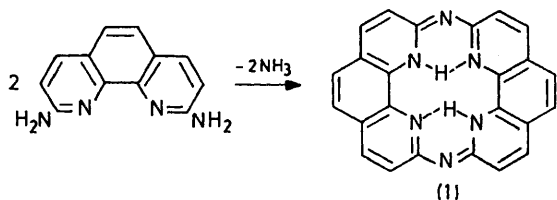


Preparation of Macrocyclic Compounds by Thermal Dimerization of 1,10-Phenanthroline Derivatives.

By Shojiro Ogawa, Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo, Japan

An efficient non-template synthesis of a new macrocycle, a conjugated tautomer of 1,14:7,8-diethenotetrapyrido-[2,1,6-*cd*:2',1',6'-*gh*:2'',1'',6''-*jk*:2''',1''',6'''-*na*][1,4,8,11]tetra-azacyclotetradecine (3), is described. The thermal behaviour of several disubstituted 1,10-phenanthrolines towards dimerization is studied by use of differential thermal analysis and thermogravimetric analysis, and some spectroscopic properties of the macrocycles produced are described.

AZAMACROCYCLIC systems have been intensively investigated in attempts to correlate their electronic properties and reactivities with those of polypyrrolic macrocycles such as porphyrins and corroles. Although a number of methods have been developed for the preparation of azamacrocyclic systems, non-template preparations of free macrocycles usually have the disadvantage that the method gives only low yield of the desired products.¹ We have recently reported a synthesis of a conjugated tautomer of a diethenodipyridohexa-azacyclotetradecine by condensing 2,9-diamino-1,10-phenanthroline with a 2,9-dihalogeno-1,10-phenanthroline in the presence of



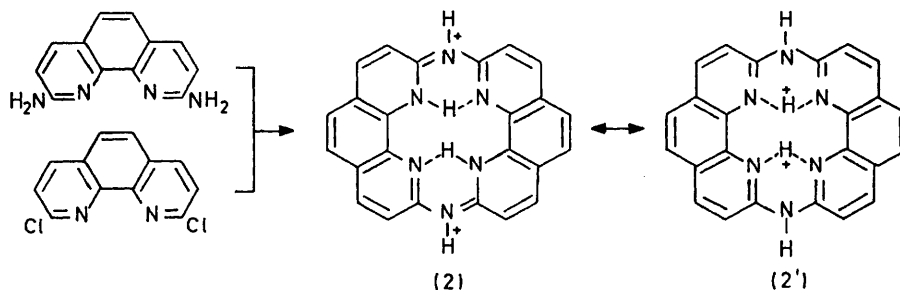
alkali in nitrobenzene, and its behaviour as a ligand.² 2,9-Diamino-1,10-phenanthroline alone also gave a cyclic dimer when heated without solvent. We describe here the thermal behaviour of several disubstituted 1,10-phenanthrolines, leading to the formation of a new macrocycle. The study was conducted by use of

evolution of ammonia. These needles were shown to be the hexa-aza-macrocyclic (1). The reaction was studied by DTA and TGA.

A thermogram of DAP shows a melting endotherm at 292 °C, followed by exothermic macrocycle formation at 306 °C and a small endothermic peak at 326 °C. The TGA curve consists of two continuous steps, which might be interpreted in terms of a two-step deamination-condensation. The weight loss in the range 290–330 °C corresponds to 1 mol of ammonia per mol of DAP.

The thermogram for an equimolar mixture of DAP and 2,9-dichloro-1,10-phenanthroline (DCP) shows an endotherm at 224 °C and a complex exotherm beginning at 230 °C with a peak at 280 °C. The TGA curve shows no substantial weight decrease. This implies that cross-condensation between DAP and DCP rather than self-condensation of DAP occurs. When an equimolar mixture of DAP and DCP was heated at 300 °C, needles separated from the melt with slight evolution of gas. Analysis showed that the needles were the dihydrochloride of the hexa-aza-macrocyclic (2).

This salt (2) is moderately soluble in water. The free base (1) was obtained as a precipitate by treating the aqueous solution with alkali. The i.r. spectrum of the free base (1) shows bands at 2780 and 900 cm⁻¹, assigned to stretching and out-of-plane deformation



differential thermal analysis (DTA), thermogravimetric analysis (TGA), and spectroscopy.

