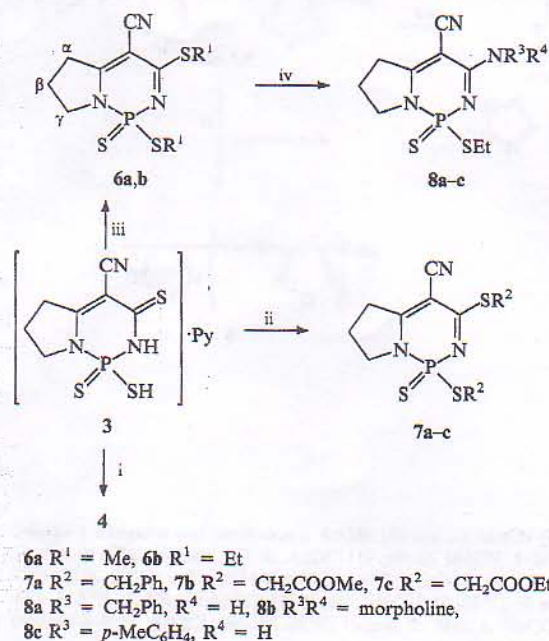


is applicable to a comparison of the ^1H NMR spectra of **6b** and **8a**.



Scheme 2 Reagents and conditions: i, MeOH/MeONa, bp, 2 h; ii, MeOH/MeONa, Hal- R^1 , 20 $^\circ\text{C}$, 12 h; iii, NaOH/ H_2O , $(\text{R}^2)_2\text{SO}_4$, 20 $^\circ\text{C}$, 2 h; iv, HNR^3R^4 , bp, 20 min.

Thus, the present work has established that P_2S_5 -pyridine shows thionating and cyclizing action relative to nonaromatic enaminoamides, enaminothioamides and enaminoitrile derivatives, leading to the formation of trimethylendiazaphosphorine derivatives.

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Hypohalites as reagents for the macrocyclization of diamines of the furazan series

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The possibility of using hypohalites for the oxidative cyclocondensation of diamines was demonstrated for the first time by the example of 3,4-diaminofurazan and 4,4'-diamino-3,3'-azofurazan and the series of macrocyclic polydiazenofurazans, including previously unknown difurazano[c,g]-1,2,5,6-tetrazocine, was synthesized.

A series of new macrocyclic systems, polydiazenofurazans,^{1,2} has been synthesized during a study of the oxidative cyclocondensation of 3,4-diaminofurazan (DAF) and 4,4'-diamino-3,3'-azofurazan (DAAF) under the action of DBI or mixtures of $\text{Pb}(\text{OAc})_4$ with bromine-containing components (Bu_4NBr , Br_2 , or NaBr). It has been supposed in ref. 1 that acetyl hypobromite (AcOBr) is the oxidant that directly reacts with diamines in their reactions with oxidizing mixtures based on $\text{Pb}(\text{OAc})_4$. In the present work, in order to confirm this assumption, the possibility of the oxidative macrocyclocondensation of DAF and DAAF under the action of AcOBr and other hypohalites (NaOBr , AcOCl and NaOCl) was studied.[†]

In fact, it turned out that the reactions of DAAF and DAF with AcOBr or NaOBr (high excess) in MeCN or EtOAc and of DAAF with these hypobromites in aqueous-methanol solutions result in the cyclocondensation of the diamines studied to form polydiazenofurazan macrocycles 1–3^{1,2} from DAAF and macrocycles 1–5^{1,2} from DAF (Scheme 1).[†]

