Chemistry of Heterocyclic Compounds, Vol. 42, No. 9, 2006

REACTION OF CROWN ETHERS WITH FIVE-MEMBERED HETEROCYCLES: 1H-IMIDAZOLE-4,5-DICARBONITRILE, 3-NITRO-1,2,4-TRIAZOLE, AND 1H-TETRAZOLE

Wen Jwu Wang[1], San Wei Tang[1], and E. V. Ganin[2]

By the reaction of 1H-imidazole-4,5-dicarbonitrile, 3-nitro-1,2,4-triazole, and 1H-tetrazole, containing one proton at each of the two proton-donating atoms separated by one covalent bond, it was shown that uncharged crystalline supramolecular compounds can be obtained on account of the proton-donating characteristics of the aromatic heterocycles.

Keywords: 1H-imidazole-4,5-dicarbonitrile, 3-nitro-1,2,4-triazole, 1H-tetrazole, crown ethers, crystalline supramolecular compounds.

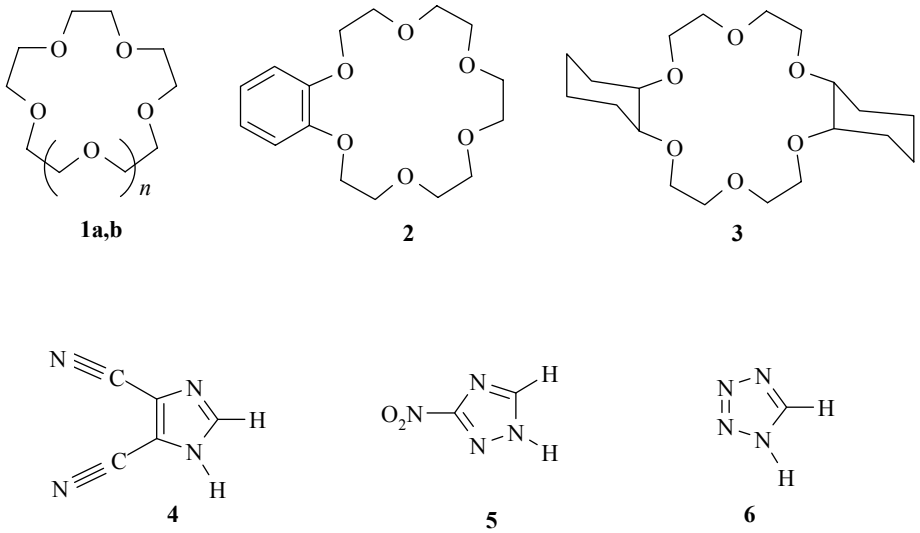
An indispensable condition for the formation of crystalline supramolecular compounds [1, 2] of crown ethers with organic molecules is the presence in the latter of proton-donating centers with one of the atoms C, N, or O, particularly H_2N–, H_2NSO_2–, H_2NCS–, H_2NHNCO–, H_2C=, H_3C–, H_3CO–, and similar groups or water molecules [1-3], securing stabilization of the components of the supramolecular compound by hydrogen bonds. As a rule a pair of protons of the substituent takes part in bonding, and the stability of the compounds decreases in the following order: OH > NH_2 > CH_2 [4]. The crystalline supramolecular compounds of crown ethers with heterocycles are stabilized by hydrogen bonds either through one of the above-mentioned substituents in the heterocycle [5-12] or the cyclic ammonium group of the protonated heterocycle [13]. A single example of the formation of a crystalline supramolecular compound of the most effective [3, 14] crown ether **1b** with unsubstituted triazole is known [15].

The aim of this work was to determine the possibility of synthesizing uncharged crystalline supramolecular compounds of various crown ethers with five-membered aromatic heterocycles, containing one proton at each of two adjacent proton-donating atoms separated by one covalent bond and securing stabilization of the supramolecular compound by analogy with the data in [15].

It was established that the crystalline supramolecular compounds [**1b**·**4**]–**7**, [**2**·**4**]–**8**, [**3**·2(**4**)]–**9**, [**1a**·**5**]–**10**, [**1b**·2(**5**)]–**11**, [**2**·2(**5**)]–**12**, [**3**·2(**5**)]–**13**, and [**3**·2(**6**)]–**14** respectively are formed during spontaneous evaporation of the solvents from solutions of the crown ethers **1-3** with the respective heterocycles **4-6**.

[1] Tamkang University, Taipei 25137, Taiwan (Chinese Republic); e-mail: wjw@mail.tku.edu.tw.
[2] Odessa State Ecological University, Ministry of Education and Science of Ukraine, Odessa 65016; e-mail: edganin@yahoo.com. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1302-1305, September, 2006. Original article submitted October 7, 2005.

