $C_{16}H_{20}ClCoN_3O_6$  in the case of more concentrated reaction mixtures and excess cobalt(II) ions. The highest yield was obtained when the initial ratio of the reactants was 2(**2**):1(Co), but the reaction still took place with much smaller rates even when the ratio was 10:1.

The almost perfectly planar structure of *trans*-2,2'-azobis(quinoxaline) determined by single crystal analysis<sup>4</sup>) is not expected in **3** because of the bulky crown ether groups attached to the aromatic rings, but **3** is also in *trans*-structure as deduced from the electronic spectrum.

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## Experimental

*2(1H)-(15-Crown-5)eno[g]quinoxalinone Oxime (2)*: To the solution of 2.98 g 2,3-diaminobenzo-15-crown-5 (**1**) (10 mmol) in absol. ethanol (100 ml) under stirring at room temperature was added a solution of *s-trans*-chloroethanedial dioxime (1.23 g, 10 mmol) in absol. ethanol (30 ml). The colour of the solution gradually turned to bright yellow and the precipitation started. The stirring was continued for 1 h. The yellow precipitate was filtered off, washed with ethanol and then with diethyl ether and dried in vacuo. Yield 2.60 g (74%), m. p. 184°C (dec.). — IR (KBr): 3370 (NH), 3170 (OH), 3035 ( $CH_{arom.}$ ), 2920, 2860 ( $CH_{aliph.}$ ), 1645 (C=N), 1405 (OH), 1265–1225 (Ar–O–C), 1190–1130 (C–O–C), 955 (N–O). — UV-VIS (ethanol):  $\lambda_{max}$  ( $\epsilon$ ) = 380 (19690), 255 (69700), 218 nm (61100). — <sup>1</sup>H-NMR ( $[D_6]DMSO$ ):  $\delta$  = 3.80 (s, 8H, C–O–CH<sub>2</sub>), 3.85 (s, 4H, Ar–O–C–CH<sub>2</sub>), 4.1 (s, 4H, Ar–O–CH<sub>2</sub>), 6.9 (s, 1H, Ar-H), 7.0 (s, 1H, Ar-H), 7.75 (s, 1H, N=CH), 9.95 (s, 1H, NH), 10.10 (s, 1H, OH). — <sup>13</sup>C NMR ( $[D_6]DMSO$ ):  $\delta$  = 68.2–70.6 (8 peaks), 99.1, 113.5, 128.2, 143.0, 147.3, 150.1. — MS (70 eV):  $m/z$  = 351 (19%, M<sup>+</sup>).

$C_{16}H_{21}N_3O_6$  (351.4) Calc. C 54.70 H 6.02 N 11.97 Found C 54.08 H 6.19 N 11.97

*2,2'-Azobis[(15-crown-5)eno[g]quinoxaline (3)*: To a solution of **2** (0.35 g, 1.0 mmol) in absol. ethanol (50 ml) was added a solution of cobalt(II) chloride hexahydrate (0.12 g, 0.5 mmol) in ethanol (10 ml). The mixture was stirred at 60°C under nitrogen atmosphere for 2 h. The colour of the solution turned to dark red from the initial blue colour. A reddish brown precipitate was obtained when the solution was cooled to room temperature. It was filtered, washed with ethanol and then with diethyl ether and dried in vacuo. Yield 0.22 g (67%), m. p. 214°C. — IR (KBr): 3055 ( $CH_{arom.}$ ), 2920, 2850 ( $CH_{aliph.}$ ), 1610 (C=N), 1290–1235 (Ar–O–C), 1160–1120 (C–O–C). — UV-VIS (chloroform):  $\lambda_{max}$  ( $\epsilon$ ) = 424 (27600), 286 (20650), 240 nm (13300). — <sup>1</sup>H NMR ( $[D_6]DMSO$ ):  $\delta$  = 3.67 (s, 16H, C–O–CH<sub>2</sub>), 3.89 (s, 8H, Ar–O–C–CH<sub>2</sub>), 4.35 (s, 8H, Ar–O–CH<sub>2</sub>), 7.44 (s, 2H, Ar-H), 7.50 (s, 2H, Ar-H), 9.22 (s, 2H, N=CH). — MS (70 eV):  $m/z$  = 668 (4%, [M + 2]<sup>+</sup>), 654 (100, M – 12).

$C_{32}H_{38}N_6O_{10}$  (666.7) Calc. C 57.66 H 5.71 N 12.61 Found C 57.23 H 5.77 N 12.88

## CAS Registry Numbers

1: 102818-74-6 / 2: 104642-08-2 / 3: 104642-09-3 / *s-trans*-chloroethanedial dioxime: 4732-58-5

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