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Synthesis of a Novel Macrocyclic Compound and of Its Copper Complex

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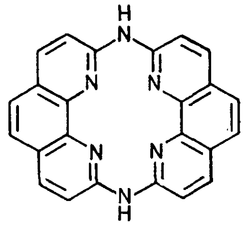
Summary Condensation of 2,9-diamino- and 2,9-dichloro-1,10-phenanthroline gave a novel macrocyclic ligand in excellent yield.

Many azaporphin derivatives have been synthesized[1] and aromatic macrocycles related to porphins containing furan and thiophen rings in addition to pyrrole have been prepared recently.[2] For a comparative study of porphyrin and phthalocyanin analogues, we have synthesized a novel conjugated macrocyclic compound containing 1,10-phenanthroline nuclei.

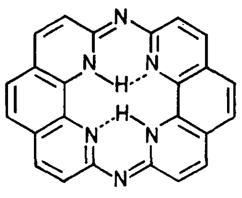
The macrocycle (I) consists of two 1,10-phenanthroline nuclei bridged by two NH groups and might be considered as a diquinolylamine derivative, similar to the basic components of many cyanine dyestuffs. It has been suggested that the acidity of the central amine bridge in diquinolylamine leads to the corresponding tautomeric species.[3] We now report the syntheses of compound (I) and also its metal complexes, by the condensation of 2,9-dichloro- and 2,9-diamino-1,10-phenanthroline.

The phenanthroline (IV)[4] was treated with Me_2SO_4 to give (V), m.p. 208°,† which was oxidized with potassium ferricyanide and NaOH to afford the phenanthrolinone (VI), m.p. 148—150° (90%). Treatment of (VI) with PCl_5 in $POCl_3$ gave (VII), m.p. 250° (90%). Ammonolysis of (VII) in a mixture of phenol and acetamide by bubbling dry ammonia gas at 160° gave (VIII) (90%), m.p. 273—275°. Ammonolysis at <160° gave a mixture of the mono- (IX) and diamino-compound (VIII).

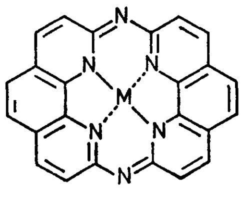
(VII) and (VIII) were heated in nitrobenzene in the presence of K_2CO_3 as acid acceptor to give the cyclic product in 94% yield. It was very insoluble in most organic solvents but could be recrystallized from quinoline, giving yellow needles, m.p. >450°. It sublimed without decomposition at 400° and 10^{-4} mmHg.



(I)



(II)



(III)

The structure of the product was verified by its mass spectrum: *m/e* 386 (M^+) and 193 (M^{2+}). In contrast to the spectrum of (VIII) the M^+ and M^{2+} peaks were much

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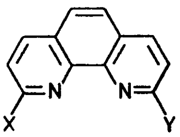
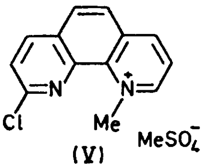
† Satisfactory C, H, and N analyses were obtained for all new compounds described.

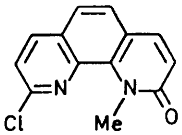
more intense than those of the fragment ions (<2% of M^+ and M^{2+}). This minor fragmentation seems to be due to aromatic stability. Hoffman[5] reported that the molecular ion of porphyrin was strong and that a relatively strong doubly charged ion spectrum was observed in most cases. The n.m.r. spectrum also supports its cyclic structure [δ ($CF_3{\cdot}CO_2H$) 8·07 (4H, d), 8·35 (4H, s), and 9·00 (4H, d) p.p.m.] and was similar to that of 2,9-disubstituted 1,10-phenanthroline. No N–H absorption was observed, presumably owing to exchange with the solvent. Although it is uncertain whether this cyclic compound exists as (I) or (II) in solution from its n.m.r. or i.r. spectrum because of its limited solubility in neutral organic solvents, its solid-state i.r. spectrum (KBr disc) shows that the solid exists in form (II). It showed no absorption in the normal N–H stretching region, but a broad absorption at *ca.* 2780 cm^{-1} indicated the formation of intramolecular N–H···N bridges. Intermolecular hydrogen bonding of (I) is excluded because carbazole, for example, shows no absorption of ν_{NH} at such low frequencies. An N–H stretching absorption at 2780 cm^{-1} is very rare, but it has been reported that imidazole shows no free N–H band at high concentration, but an absorption due to polymer appears near 2800 cm^{-1}. Zimmerman[6] has shown that these bands arise from very strong hydrogen bonding. Heating of (VII) and (VIII) in the presence of $CuCl_2$ and K_2CO_3 in nitrobenzene followed by recrystallization from quinoline gave tan yellow needles of the copper complex (III; M = Cu) (94%), whose structure was supported by its mass spectrum [highest peaks at *m/e* 447 and 449 (M^+) and M^{2+} peaks at 223·5 and 224·5 with abundance ratios consistent with the isotopic abundance of copper]. (III; M = Cu) was also prepared by heating the cyclic product and $CuCl_2$ in nitrobenzene.



(IV ; X = Cl, Y = H)
(VII ; X = Y = Cl)
(VIII ; X = Y = NH$_2$)
(IX ; X = NH$_2$, Y = Cl)



(V)



(VI)

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