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The chemistry of cycloocta [2,1-b:3,4-b'] dipyridine and its derivatives

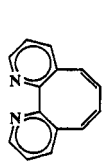
Xiu Chun Wang and Henry N.C. Wong*

Department of Chemistry, The Chinese University of Hong Kong,
Shatin, New Territories, Hong Kong.

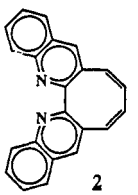
Abstract - Compounds containing dipyridine, diquinoline or 1,8-dinaphthyridine nucleus fused to the molecular framework of cyclooctatetraene were synthesized. The X-ray analysis of cycloocta[2,1-*b*:3,4-*b*']diquinoline reveals that the molecule contains a C_2 axis. The energy barriers for ring inversion of these compounds and their derivatives were studied by various methods including variable temperature CD study of their chiral forms, proton NMR measurements, MNDO calculation as well as mutarotation study. Metal complexes were prepared for these compounds. The structures of these complexes were studied by X-ray crystallography whose results demonstrate that the cyclooctatetraene rings of the ligands have been flattened after metal coordination.

INTRODUCTION

One of the major chemical advances in recent years has been the use of metal complexes containing 2,2'-diazabiaryl ligands (ref.1) because they have found applicability in the domains of host-guest chemistry (ref.2), photochemistry (ref.3), biochemistry (ref.4) and organic synthesis (ref.5). In light of this fact, it is thus important to design and to synthesize new 2,2'-diazabiaryl ligands in order to fully understand their coordination chemistry. Of great interest is the 2,2'-diazabiaryl ligands belonging to the C_2 symmetry point group because they might be capable of being resolved into their corresponding antipodes and thus might serve as optically active ligands. Noteworthy is that the chain-length of the annelating bridge of a series of 3,3'-annelated-2,2'-diquinolines manipulates the relative orientation of the two quinoline rings and therefore influences the geometry of the chelating envelope (ref.6). In this connection, fusion of a cyclooctatetraene nucleus to 2,2'-diazabiaryl ligands will result in novel systems containing an unsaturated annelating bridge with full retention of the required C_2 symmetry. We have now synthesized cycloocta[2,1-*b*:3,4-*b*']dipyridine 1, cycloocta[2,1-*b*:3,4-*b*']diquinoline 2 and cycloocta[2,1-*b*:3,4-*b*']di[1,8]naphthyridine 3. In conjunction with our long-standing quest for novel planar eight-membered ring compounds (ref.7), it is envisaged that the metal complexes of 1,2 and 3 might possibly comprise such coplanar rings. On the other hand, optical resolution of 1,2 and 3 might provide useful chiral ligands with C_2 symmetry.



1



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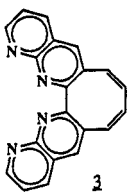
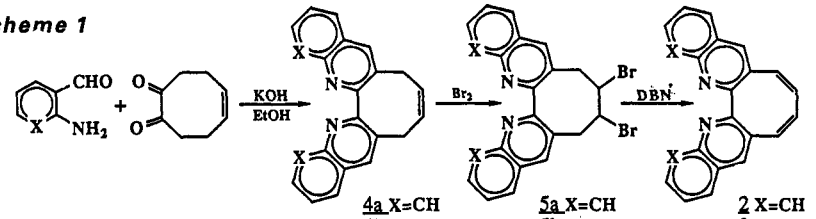


3

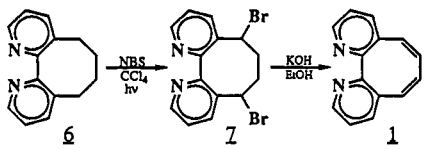
SYNTHESIS OF THE LIGANDS

Friedlander's method (ref.6,8,9) was employed to construct the diquinoline and dinaphthyridine skeleton of 2 and 3 [Scheme 1] (ref.10). The realization of compound 1 was however not trivial. In order to achieve the synthesis of 1, we prepared the known compound 6 (ref.11). Radical initiated bromination of 6 resulted in the isolation of the dibromide 7. Subsequent double dehydrobromination converted 7 to 1 [Scheme 2]. Figure 1 shows the molecular structure of 2, which has been determined by X-ray crystallography (ref.10). It is noteworthy that the structure of 2 by all means belongs to the C_2 symmetry point group. Compounds 1 and 3, whose structures are in principle similar to 2, should also belong to the same symmetry point group.

