

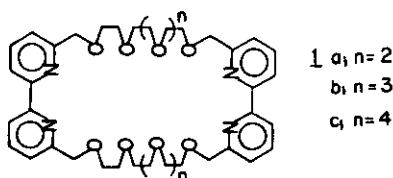
DIPYRIDINE CROWN ETHERS. SYNTHESIS AND CONFORMATIONAL ASPECTS
OF A TETRAAZADITHIA-18-CROWN-6 ANALOG.[†]

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Abstract. The synthesis and conformational analysis by VTNMR of a bis-dipyridylthia-18-crown-6-ether (4) are described. The energy barrier of inversion ΔG^\ddagger is 10.4 kcal/mol and measures a transverse isomerization inversion process.

The chemistry of macrocyclic molecules possessing subheterocyclic rings within the crown ether framework has received considerable attention in past few years¹. During our studies related with the synthesis and complexation of 2,2'-dipyridine crown ethers, e.g., 1, we observed that the conformational preferences of these molecules are dictated by the size of the bridge connecting the two dipyridine subunits^{1b,2}. As part of our continuing investigation in the area of



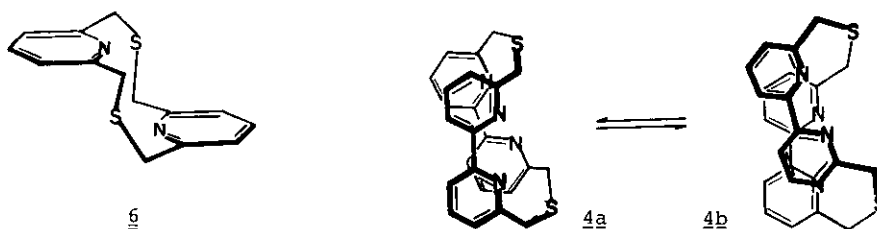
binuclear complexes, we synthesized macrocycles in which the two dipyridine units are held as close to one another as possible. In this communication, we wish to report the synthesis and NMR study of 4, which is an analog of 18-crown-6 as well as a novel [3:3]dithiametacyclophane.

The 6,6'-dichloromethyl-2,2'-dipyridine^{1c} (2) was treated with thiourea followed by base hydrolysis to provide the dithiol 3⁴, as a white solid: mp 107-108°C (hexane); NMR (CDCl₃) δ 2.1 (t, -SH, J = 8.0Hz, 1H), 3.92 (d, -CH₂SH, J = 8.0 Hz, 2H), 7.35 (d, 5-Pyr-H, J = 7.5Hz, 1H), 7.78 (t, 4-Pyr-H, J = 7.5Hz, 1H), 8.37

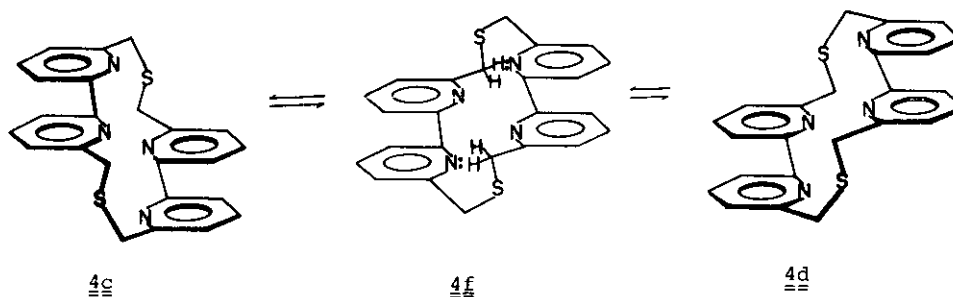
[†]Dedicated to Professor Tetsuji Kametani on the occasion of his retirement.

macrocycle is calculated to be 10.4 kcal/mole. This high energy barrier for the transverse isomerization process⁷ in 4 is in contrast to the case of the related pyridine dithiacyclophane 6, in which the inversion of the central ring is found to be too fast for dynamic NMR.⁸

Examination of the molecular models of 4 reveals a number of probable conformations, in which the dipyridyl moiety can exist in an anti conformation;



however, these anti structures can be disregarded on the basis of the chemical shift for the 3-pyridine hydrogen. Conformations 4a and 4b will account for the upfield shift of all aromatic hydrogens but they do not account for a high barrier



for the ring inversion in 4. Two chair conformations, 4c and 4d, are possible for 4, which must interconvert via a near planar, strained conformation 4f. In this transitional conformation the two α -methylene hydrogens are thrust into the immediate proximity of the pyridine N-electrons. This unfavorable interaction during the interconversion of 4c and 4d may account for a high $\Delta G^\ddagger_{\text{inversion}}$ observed for 4, as compared to similar systems.

We are currently investigating the x-ray crystal structure of 4, its conversion into the corresponding [2:2]-metacyclophane, and the complexation behavior of these 18-crown-6 analogs.

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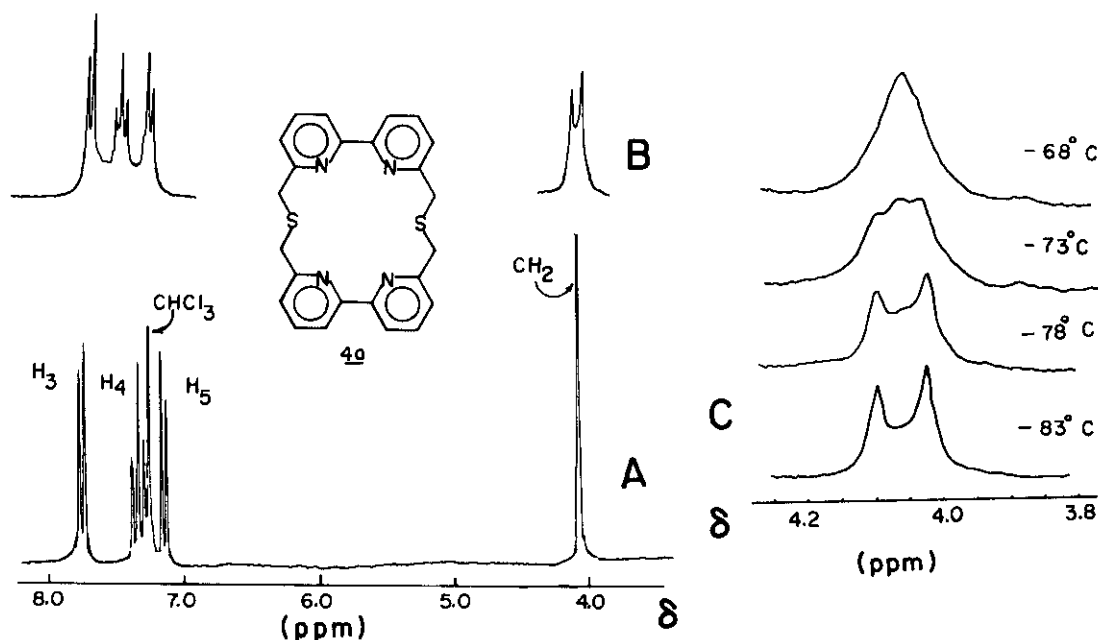


Figure 1. A. 200 MHz NMR of 4 in CDCl_3 . B. NMR spectrum at 190°K .
C. VT-NMR spectrum of 4 methylene region.

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