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REACTIVITY OF MACROHETEROCYCLES WITH RESPECT TO SULFAMIC ACID

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It has been established, on the basis of the formation of a 1:1:1 inclusion compound of 18,19-benz-1,16-diaza-4,7,10,13-tetraoxoeicosa-17,20-dione with sulfamic acid and water from the interaction of 11-20-membered macrocyclic oxyethyleneamides of phthalic acid with sulfamic acid, that 18-20-membered oxyethylene macrocycles containing six oxygen donor atoms in the macrocycle are effective in the formation of "host–guest" complexes.

The observation that crown ethers ("hosts") are able to form crystalline "host–guest" (inclusion) compounds with proton donor molecules ("guests") [1, 2] is based on a system of hydrogen bonds in a nontraditional class of heterocyclic systems, the reactivity of which depends on their size, and the steric and stereoelectronic structure of the cavity of the macroheterocycle. The requirements for a "guest" to combine with an oxygen containing crown ether have been discussed with 18-crown-6 as the example [3]. The "guest" should be a small molecule containing CH, NH, and OH proton donors and a clear dipole moment. The characteristics of crown ethers needed for effective "host–guest" formation have not been discussed in the literature.

Sulfamic acid was chosen as the "guest" molecule in determining the characteristics of oxygen containing crown ethers necessary for bonding with hydrogen donors in "host–guest" molecules because it has all of the requirements noted previously [3]. It is a strong acid with *pKa* 0.130 (25°C) [4] which has the zwitterionic structure ($H_3N^+S^-O_3$) in solution and in the solid state. The properties of the "guest" allow the limits of the effective reactivity (macrocyclic effect [5]) to be determined for oxygen containing crown ethers for the interactions under discussion. Stable crystalline 1:1 "host–guest" compounds have been obtained in practically quantitative yield from the reaction of sulfamic acid in aqueous ethanol with 12- to 24-membered oxygen containing crown ethers and their benzo- and cyclohexano-analogs [6-9]. The distances (Å) between the N atom of sulfamic acid and the mean plane of the heteroatoms of the heterocycles were as follows: 12-crown-4 (2.979-3.130 (shortest contacts) — composition of "host–guest," 6:4 [6]), 15-crown-5 (1.76 [7]), benzo-15-crown-5 (1.86 [7]), 18-crown-6 (0.97 [8]), benzo-18-crown-6 (0.98 [8]), benzocyclohexano-18-crown-6 (not determined [9]), *cis-cis-cis*-diastereoisomer of dicyclohexano-18-crown-6 (1.58 [8]), *cis-anti-cis*-diastereoisomer of dicyclohexano-18-crown-6 (1.97 [8]). In the "host–guest" compound the 18-membered crown ether is linked to the "cationic" part of sulfamic acid via three classical hydrogen bonds to successive oxygen atoms of the heterocycle [8]. For the 15-membered crown ether the possibility of bonding to the "guest" molecule has a collective character (bi- or trifunctional), but a component which reflects the effectiveness of the bonding is absent. The effectiveness is notably greater for the 15-membered ring than for the 18-membered. In the 6:4 compound of sulfamic acid with 12-crown-4 the "host" molecules which do not take part in bonding to the "guest" molecules are placed away from center of the plane of the host and have the role of solvent [6]. The increased distance between the components, the possibility of coordination and the incomplete bonding of the "guest" in the "host–guest" compounds makes these compounds nonclassical, nevertheless 12-crown-4 is a limit for the effectiveness of crown ethers in the interactions discussed. The 22- and 24-membered crown ethers with eight oxygen atoms do not form "host–guest" with sulfamic acid, limiting the choice of crown ethers suitable for bonding to a "guest" with a single proton donor group in "host–guest" compounds.

The presence of 6 oxygen atoms in 18-membered and 15-membered crown ethers be suitable for the stabilization of a proton donor "guest" in a "host–guest" compound from the discussion above.

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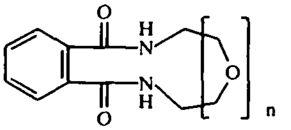
To confirm these conclusions and to decide whether the size or the number of oxygen atoms in the cavity of the macromolecule is the more important, the reaction of the 11-, 14-, 17-, and 20-membered macrocyclic oxyethylene diamides of phthalic acid, Ia-d, containing 3, 4, 5, and 6 oxygen atoms in the heterocycle respectively, with sulfamic acid aqueous methanol was carried out. A stable crystalline "host–guest" compound was obtained only with the 20-membered macrocyclic diamide Id, containing 6 oxygen atoms, which indicates that the number of electron donor oxygen atoms in the heterocyclic crown ethers plays the more important role.