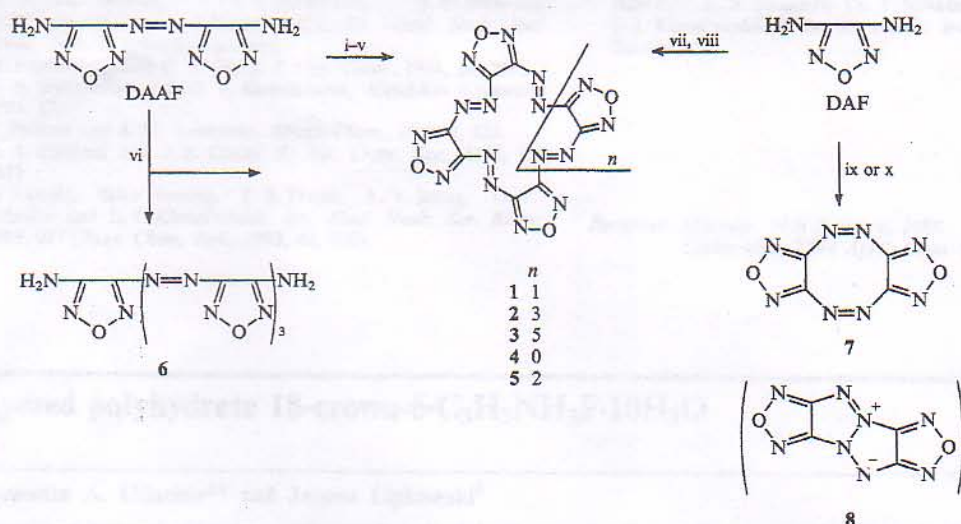
It is noteworthy that the formation of the four-membered macrocycle 1, which was isolated in the majority of the

reactions in high yields (55 to 93%), is the preferential process under the conditions studied upon both the action of DBI² and $\text{Pb}(\text{OAc})_4$ with Bu_4NBr .[†] Macrocycles 2–5 were not isolated. They were identified in the mixtures by comparison with known samples,¹ by mass spectral and TLC data.

The study of the oxidation of DAAF in MeCN by a small

[†] Acetyl hypohalites were obtained by a procedure similar to that described in ref. 3 from AcONa and the corresponding halogen in a particular solvent and were used *in situ*. The reactions with aqueous solutions of NaOCl or NaOBr were performed in homogeneous (aqueous-methanol) or heterogeneous (water-organic solvent-MeCN, EtOAc) media. The reaction was controlled by TLC with Silufol UV-254, C_6H_6 -EtOAc (5:1) as eluent.

Compound 1 or a mixture of macrocycles was isolated by chromatography on a column (silica gel LS 40/100) using benzene or CH_2Cl_2 -hexane (3:1) as eluent, respectively. A mixture of benzene-EtOAc (3:1) was used as eluent for the isolation of compound 6. Compound 7: mp 232 $^\circ\text{C}$ (decomp.), R_f 0.9 (benzene-EtOAc, 5:1); R_f 0.78 (CH_2Cl_2 -hexane, 1:1); MS m/z (I, %): 192 (70) [M^+]; IR (KBr) ν/cm^{-1} : 1635, 1410, 1260, 1035, 910, 760; ^{13}C NMR (HNO_3 , δ 1.5, external standard $^2[\text{H}_6]\text{acetone}$), δ 158.30 ppm.



Scheme 1 Reagents and conditions: i, AcOBr (40 mmol), MeCN (EtOAc), 5–10°C, 15 min, 1: 90% (85%); ii, AcOBr (40 mmol), MeCN, 5–10°C, 30 min, 1: 67%, mixture 1, 3; iii, AcOCl (10 mmol), MeCN, 5–10°C, 4 h, 1: 90%; iv, NaOBr (50 mmol), MeCN (EtOAc, MeOH), 0–2°C, 1 h, 1: 93% (85%, 50%); v, NaOCl (45 mmol), MeCN (EtOAc), 0–2°C, 4 h, 1: 90% (1 h, 1: 65%, mixture 1, 3, 6); vi, AcOBr (4 mmol), MeCN, 5–10°C, 20 h, 6: 37%, 1: 6%; vii AcOBr (20 mmol), MeCN, 10–15°C, 30 min, 1: 55%, mixture 2–5; viii, NaOBr (25 mmol), MeCN, 0–2°C, 30 min, 1: 41%, mixture 2–5; ix, AcOCl, MeCN, 20°C, 15 min, 7: 70%; x, NaOCl, MeCN (5–7°C, 30 min, 7: 65%), EtOAc (5–7°C, 4 h, 7: 40%).

excess AcOBr (1:4) shows that DAAF does not react completely under the conditions employed here. Cyclocondensation occurs only insignificantly (1, 6%) and largely ceases at the stage of the formation of the linear product of the oxidative dimerization of DAAF (diamine 6²), which was isolated in a yield of 37%. The same compound and DAAF were observed by TLC as intermediates in the oxidation of DAF by hypobromites.

