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LETTERS TO THE EDITOR

Host–Guest Complexes. Selective Reaction of Crown Ether Hosts with Triphenylmethane Derivatives

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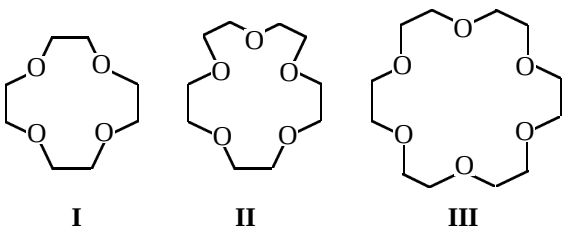
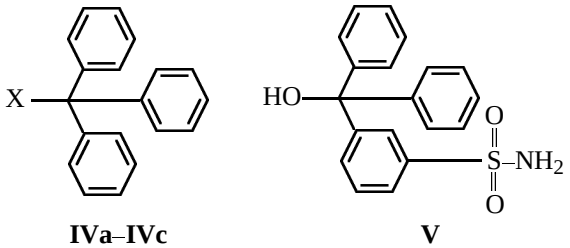
One of priority tasks of guest-host chemistry is search for selective interactions of neutral molecules, leading to formation of molecular complexes to model processes widely occurring in biological systems [1]. In [2], crown ethers and triphenylmethane derivatives are referred to as host molecules capable of binding smaller size host molecules [3–5] into complexes. The aim of the present work was synthesize crystalline molecular complexes of crown ethers **I**–**III** with triphenylmethane derivatives and examine selectivity of the complex-formation reaction between these partners.

It was found that spontaneous evaporation of solvents from solutions of the small crown ether **I** with triphenylmethanol (**IVa**), 1,1,1-triphenylamine (**IVb**), and triphenylmethanethiol (**IVc**) gives rise to crystalline molecular complexes **I** · $2(C_6H_5)_3COH$ (**VI**), **I** · $2(C_6H_5)_3CNH_2$ (**VII**), and **I** · $2(C_6H_5)_3CSH$ (**VIII**), respectively.



I **II** **III**



IVa–**IVc** **V**

IV, X = OH (**a**), NH_2 (**b**), SH (**c**).

When a mixture of crown ethers **I**–**III** is used, triphenylmethane derivatives **IVa** and **IVb** selectively form crystalline complexes with crown ether **I** only. Introduction of the H-donor sulfamide substituent in one of the aromatic rings of triphenylmethanol radically changes the result of the complex formation. Thus, the reaction of 3-(hydroxydiphenylmethyl)benzenesulfonamide (**V**) with a mixture of crown ethers **I**–**III** results in selective isolation of crystalline complex **III** · 2*m*-$H_2NSO_2C_6H_4(C_6H_5)_2COH$ (**IX**). Earlier [6] no selectivity was observed in reactions of the above crown ethers with neutral molecules. By contrast, *N*-(phenylsulfonyl)benzenesulfonamide $HN(SO_2C_6H_5)_2$ gives crystalline molecular complexes both with crown ether **I** [7] and with crown ether **III** [8–10].

Thus, we are the first to describe selective interactions of crown ethers with bulky triphenylmethane derivatives, yielding crystalline molecular complexes **VI**, **VII**, and **IX**, which can be used for modeling molecular interactions of fairly large natural molecules [11] and also form a chemical basis for separation of crown ethers [12] as it has been done in [13–15]. Note also that the preparation of compound **VIII** is a first example of fixation of a thiol with a crown ether to form a crystalline host–guest molecular complex.

3-(Hydroxydiphenylmethyl)benzenesulfonamide (V). A mixture of 10 mmol of chlorotriphenylmethane and 10 ml of chlorosulfonic acid was heated for 8 h at 150C and then cooled and poured onto 50 g of ice. The crystals were separated, placed into 40 ml of 25% aqueous ammonia, and heated with stirring for 12 h. The crystals that formed at 20°C were washed with water, dried in air, and recrystallized from acetone–hexane. Yield 53%, mp 188–190°C. Found, %: C 67.24; H 5.05; N 4.13; S 9.45. $C_{19}H_{17}NO_3S$. Calculated, %: C 67.21; H 5.09; N 4.19; S 9.55.

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Crystalline molecular complexes VI–VIII. A solution of 1 mmol of compound **IVa**–**IVc** in 10 ml of methanol or of 1 mmol of compound **V** in a mixture of 5 ml of acetone and 5 ml of hexane was added to a mixture of 1 mmol of crown ether **I**, 1 mmol of crown ether **II**, and 1 mmol of crown ether **III**. The solvents were allowed to evaporate at 20°C. Crystals formed and were washed with ethyl acetate and dried in air. In the synthesis of complex **VIII**, an individual crown ether **I** and a solution of compound **Ic** in a mixture of 1.5 ml of benzene and 3 ml of diethyl ether were used.

Complex of 1,4,7,10-tetraoxacyclododecane with triphenylmethanol, 1 : 2 (**VI**), yield 85%, mp 147–148°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.62 s (2H, OH), 3.70 s, (16H, CH_2), 7.24–7.35 m (30H, ArH). Found, %: C 79.28; H 6.94. $C_{46}H_{48}O_6$. Calculated, %: C 79.33; H 6.90.

Complex of 1,4,7,10-tetraoxacyclododecane with 1,1,1-triphenylmethylamine, 1 : 2 (**VII**), yield 81%, mp 94–95°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.86 s (4H, NH), 3.70 s (16H, CH_2), 7.20–7.32 m (30H, ArH). Found, %: C 79.51; H 7.25; N 4.03. $C_{46}H_{50}N_2O_4$. Calculated, %: C 79.53; H 7.24; N 4.05.

Complex of 1,4,7,10-tetraoxacyclododecane with triphenylmethanethiol, 1 : 2 (**VIII**), yield 83%, mp 68–70°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.61 s (2H, SH), 3.71 s (16H, CH_2), 7.22–7.30 m (30H, ArH). Found, %: C 75.79; H 6.64; S 8.80. $C_{46}H_{48}\cdot O_4S_2$. Calculated, %: C 75.81; H 6.69; S 8.77.

Complex of 1,4,7,10,13,16-hexaoxacyclooctadecane with 3-(hydroxydiphenylmethyl)benzenesulfonamide, 1:2 (**IX**), yield 98%, mp 174–176°C. ^{1}H NMR spectrum (CD_3OD), δ, ppm: 3.62 s (24H, CH_2), 7.27–7.44 m (28H, ArH). Found, %: C 63.66; H 6.20; N 2.97; S 6.80. $C_{50}H_{58}N_2O_{12}S_2$. Calculated, %: C 63.71; H 6.24; N 2.99; S 6.85.

The ^{1}H NMR spectra were recorded on a Varian VXR-300 instrument (300 MHz), internal reference TMS.

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