Ia–d

Ia n = 1, b n = 2, c n = 3, d n = 4

EXPERIMENTAL

IR Spectra were recorded in KBr disks on an IKC-20 spectrometer. ^{1}H NMR Spectra of $CDCl_3$ solutions with HMDS as internal standard were recorded with a Tesla BS-467 machine. TLC was carried out on Silufol strips with 1:8 methanol–chloroform as eluent and exposure with ninhydrin at 200°C. Decomposition occurred during TLC and the diamide Id appeared as a hole while sulfamic acid appeared as a grey spot on a rose background with R_f = 0.51 and 0.46 respectively. The macrocyclic amides Ia-Id were prepared as described previously [10].

The 1:1:1 Inclusion Compound of 18,19-benz-4,7,10,13-Tetroxacycloeicosa-17,20-dione with Sulfamic Acid and Water. A solution of sulfamic acid (97 mg, 1 mmole) in water (5 cm^3) to a solution of the diamide Id (366 mg, 1 mmole) in methanol (20 cm^3) at 64°C and the product was allowed to crystallize at 20°C. Yield of the inclusion compound 435 mg (90%), mp 166-168°C. IR Spectrum: 3420 (H_2O), 3290 (NH), 1625 (CO), 1100 cm^{-1} (COC). ^{1}H NMR Spectrum: 3.10 (2H, s, H_2O), 3.97 (20H, m, CH_2O and CH_2N), 7.60 (2H, br s, NH), 7.80 (4H, m, Ph), 8.50 ppm (3H, br s, H_3N^+). Found, %: C 44.71, H 6.40, N 8.93, S 6.80. Calc. for $C_{18}H_{31}N_3O_{10}S$, %: C 44.90, H 6.49, N 8.73, S 6.66. When a 100 mg sample was heated at 100°C and 0.1 mmHg for 1 h, a 3.8% loss in weight occurred, which corresponds to 1 mole of water (calculated 3.75%).

REFERENCES

1. D. J. Cram and J. M. Cram, Acc. Chem. Res., No. 11, 8 (1978).
2. F. Fegtle and É. Weber (ed.), "Host–Guest" Complexes. Synthesis, Structure and Use [Russian translation], Mir, Moscow (1988).
3. A. Elbasyony, H. J. Brügge, K. Deuten, M. Dickel, A. Knochel, K. U. Koch, J. Kopf, D. Melzer, and S. Rudolph, J. Am. Chem. Soc., **105**, 6568 (1983).
4. H. Brauer (ed.), Handbook of Inorganic Synthesis, Vol. 2 [Russian translation], Mir, Moscow (1985), p. 338.
5. K. B. Yatsimirskii, Teor. Éksp. Khim., **16**, 34 (1980).
6. Y. A. Simonov, M. S. Fonari, A. A. Dvorkin, T. I. Malinowsky (Malinovskii), J. Lipkowski (Ya. Lipkovskii), and E. V. Ganin, J. Incl. Phenomena, **16**, 315 (1993).
7. A. A. Dvorkin, Yu. A. Simonov, K. Suvinska, Ya. Lipkovskii, T. I. Malinovskii, É. V. Ganin, and S. A. Kotlyar, Kristallografiya, **36**, 62 (1991).
8. M. S. Fonar, Y. A. Simonov, A. A. Dvorkin, T. I. Malinowsky (Malinovskii), E. V. Ganin, S. A. Kotlyar, and V. F. Makarov, J. Incl. Phenomena, **7**, 613 (1989).
9. É. V. Ganin, V. F. Makarov, S. A. Kotlyar, and N. G. Luk'yanenko, Ukr. Khim. Zh., **56**, 440 (1990).
10. É. V. Ganin, V. F. Anikin, and G. L. Kamalov, Khim. Geterotsikl. Soedin., No. 6, 846 (1981).
11. V. F. Anikin, É. V. Ganin, B. V. Rozynov, R. M. Zakharova, and G. L. Kamalov, Khim. Geterotsikl. Soedin., No. 2, 246 (1982).