A study of the reactions of DAAF and DAF with hypochlorites (AcOCl, NaOCl) in aqueous-organic (MeCN or EtOAc) media made it possible to establish that the reactivities of the diamines studied with respect to these reagents differ substantially.

Macrocycle 1 was mainly obtained from DAAF under the action of hypobromites, while the reaction of DAF resulted in the formation of the previously unknown compound difurazano[*c,g*]-1,2,5,6-tetrazocine 7 as the sole reaction product, the result of the oxidative cyclocondensation of two DAF molecules.

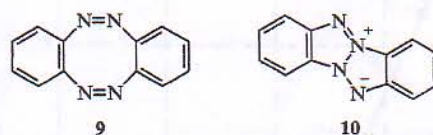
It follows from this result that the reactivity of DAF with respect to hypochlorites differs from the behaviour of DAAF with respect to these reagents and from that of DAF itself with respect to the corresponding hypobromites and other oxidants used previously.^{1,3}

The structure of compound 7 was determined on the basis of elemental analysis (corresponding to the empirical formula C₂N₄O), IR (absorption in the range from 3200 to 3500 cm⁻¹, which is typical of amines, is absent), ¹³C NMR and mass (an intense peak with the corresponding molecular mass) spectra. The ¹³C NMR spectrum of 7 exhibits only one signal of the furazan cycle, indicating the equivalence of its carbon atoms, which allows one to exclude the alternative tetraazapentalene structure 8 (Scheme 1).

The formation of the dimer 7 agrees with calculations⁵ made on the electrostatic potentials and relative energies of the

hypothetical structures 7 and 8. These calculations show that structure 7 is considerably more energetically favorable (by 33 kcal mol⁻¹)⁵ than structure 8. According to these calculations, structure 7 should have the form of a 'boat' with a *cis*-configuration of the furazan units relative to the diazene bridges.

It is known⁶ that the pentalene structure is thermodynamically preferred for the isomeric compounds dibenzo[*c,g*]-1,2,5,6-tetrazocine 9 and the tetraazapentalene 10. It follows from the calculations presented in ref. 5 that tetraazapentalene itself should also be more energetically favorable than the isomeric 1,2,5,6-tetrazocine. The inverse dependence observed for the corresponding difurazan derivatives 7 and 8 is likely to be related to the instability of the system consisting of four fused five-membered polyheterocycles.⁷



It is significant that compound 7 is not formed from DAAF^{1,2} because of its intramolecular cyclization and owing to the treatment of DAF with other reagents favorable for cyclocondensation of these compounds, including hypobromites, i.e. in the reactions in which DAAF is observed as an intermediate. In turn, no macrocycles with more than two diazenofurazan units were observed in the reactions of DAF with hypochlorites. It is likely that macrocycle 7 is formed by a different route rather than *via* DAAF in which furazan cycles would be likely to have the *trans*-configuration relative to the diazene fragment (according to the X-ray diffraction data^{2,8} of macrocycles obtained from it).

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⁵ 1 cal = 4.184 J.

[†] IR spectra were recorded on a UR-20 instrument. Mass spectra of the reaction products were recorded on a Varian MAT CH6 spectrometer, and the mass spectrum of compound 7 was obtained using an aliquot of a solution of the substance in the organic layer that was separated from the aqueous layer after the cessation of the reaction. ¹³C NMR spectra were recorded on a Bruker AM-300 spectrometer.