 0009-3122/06/4209-1126



1a,b **2** **3**

4 **5** **6**

(**1a**) 1,4,7,10,13-pentaoxacyclopentadecane, (**1b**) 1,4,7,10,13,16-hexaoxacyclooctadecane; (**1a**) n = 1, (**1b**) n = 2;
(**2**) 2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecene;
(**3**) *cis*-*anti*-*cis*-eicosahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecene;
(**4**) 1H-imidazole-4,5-dicarbonitrile; (**5**) 3-nitro-1,2,4-triazole; (**6**) 1H-tetrazole

The formation of stable crystalline compounds between the neutral heterocycles **4-6** and crown ethers having macrocycles of different sizes (compounds **1a**,**b**) and also differently sterically screened sides of the macrocyclic cavity (compounds **2** and **3**) makes it possible to suppose that the bonding of the crown ethers into the supramolecular compounds by the pairs of protons of the aromatic heterocycles is not accidental in nature. The data can be used for analysis and modelling of the molecular interactions of uncharged natural molecules [1, 2, 16] and also for the direct synthesis of crystalline supramolecular compounds of crown ethers with heterocycles.

The structure of all the subjects described in the article was also determined by X-ray crystallographic analysis. These data are of independent interest and will form the subject of a separate series of publications.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker AC 300 instrument (300 MHz) in acetone-d_6 with TMS as internal standard. Thin-layer chromatography was conducted on Silufol plates with 1:8 methanol–chloroform as eluant and ninhydrin as developer. The crown ethers appeared as gray spots against a pink background. The crown ether **3** was obtained as described in [17], and the compounds **1**, **2**, and **4-6** were commercial products supplied by Aldrich and were used without additional purification.

Supramolecular Compounds 7-14. To the crown ether **1a** (0.220 g, 1 mmol), **1b** (0.264 g, 1 mmol), **2** (0.312 g, 1 mmol), or **3** (0.372 g ,1 mmol) we added a solution of the heterocycle **4** (0.118 g, 1 mmol), **5** (0.114 g, 1 mmol), or **6** (0.070 g, 1 mmol) in a 1:1 mixture of acetone and hexane. The mixture was left to evaporate at 20°C. The single crystals that separated were removed, washed with the same mixture of solvents, and dried in air.

Compound 7 – 1,2,7,10,13,16-Hexaoxacyclooctadecane (1b) with 1H-Imidazole-4,5-dicarbonitrile (4), 1:1. Yield 0.35 g (91%); mp 146-147°C. ^{1}H NMR spectrum, δ, ppm:3.58 (24H, s, CH_2O); 8.29 (1H, s, CH). Found, %: C 53.44; H 6.89; N 14.63. $C_{12}H_{24}O_6 \cdot C_5H_2N_4$. Calculated, %: C 53.39; H 6.85; N 14.65.

Compound 8 – 2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecene (2) with 1H-imidazole-4,5-dicarbonitrile (4), 1:1. Yield 0.4 g (92%); mp 87-90°C. ^{1}H NMR spectrum, δ, ppm: 3.58, 3.61, 4.11 (20H, m, CH_2O); 6.88 (4H, m, C_6H_4); 8.27 (1H, s, CH). Found, %: C 58.28; H 6.17; N 12.83. $C_{16}H_{24}O_6 \cdot 2C_5H_2N_4$. Calculated, %: C 58.59; H 6.09; N 13.02.

Compound 9 – *cis-anti-cis*-Eicosahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecene (3) with 1H-Imidazole-4,5-dicarbonitrile (4), 1:2. Yield 0.29 g (96%); mp 155-156°C. ^{1}H NMR spectrum, δ, ppm: 1.24-1.81, 3.59 (36H, m, CH_2O, CH_2, CH); 8.24 (2H, s, CH). Found, %: C 59.24; H 6.59; N 18.47. $C_{20}H_{36}N_6 \cdot 2C_5H_2N_4$. Calculated, %: C 59.20; H 6.62; N 18.41.

Compound 10 – 1,4,7,10,13-Pentaoxacyclopentadecane (1a) with 3-Nitro-1,2,4-triazole (5), 1:1. Yield 0.3 g (90%); mp 110-112°C. ^{1}H NMR spectrum, δ, ppm: 3.53 (20H, s, CH_2O); 8.86 (1H, s, CH). Found, %: C 43.15; H 6.61; N 16.84. $C_{10}H_{20}O_5 \cdot C_2H_2N_4O_2$. Calculated, %: C 43.11; H 6.63; N 16.76.

Compound 11 – 1,4,7,10,13,16-Hexaoxacyclooctadecane (1b) with 3-Nitro-1,2,4-triazole (5), 1:2. Yield 0.215 g (88%); mp 184-186°C. ^{1}H NMR spectrum, δ, ppm: 3.50 (24H, s, CH_2O); 8.86 (2H, s, CH). Found, %: C 39.11; H 5.76; N 22.84. $C_{12}H_{24}O_6 \cdot 2C_2H_2N_4O_2$. Calculated, %: C 39.03; H 5.73; N 22.75.

Compound 12 – 2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecene (2) with 3-Nitro-1,2,4-triazole (5), 1:2. Yield 0.22 g (81%); mp 94-96°C. ^{1}H NMR spectrum, δ, ppm: 3.58, 3.72, 4.05 (20H m, CH_2O); 6.88 (4H, m, C_6H_4); 8.86 (2H, s, CH). Found, %: C 44.41; H 5.28; N 20.77. $C_{16}H_{24}O_6 \cdot 2C_2H_2N_4O_2$. Calculated, %: C 44.45; H 5.22; N 20.73.