Scheme 1



Scheme 2



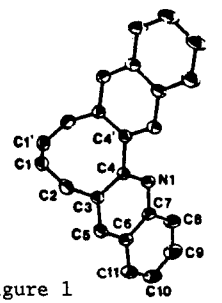
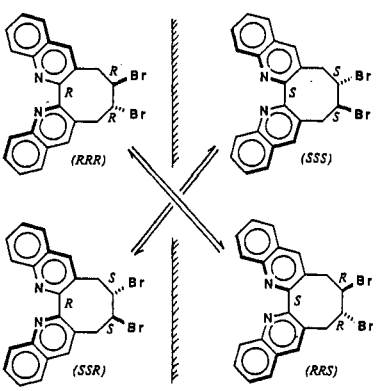


Figure 1

DETERMINATION OF ENERGY BARRIERS FOR RING INVERSION

The dibromide 5a should have two diastereomeric forms, namely, the (*RRR/SSS*) form and the (*SSR/RRS*) form. Each of this diastereomeric form should contain two enantiomers as illustrated in Scheme 3 (ref.12,13). These diastereomeric forms are interconvertable at elevated temperature through a mutarotation process (ref.12). In order to study the ring inversion process in association with mutarotation, it is important to isolate the diastereomeric mixture into the two corresponding pure diastereomers. Consequently, the separation of the diastereomers was achieved by thin layer chromatography, albeit in only very poor yield. Another way in which the (*RRR/SSS*) diastereomeric form of 5a could be prepared would be by the bromination of 4a in THF-H_2O at low temperature [Scheme 4]. The stereochemistry of this (*RRR/SSS*) compound was assigned by proton NMR spectrometry [Figure 2]. Figure 3 shows the proton NMR spectrum of the diastereomeric mixture. The most significant absorption peaks in Figure 2 and 3 are those due to the methine proton of 5a, which show absorptions at δ4.54(d) for the (*RRR/SSS*) diastereomer and δ5.10(d) for the (*SSR/RRS*) diastereomer [Figure 2,3]. Upon heating of the (*RRR/SSS*) diastereomer 5a (with methine absorption peaks at δ4.54 only) to 140°C, mutarotation process presumably took place, which can be confirmed by cooling of the NMR sample to room temperature. Consequently, the spectrum shows two absorption peaks in the ratio of approximately 1:1, which are due to the signals of the methine protons of the (*RRR/SSS*) and (*SSR/RRS*) mixture [Figure 4]. The coalescence temperature (T_c) has been found to be 110°C and the corresponding $\Delta G^{\neq}_c$ is therefore 22 kcal/mol.

Scheme 3



Scheme 4

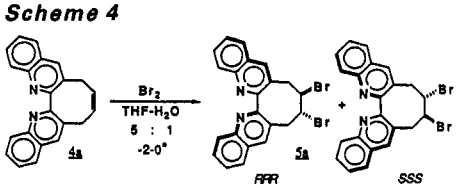


Figure 2

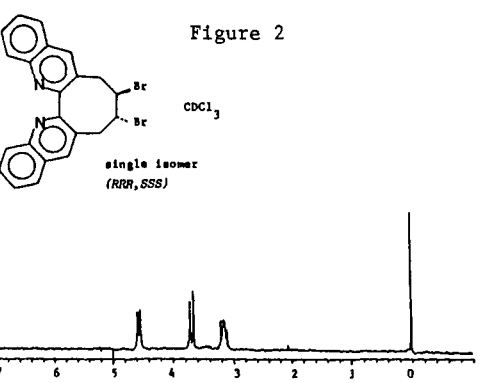


Figure 3

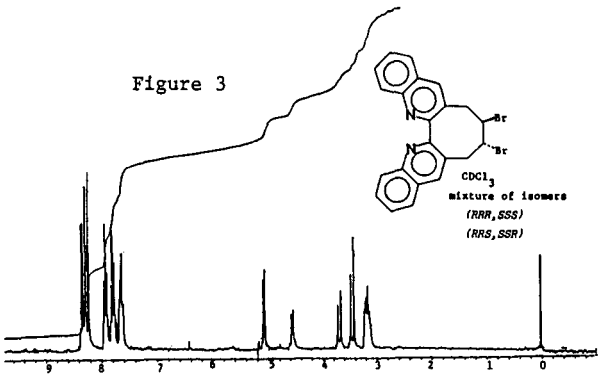
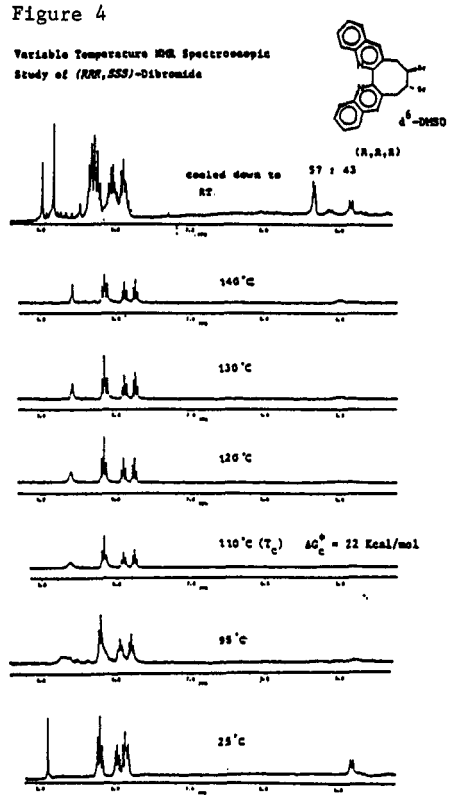