When 2,9-diamino-1,10-phenanthroline (DAP) was heated slightly above its m.p., the formation of needle crystals was observed just after melting, with vigorous

N-H vibrations, which disappear on N-deuteration. The ν_{NH} value is much lower and the δ_{NH} value much higher than those of porphyrins (near 3310 cm⁻¹ and between 680 and 675 cm⁻¹, respectively³). This may be explained in terms of strong intramolecular hydrogen bonding. The salt (2) shows a very intense N-H stretching band at 2780 cm⁻¹; this high frequency in

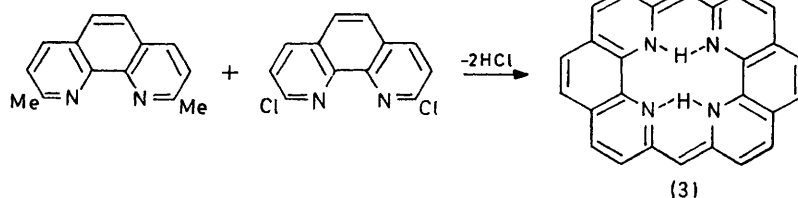
¹ J. J. Christensen, D. J. Eathough, and R. M. Izatt, *Chem. Rev.*, 1974, **74**, 353.

² S. Ogawa, T. Yamaguchi, and N. Gotoh, *J.C.S. Perkin I*, 1974, 976.

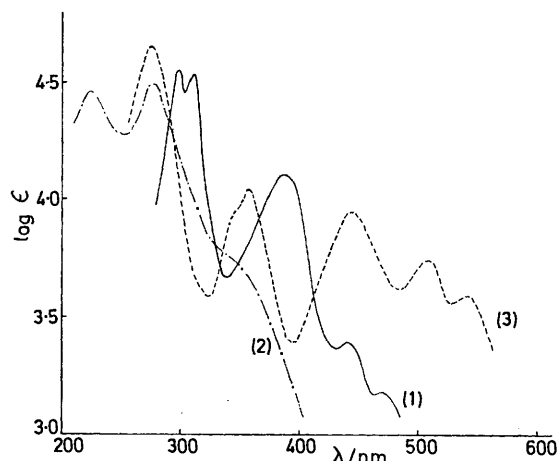
³ W. S. Caughey, J. O. Alben, W. Y. Fujimoto, and J. L. York, *J. Org. Chem.*, 1966, **31**, 2631.

comparison with pyridinium salts ($2\ 325\text{--}2\ 500\ \text{cm}^{-1}$)⁴ may be due to a contribution from the resonance structure (2'), strengthening the outer N-H bond. The fact that the N-H out-of-plane bending band at $910\ \text{cm}^{-1}$ is very weak supports this idea. The ^1H n.m.r. spectrum of the free base in trifluoroacetic acid [in which it is assumed that the compound is present as the dication (2)] shows that the inner NH protons are abnormally deshielded ($\tau -8.5$); in other words these protons are very acidic and the contribution of (2') is important. Since the amine bridge structure (2') is less effectively electron-delocalized than imine bridge structure (1), a hypsochromic shift is expected in the u.v. spectrum of the salt relative to the free base (1); this is in fact observed (see Figure).

The ease of cyclisation of DAP to the hexa-aza-macrocycle led us to examine the possibility of co-cyclisation of 2,9-dimethyl-1,10-phenanthroline (DMP) and DCP to give a methine-bridged tetra-aza-macrocycle. However, our attempts to condense DMP with DCP in solution were unsuccessful. Nevertheless, a thermogram of an equimolar mixture of DMP and DCP shows endotherms at 118 and 193 °C and a distinct



exotherm at 269 °C. The TGA curve shows weight loss at 45–120 °C corresponding to 0.5 mol of water per



Electronic spectra of the hexa-aza-macrocycle (1) in chloroform, the tetra-aza-macrocycle (3) in methanol, and the hexa-aza-macrocycle dihydrochloride (2) in water

mol of DMP hemihydrate, and another weight loss at *ca.* 250 °C. The second weight loss corresponded to 2 mol of hydrogen chloride per mol each of DMP and DCP. This suggested that an equimolar mixture of DMP and DCP would give a macrocycle (3) on heating at *ca.*

250 °C, and this was the case. The reaction gave a red product and its structure was confirmed as (3) by elemental analysis and spectral evidence.