Compound 13 – *cis-anti-cis*-Eicosahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecene (3) with 3-Nitro-1,2,4-triazole (5), 1:2. Yield 0.26 g (87%); mp 178-180°C. ^{1}H NMR spectrum, δ, ppm: 1.20-1.71, 3.52 (36H, m, CH_2O, CH_2, CH); 8.86 (2H, s, CH). Found, %: C 48.08; H 6.76; N 18.73. $C_{20}H_{36}O_6 \cdot 2C_2H_2N_4O_2$. Calculated, %: C 47.99; H 6.71; N 18.66.

Compound 14 – *cis-anti-cis*-Eicosahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecene (3) with 1H-Tetrazole (6), 1:2. Yield 0.22 g (86%); mp 140-142°C. ^{1}H NMR spectrum, δ, ppm: 1.23-2.05, 3.59 (36H, m, CH_2O, CH_2, CH); 9.19 (2H, s, CH). Found, %: C 51.51; H 7.83; N 21.82. $C_{20}H_{36}O_6 \cdot 2CH_2N_4$. Calculated, %: C 51.54; H 7.87; N 21.87.

The work was carried out under Project No. NCS 94-2811-M-032.

REFERENCES

1. F. Vogtle and E. Weber (editors), *Chemistry of Guest–Host Complexes* [Russian translation], Mir, Moscow (1988).
2. J.-M. Lehn, J. L. Atwood, J. E. D. Davies, D. D. MacNicol, and F. Vogtle (editors), *Comprehensive Supramolecular Chemistry*, Pergamon, Oxford, New York, Tokyo (1996).
3. A. Elbasyony, J. Klimes, A. Knochel, J. Oehler, and S. Rudolp, *Z. Naturforsch.*, **31b**, 1192 (1976).
4. A. Elbasyony, H. J. Brugge, K. Deuten, M. Dickek, A. Knochel, J. Kopf, D. Mezer, and S. Rudolp, *J. Am. Chem. Soc.*, **105**, 6568 (1983).
5. M. S. Fonar', A. A. Dvorkin, E. V. Ganin, Yu. A. Simonov, S. A. Kotlyar, and T. I. Malinovskii, *Zh. Obshch. Khim.*, **59**, 2302 (1989).
6. A. A. Dvorkin, Yu. A. Simonov, Ya. Lipkovskii, M. S. Fonar', T. I. Malinovskii, E. V. Ganin, and S. A. Kotlyar, *Kristallografiya*, **35**, 682 (1990).
7. R. Lyuboradzki, J. Lipkowski, Yu. A. Simonov, M. S. Fonar', E. V. Ganin, and A. A. Yavolovskii, *Crystallogr. Reports*, **42**, 67 (1997).
8. M. S. Fonar', Yu. A. Simonov, V. Kh. Kravtsov, Ya. Lipkovskii, A. A. Yavolovskii, and E. V. Ganin, *Zh. Strukt. Khim.*, **42**, 550 (2001).

9. Yu. A. Simonov, M. S. Fonar', B. Kh. Kravtsov, Ya. Lipovskii, E. V. Ganin, and A. A. Yavolovskii, *Kristallografiya*, **47**, 93 (2002).
10. Yu. A. Simonov, M. S. Fonari, J. Lipkowski, E. V. Ganin, and A. A. Yavolovskii, *J. Supramol. Chem.*, **2**, 415 (2002).
11. M. S. Fonari, Yu. A. Simonov, V. Ch. Kravtsov, J. Lipkowski, E. V. Ganin, and A. A. Yavolovskii, *J. Mol. Struct.*, **647**, 129 (2003).
12. Yu. A. Simonov, M. S. Fonari, G. G. Duca, M. V. Gonta, E. V. Ganin, A. A. Yavolovskii, M. Gdaniec, and J. Lipkowski, *Tetrahedron*, **61**, 6596 (2005).
13. S. Kiviniemi, M. Nissinen, M. T. Lamsa, J. Jalonen, K. Rissanen, and J. Pursiainen, *New J. Chem.*, **24**, 47 (2000).
14. E. V. Ganin, *Khim. Geterotsikl. Soedin.*, 1571 (1997). [*Chem. Heterocycl. Comp.*, **33**, 1360 (1997)].
15. R. Lyuboradskii, Ya. Lipkovskii, E. V. Ganin, A. A. Yavolovskii, M. S. Fonar', and Yu. A. Simonov, *Kristallografiya*, **40**, 664 (1995).
16. Zh.-M. Len, *Supramolecular Chemistry: Conceptions and Perspectives* [in Russian], Nauka, Novosibirsk (1998).
17. E. V. Ganin, V. F. Makarov, S. A. Kotlyar, and N. G. Luk'yanenko, *Zh. Obshch. Khim.*, **58**, 1309 (1988).