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Layered polyhydrate 18-crown-6·C₃H₇NH₃F·10H₂O

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New polyhydrate 18-crown-6·C₃H₇NH₃F·10H₂O which melts incongruently at -0.8°C has been found in the 18-crown-6–C₃H₇NH₃F–H₂O system; a single crystal X-ray structure of this layered hydrate is reported, in which layers of water molecules and fluoride anions are made up of tetra-, penta- and heptagons and also contain vacant polyhedral cavities; the crown ether complexes with cations C₃H₇NH₃⁺ are situated between water–fluoride layers and do not form hydrogen bonds with the molecules of the layers.

Among numerous framework water structures there are quite a few in which water forms cavities. This is typical of gas hydrates^{1,2} and many similar clathrate compounds of peralkylammonium salts and their analogues.^{2,3} However, it was only recently that we found a channel structure hydrate with vacant polyhedral cavities.⁴ Therefore, a layered hydrate with polyhedral cavities of molecular size is not common and of particular interest. We found it while studying the hydrate formation of crown ethers and complexes. This paper discusses the layered polyhydrate found in 18-crown-6–C₃H₇NH₃F–H₂O.

Figure 1 shows a section of the tertiary system 18-crown-6–C₃H₇NH₃F–H₂O with a constant molar ratio of 18-crown-6 and C₃H₇NH₃F of 1:1 and variable water content. It is seen from the figure that in the studied interval of the phase diagram a hydrate forms of composition 18-crown-6·C₃H₇NH₃F·10H₂O which melts incongruently at -0.8°C . The hydrate crystals exist in equilibrium with an aqueous solution in a very narrow temperature and concentration range. At -0.8°C the hydrate melts, forming a solution of composition 18-crown-6·C₃H₇NH₃F·12.8H₂O and a hydrate containing less water than the initial one. Analysis of the hydrate crystals for water content by Fischer's technique⁵ gave the composition 18-crown-6·C₃H₇NH₃F·10.05(6)H₂O (in brackets we give the standard deviation for five independent measurements). Using the phase diagram data, we grew single crystals of this hydrate, from water solutions, of composition 18-crown-6·C₃H₇NH₃F·12H₂O at -5°C . Under these conditions the solid and liquid phases were present in approximately the same proportions, which favoured the growth and selection of single crystals. The solutions were rapidly cooled until crystallization began; the temperature was then increased to -5°C . The solution with crystals was then kept at this temperature for several days; the temperature was regularly increased to above the melting point of the crystals for several minutes which resulted in the melting of some crystals. Subsequently the temperature was decreased to -5°C . The

single crystals obtained in this way had clear-cut faces and looked like needles with square cross-sections.

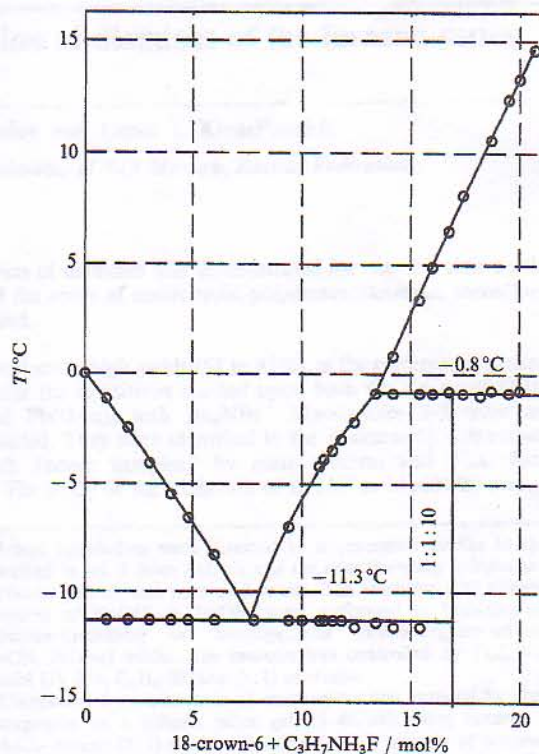


Figure 1 Section of the tertiary system 18-crown-6–C₃H₇NH₃F–H₂O with constant molar ratio of 18-crown-6 to C₃H₇NH₃F of 1:1 and variable water content.