The elimination of hydrogen chloride in this reaction is in contrast to the reaction of DAP and DCP, which shows little weight loss on the exothermic reaction. The mass spectrum of the product shows the molecular ion at $m/e\ 384$ and also an intense doubly charged molecular ion at $m/e\ 192$. The ^1H n.m.r. spectrum could not be determined owing to solubility problems.

In marked contrast to the hexa-aza-macrocycle (1), which gives a yellow solution in chloroform, the tetra-aza-macrocycle (3) gives an intensely red solution. The electronic spectrum of (3) is qualitatively similar to that of (1) (see Figure). The bathochromic shift with respect to the hexa-aza-macrocycle, might be due to more effective electron delocalization in the former.

In the i.r. spectrum of (3) the ν_{NH} band is too weak to be observed. Bands at 1 280 and 960 cm^{-1} were assigned to N-H in-plane and out-of-plane deformation, respectively, on the basis of their disappearance on deuteration [effected by treating (3) with D_2SO_4 and then with K_2CO_3 in D_2O]. The tetra-aza-macrocycle (3) is stable in

the dark, but the absorption spectrum changed significantly when the solution was exposed to light. The photochemistry of this system will be reported in a forthcoming paper.

EXPERIMENTAL

Thermal analysis was conducted by using a Thermoflex 8021 instrument (Rigaku Denki) under nitrogen at a heating rate of $5\ \text{°C}\ \text{min}^{-1}$. Sample size was in the range 83.0–200 mg. Equimolar proportions of reactants were mixed thoroughly in a mortar. N.m.r. spectra were determined with a Hitachi R-20A instrument operating at 60 MHz, with tetramethylsilane as internal reference. U.v. and visible spectra were measured with a Union Giken SM 401 spectrophotometer. I.r. spectra were measured with a Hitachi-Perkin-Elmer 125 spectrophotometer. Mass spectra were obtained by direct insertion into the ion source of a Hitachi RMU-6D instrument.

2,9-Dichloro- and 2,9-diamino-1,10-phenanthroline were prepared by published methods.² 2,9-Dimethyl-1,10-phenanthroline hemihydrate was obtained commercially (Tokyo Kasei Kogyo Co., Tokyo), and was used without further purification.

Dihydrochloride of 1,14 : 7,8-Diethenotetrapyrido[2,1,6-de : 2'1',6'-gh : 2''1'',6''-kl : 2'''1'''',6'''-na][1,3,5,8,10,12]-hexa-azacyclotetradecine (2)—2,9-Diamino-1,10-phenanthroline (42 mg) and 2,9-dichloro-1,10-phenanthroline (50 mg)

⁴ L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' 2nd edn., Wiley, New York, 1958, p. 260.

were mixed thoroughly in a mortar and heated in an atmosphere of nitrogen. Yellow needles began to separate at 230 °C. After solidification was completed, heating was continued at 260 °C for 1 h. The product was washed with chloroform, giving yellow *needles* (77 mg, 83.7%) (Found: C, 63.4; H, 3.6; N, 18.8. $C_{24}H_{16}Cl_2N_6$ requires C, 62.8; H, 3.5; N, 18.3%). The free base (1), identical with the sample already prepared,² was obtained by dissolving the salt (50 mg) in water (100 ml) and adding aqueous ammonia (*d* 0.88; 5 ml) in water (10 ml).

Conjugated Tautomer of 1,14:7,8-Diethenotetrapyrido-[2,1,6-cd:2',1',6'-gh:2'',1'',6''-jk:2''',1''',6'''-na][1,4,8,11]tetra-azacyclotetradecine (3).—A mixture of 2,9-dimethyl-

1,10-phenanthroline hemihydrate (83 mg) and 2,9-dichloro-1,10-phenanthroline (70 mg) was heated to 260 °C in an atmosphere of nitrogen. After the vigorous evolution of hydrogen chloride ceased, heating was continued at 260 °C for a further 4 h. The solidified mixture was washed with acetone, giving red *crystals* (101 mg, 93.6%) (Found: C, 80.85; H, 4.45; N, 14.75. $C_{26}H_{16}N_4$ requires C, 81.2; H, 4.2; N, 14.6%).

I thank Mr. K. Kataoka for experimental assistance and Professors J. Kumanotani and S. Shiraishi for comments.

[6/542 Received, 22nd March, 1976