28. M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, 4907 (1977).
29. C. Thomson and C. Glidewell, J. Comput. Chem., 4, 1 (1983).
30. K. Raghavachari, R. C. Haddon, and J. S. Binkley, Chem. Phys. Lett., 122, 219 (1985).
31. G. Tringquer, J.-P. Daudey, and N. Komiha, J. Am. Chem. Soc., 107, 7210 (1985).
32. R. Ahlrichs, S. Brode, and C. Ehrhardt, J. Am. Chem. Soc., 107, 7620 (1985).
33. M. W. Schmidt and M. S. Gordon, Inorg. Chem., 24, 4503 (1985).

NEW HETEROCYCLIC SYSTEM – BIS[1,2,3-BENZOTRIAZOLO[5,6-b;5',6'-k]]-18-CROWN-6

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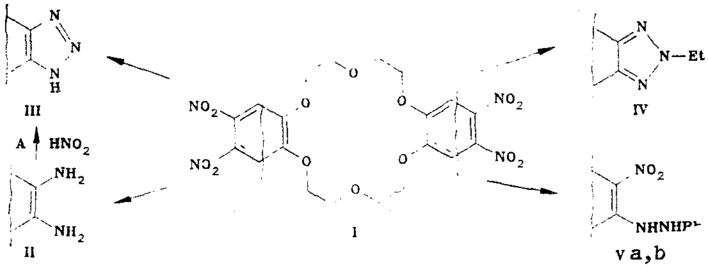
It was shown that 1,2,3-triazole derivatives are formed in the reaction of tetranitrodibenzo-18-crown-6 with excess hydrazine or ethylhydrazine in DMSO, while the reaction with phenylhydrazine leads to isomeric products of nucleophilic substitution of the nitro group.

Substituted dibenzo-18-crown-6 compounds are fungicides and plant-growth regulators [1, 2]. Derivatives of crown ethers that fragmentarily include thiazole, imidazole, 2,1,5-oxadiazole, pyridine, pyrazine, pyrimidine, and 1,4-diazepine rings were described relatively recently [3-6]. Substances that have ergotropic and bactericidal activity have been found among the synthesized compounds [5, 6].

In attempts to obtain triazole derivatives of the III type we found that it was necessary to reject the traditional method of synthesis (scheme A), since the corresponding tetramine II could not be isolated. The formation of a vis-triazole ring, which is based on the reaction of hydrazine and 5,6-dinitrobenzimidazoles [7], has not been widely used in the arene series, since 1,2-dinitrobenzenes are less accessible than the corresponding o-phenylenediamines. On the other hand, tetranitrodibenzo-18-crown-6 (I) can be easily obtained [8], and this makes the scheme presented below suitable for the synthesis of bistriazole analogs of crown ethers.

The corresponding bis(1,2,3-benzotriazole) derivative III was obtained by the reaction of crown ether I with excess hydrazine hydrate in DMSO at room temperature. Under these conditions the reaction of I with ethylhydrazine leads to 2H-benzotriazole derivative IV, while nucleophilic substitution products Va, b are formed with phenylhydrazine.



The formation of isomeric V, which contains 2-phenylhydrazino groups in the 2.14 or 2.13 positions of the crown ether, constitutes evidence that the reaction does not proceed regioselectively and in a stepwise manner; the initial step is replacement of a nitro group by a hydrazine residue. The ease of formation of a cyclic compound in this case evidently depends on the basicity of the nitrogen atom of the hydrazine fragment.

Three absorption bands at 238-242, 300-324, and 335-445 nm appear in the UV spectra of the synthesized compounds. The first two bands correspond to excitation of the aromatic

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chromophores, and the third long-wave band can be assigned to azo or hydrazo groups conjugated with a benzene ring.

EXPERIMENTAL

The IR spectra were obtained with a Specord IR-75 spectrometer. The UV spectra were obtained with a Specord UV-vis spectrophotometer. The mass spectra were recorded with a Varian MAT-112 spectrometer. Silufol UV-254 plates in an acetone–hexane system (1:2) were used for TLC.