Figure 4



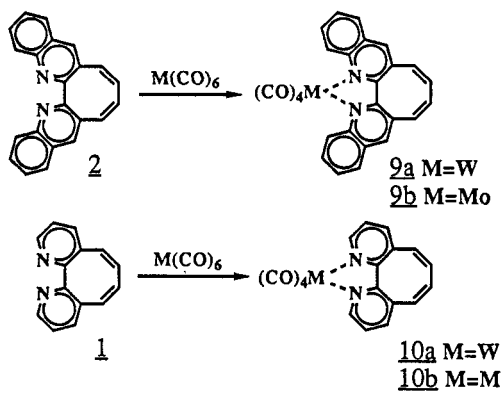
In collaboration with Prof. Jan Sandström of University of Lund, Sweden, we were able to separate the two enantiomers of compound 2 by means of column chromatography on triacetylcellulose (ref.14). Variable temperature CD study reveals that the energy barrier of the racemization of 2 is approximately 25 kcal/mol (ref.14).

MNDO calculations (ref.15) suggest an amount of 33 kcal/mol for the energy difference between the C_{2v} and the C_2 symmetry point group of 1 (ref.16). This energy barrier of 1 is apparently higher than that of 2. The reason for this can be attributed to the extra benzo-fusion of diquinoline as compared with dipyridine. We believe that at the transition states the conjugative stabilization of the coplanar diquinoline should be greater than that of the coplanar dipyridine.

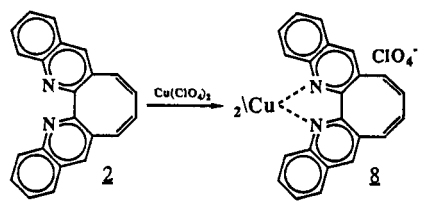
SYNTHESIS OF METAL COMPLEXES

Due to the sparing solubility of compound 3 in common organic solvents, it is rather difficult in practice to prepare its metal complex. In addition to this disadvantage, compound 3 possesses of four coordination sites which can in principle complicate the complex formation process. We shall therefore restrict our attention here only on the coordination chemistry of compounds 1 and 2. In order to test the practicability of 1 and 2 as chelating ligands and to observe their conformational change due to metal complexation, we undertook the preparation of the copper(I) perchlorate complex of 2 (ref.10)[Scheme 5], as well as tetracarbonyl tungsten and tetracarbonyl molybdenum complexes of 1 and 2 [Scheme 6].

Scheme 6



Scheme 5



The structure of the copper(I) perchlorate complex 8 and the tetracarbonyl molybdenum complex 10b are unequivocally established by X-ray crystallography (ref.10,17)[Figure 5,6] In each organic ligands of 8 and 10b, although the cyclooctatetraene moieties take the usual "tub" conformation, it is clear that their N-C-C-N torsion angles as well as their dihedral angles between the two olefinic bonds are smaller than those of the free ligands, such as 2 [Figure 7]. The much smaller dihedral angles of the complexes thus indicate a considerable flattening of the cyclooctatetraene rings through metal complexation. In support of this we have very recently discovered that the proton NMR signals of the olefinic protons of 10a absorb at relatively higher field than those of the free ligand 1 [Figure 8]. This phenomenon might be caused by the possible paratropic property of the ligand of 10a, which is reminiscent of a nearly planar $4n\pi$ systems.

Figure 5

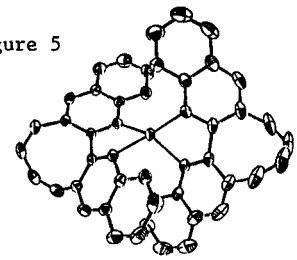


Figure 6

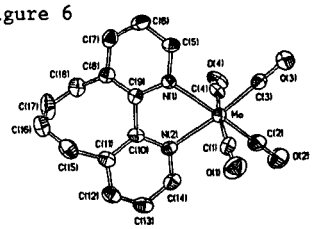


Figure 7

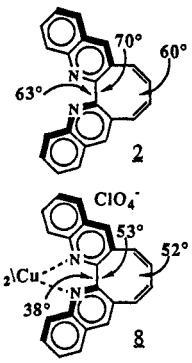
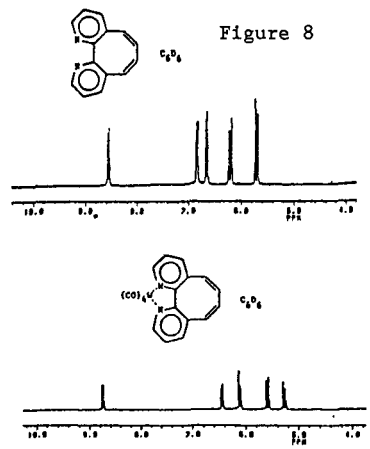


Figure 8



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17. Study undertaken by Prof. T.C.W.Mak, Department of Chemistry, The Chinese University of Hong Kong.