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LETTERS TO THE EDITOR

Complexes of Crown Ethers with Diaminomaleodinitrile

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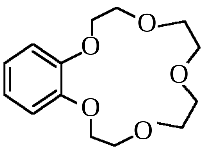
1,2-Diaminomaleodinitrile (HCN tetramer) is usually considered as one of the key steps of chemical evolution [1–4] on the pathway of transformation of hydrogen cyanide into amino acids and heterocycles [4–6]. According to [7, 8], in simulation of biochemical processes, it is important to reveal noncovalent interactions of relatively small molecules with cavity-containing structures, in particular, with crown ethers.

The goal of this work was to examine the possibility of preparing crystalline molecular complexes of crown ethers with 1,2-diaminomaleodinitrile and to reveal the selectivity of such host–guest interactions.

We found that spontaneous evaporation of solvents from solutions of crown ethers [benzo-15-crown-5, **I**; 18-crown-6, **II**; benzo-18-crown-6, **III**; mixture of *cis,syn,cis* (**IV**) and *cis,anti,cis* (**V**) isomers of dicyclohexano-18-crown-6] with 1,2-diaminomaleodinitrile **VI** results in crystalllization of molecular complexes **VII**–**X**.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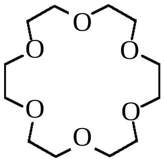
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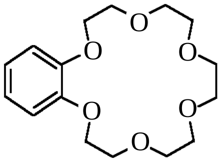
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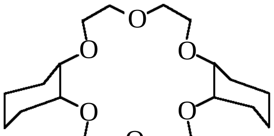
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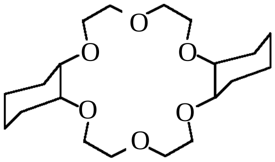
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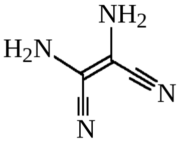

VI

I, 2,3,5,6,8,9,11,12-octahydrobenzo-1,4,7,10,13-pentaoxacyclopentadecin; **II**, 18c6, 1,4,7,10,13,16-hexaoxacyclooctadecane; **III**, 2,3,5,6,8,9,11,12,14,15-decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin; **IV**, *cis,syn,cis*-perhydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecin; **V**, *cis,anti,cis*-perhydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecin; and **VI**, 1,2-diaminomaleodinitrile.

Note that, in interaction of 1,2-diaminomaleodinitrile with a mixture of *cis,syn,cis* (**IV**) and *cis,anti,cis* (**V**) isomers of dicyclohexano-18-crown-6, complex **X** is selectively formed with the *cis,anti,cis* isomer only, in which the steric shielding of the macroring cavity is equivalent from both sides (cf. [9]). These interactions can be taken into account in simulation of molecular interactions of natural molecules [7]. Complexes **VII**–**X** may be of interest as containers [10] of highly reactive 1,2-diaminomaleodinitrile.

Crystalline molecular complexes VII–X. Solutions of 1.5 mmol of diaminomaleodinitrile **VI** and

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1 mmol of crown ether **I**–**III** or **V**, or 2 mmol of equimolar commercial mixture of **IV** and **V** in 3 ml of methanol and 3 ml of benzene were filtered and evaporated at 20°C. The colorless crystals were separated, washed with ether, and dried in air.

Complex of 2,3,5,6,8,9,11,12-octahydrobenzo-1,4,7,10,13-pentaoxacyclopentadecin with 1,2-diaminomaleodinitrile, 1 : 1 (VII). Yield 52%, mp 109–110°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.60 m, 3.77 m, 4.02 m (16H, 8CH$_2$), 5.28 s (4H, NH), 6.90 m (4H, CH). Found, %: C 57.39; H 6.48; N 14.93. $C_{18}H_{24}N_4O_5$. Calculated, %: C 57.44; H 6.43; N 14.88.

Complex of 1,4,7,10,13,16-hexaoxacyclooctadecane with 1,2-diaminomaleodinitrile, 1 : 1 (VIII). Yield 65%, mp 76–78°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.50 s (24H, 12CH$_2$), 5.28 s (4H, NH). Found, %: C 51.56; H 7.63; N 15.10. $C_{16}H_{28}N_4O_6$. Calculated, %: C 51.60; H 7.58; N 15.04.

Complex of 2,3,5,6,8,9,11,12,14,15-decahydrobenzo-1,4,7,10,13,16-hexaoxacyclooctadecin with 1,2-diaminomaleodinitrile, 1 : 1 (IX). Yield 67%, mp 108–110°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.60 m, 3.74 m, 4.05 m (20H, 10CH$_2$), 5.29 s (4H, NH), 6.90 m (4H, CH). Found, %: C 57.08; H 6.67; N 13.39. $C_{20}H_{28}N_4O_6$. Calculated, %: C 57.13; H 6.71; N 13.33.

Complex of *cis,anti,cis*-perhydro[*b,k*][1,4,7,10,-13,16]hexaoxacyclooctadecin with 1,2-diaminomaleodinitrile, 1 : 1 (X). Yield 78%; with an equimolar mixture of isomers **IV** and **V**, the yield of the complex of **IV** was 62%, mp 150–152°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.19–1.71 m and 3.53 m (36H), 5.28 s (4H, NH). Found, %: C 59.95; H 8.43; N 11.77. $C_{24}H_{40}N_4O_6$. Calculated, %: C 59.98; H 8.39; N 11.66.

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

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REFERENCES

1. Calvin, M., *Chemical Evolution*, Oxford: Oxford Univ. Press, 1969, p. 358.
2. Mozhaev, P.S., Kichigina, G.A., Aliev, Z.G., Kiryukhin, D.P., Atovmyan, L.O., and Barkalov, I.M., *Dokl. Ross. Akad. Nauk*, 1994, vol. 335, no. 6, p. 747.
3. Mozhaev, P.S., Kiryukhin, D.P., Kichigina, G.A., and Barkalov, I.M., *Mendeleev Commun.*, 1994, no. 1, p. 17.
4. Nelson, K.E., Levy, M., and Miller, S.L., *Proc. Nat. Acad. Sci. USA*, 2000, vol. 97, no. 8, p. 3868.
5. Begland, R.W., Hartter, D.R., Jones, F.N., Sam, D.J., Sheppard, W.A., Webster, O.W., and Weigert, F.J., *J. Org. Chem.*, 1974, vol. 39, no. 16, p. 2341.
6. Hulshof, J. and Ponnamperuma, C., *Origins Life*, 1976, vol. 7, no. 3, p. 197.
7. Lehn, J.M., *Supramolecular Chemistry*, New York: VCH, 1995.
8. *Host Guest Complex Chemistry. Macrocycles. Synthesis, Structure, Applications*, Vögtle, A. and Weber, E., Eds., Berlin: Springer, 1985.
9. Ganin, E.V., Makarov, V.F., Kotlyar, S.A., and Luk'yanenko, N.G., *Zh. Obshch. Khim.*, 1988, vol. 58, no. 6, p. 1309.
10. *Comprehensive Supramolecular Chemistry*, Lehn, J.-M., Atwood, J.L., Davies, J.E.D., MacNicol, D.D., and Wogtle, F., Eds., Oxford: Pergamon, 1996, vol. 10, p. 418.