Bis[1,2,3-benzotriazolo[5,6-b;5',6'-k]]-18-crown-6 (III). A 0.8-g (0.02 mole) sample of 85% hydrazine hydrate was added to a solution of 0.54 g (0.001 mole) of tetranitrodibenzo-18-crown-6 (I) in 100 ml of DMSO, and the reaction mixture was allowed to stand at 20°C for 2 h. The precipitated crystals were removed by filtration to give a product with mp 234-235°C in 86% yield. IR spectrum (KBr): 3360 (NH), 1615 (C=C), and 1120 cm^{-1} (C–O–C). UV spectrum (EtOH): 240, 320, 445 nm. Mass spectrum: 442 (M^+). Found: C 54.4; H 5.1; N 18.7%. $C_{22}H_{22}N_6O_6$. Calculated: C 54.3; H 5.0; N 19.0%.

2,14-Diethylbis[2H-1,2,3-benzotriazolo[5,6-b;5',6'-k]]-18-crown-6 (IV). This compound was similarly obtained by the reaction of crown ether I with excess ethylhydrazine. The yield of product with mp 163-165°C was 78%. IR spectrum (KBr): 1615 (C=C) and (C=N), 1115 cm^{-1} (C–O–C). UV spectrum (EtOH): 242, 300, 335 nm. Mass spectrum: 498 (M^+). Found: C 57.6; H 6.1; N 17.1%. $C_{24}H_{30}N_6O_6$. Calculated: C 57.8; H 6.0; N 16.9%.

2,14-Di(2-phenylhydrazino)-3,13-dinitrodibenzo-18-crown-6 (Va) and 2,13-Di(2-phenylhydrazino)-3,14-dinitrodibenzo-18-crown-6 (Vb). These compounds were similarly obtained by the reaction of crown ether I with phenylhydrazine. The isomers were separated by chromatography on silica gel. Compound Va, with mp 103-104°C, was obtained in 41% yield. IR spectrum (KBr): 3335, 3450 (NH); 1590 (C=C); 1505 (NO_2); 1110 cm^{-1} (C–O–C). UV spectrum (EtOH): 238, 324, 432 nm. Mass spectrum: 662 (M^+). Found: C 57.9; H 7.3; N 12.5%. $C_{32}H_{48}N_6O_{10}$. Calculated: C 58.0; H 7.3; N 12.7%. Compound Vb, with mp 128-129°C, was obtained in 41% yield. IR spectrum (KBr): 3330, 3460 (NH); 1590 (C=C); 1505 (NO_2); 1115 cm^{-1} (C–O–C). UV spectrum (EtOH): 238, 310, 436 nm. Mass spectrum: 662 (M^+). Found: C 57.8; N 7.2; N 12.9%. $C_{32}H_{48}N_6O_{10}$. Calculated: C 58.0; H 7.3; N 12.7%.

LITERATURE CITED

1. L. I. Reidalova, T. N. Kudrya, and L. M. Tochilkina, in: Physicologically Active Substances [in Russian], Vol. 17, Naukova Dumka, Kiev (1985), p. 41.
2. T. I. Cherepenko, T. N. Kudrya, and G. V. Protopopova, in: Physiologically Active Substanes [in Russian], Vol. 17, Naukova Dumka, Kiev (1985), p. 93.
3. É. I. Ivanov, A. V. Bogatskii, and A. A. Polishchuk, Ukr. Khim. Zh., 52, 197 (1986).
4. É. I. Ivanov, A. V. Bogatskii, and A. A. Polishchuk, All-Union Institute of Scientific and Technical Information Deposited Paper No. 6920–84 Dep.; Ref. Zh. Khim., 2Zh282 (1985).
5. H. J. Forster, H. J. Niclas, and N. G. Lukyanenco, Z. Chem., 25, 16 (1985).
6. H. J. Forster, H. J. Niclas, and N. G. Lukyanenco, Z. Chem., 25, 102 (1985).
7. F. R. Benson and W. L. Savell, Chem. Rev., 46, 1 (1950).
8. A. S. Gomes, Thermochim. Acta, 17, 107 (1976).