

## Isolation and Conformation of a Fully Unsaturated Nitrogen Analogue of 18-Crown-6

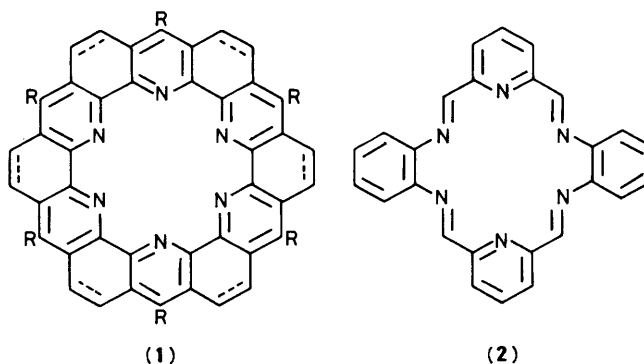
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Reaction of the potassium complex of a hexa-aza macrocycle with 18-crown-6 affords the free ligand, which undergoes a conformational change upon complexation, according to spectroscopic and crystallographic studies.

The cryptands<sup>1</sup> and spherands<sup>2</sup> were successfully designed to improve upon useful alkali metal binding properties (selectivity and complex stability) exhibited by crown ethers.<sup>3</sup> These more rigid, encapsulating hosts suffer, however, from lower rates of complex equilibration, reducing their utility in separation processes. In principle, the open-face design of a rigidly planar host would allow rapid access of metal ions to the molecular cavity. Derivatives of hexa-azakekulene (1)<sup>4</sup> are of interest as reversible potassium receptors of this type, and we have recently demonstrated that a hexa-aza macrocycle model system (2) forms a stronger potassium complex than that of 18-crown-6.<sup>5</sup> We now report the isolation of metal-free (2) and present evidence for a remarkable change in conformation that occurs during complex formation.

Although numerous metal complexes of (2) are known,<sup>5,6</sup> isolation of the free ligand has not been reported. Our synthesis of metal-free (2) (Scheme 1) begins with the Sr<sup>II</sup> templated condensation of *o*-phenylenediamine with pyridine-2,6-dicarboxaldehyde.<sup>6</sup> We have found that if strontium trifluoromethanesulphonate (triflate) is substituted for strontium perchlorate, the complex (2)·Sr<sup>2+</sup> is obtained in 57% yield after recrystallization. As previously described for the corresponding perchlorates,<sup>5</sup> the potassium triflate complex (2)·K<sup>+</sup> may be obtained by treating (2)·Sr<sup>2+</sup> with an excess of potassium fluoride. After removal of precipitated strontium salts, (2)·K<sup>+</sup> is isolated from the filtrate and recrystallized from acetonitrile-benzene (74%).<sup>†</sup> Even though host (2) competes successfully with 18-crown-6 for potassium,<sup>5</sup> (2) is liberated by precipitation from an aceto-

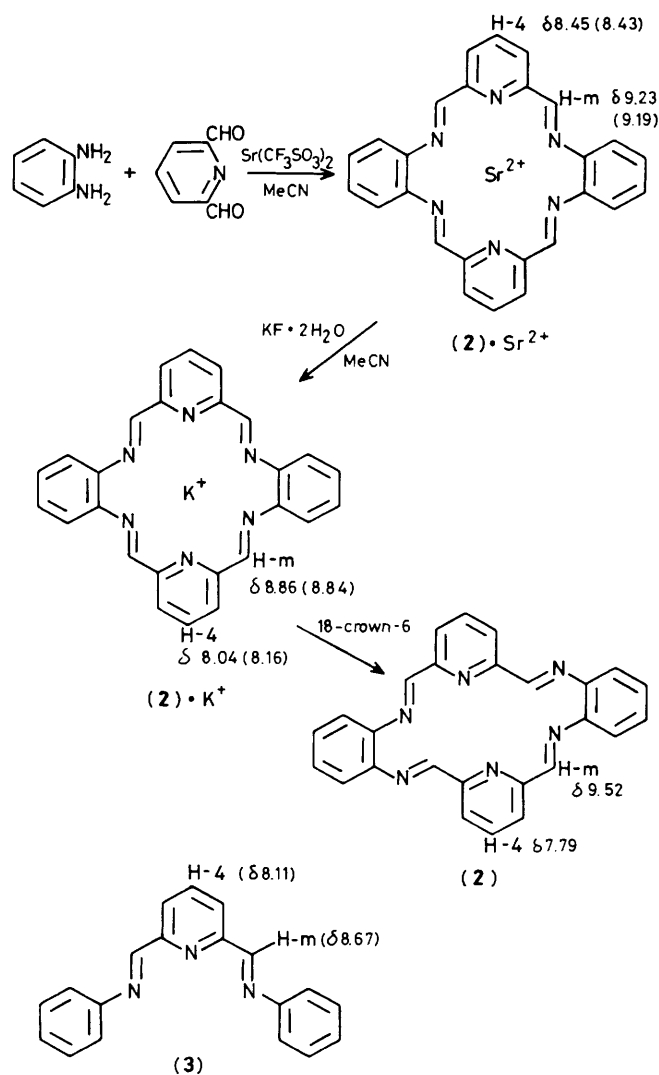


nitrile solution of 10:1 (molar ratio) 18-crown-6/(2)·K<sup>+</sup>. Stoichiometric [2.2.2]cryptand may also be employed in a more expensive variation of this experiment.

Free ligand (2) has very low solubility in all common organic solvents and is insoluble in water. Crude (2) may be recrystallized from 2:1 (v/v) pyridine/benzene, affording analytically pure yellow prisms in 58% yield. Single crystal X-ray diffraction<sup>‡</sup> revealed that (2) adopts the conformation

<sup>‡</sup> Crystal data for (2): C<sub>26</sub>H<sub>18</sub>N<sub>6</sub>, *M* = 414.47, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 12.771(2), *b* = 15.058(2), *c* = 11.087(2) Å, β = 109.73°, *U* = 2007 Å<sup>3</sup>, *D*<sub>c</sub> = 1.372, *D*<sub>m</sub> = 1.333 g cm<sup>-3</sup>, *Z* = 4. The structure was solved by direct methods using 709 of the 2404 reflections measured. Final refinement after fixing hydrogen positions using standard geometries gave *R* = 0.04. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

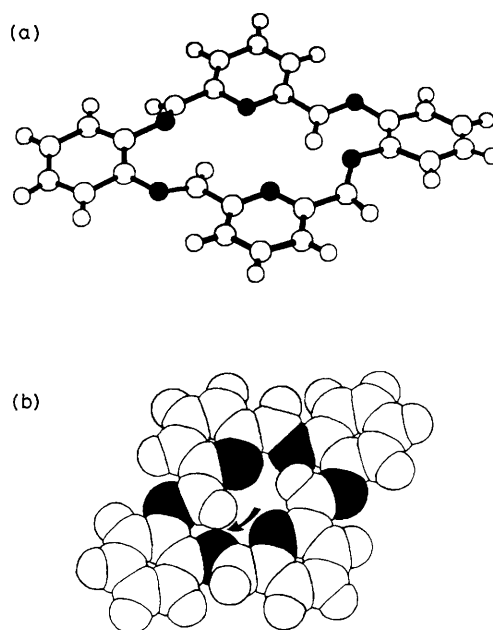
<sup>†</sup> Microanalytical data (C, H, N, K) for (2)·K<sup>+</sup> were consistent with the formula (2)·KCF<sub>3</sub>SO<sub>3</sub>·½C<sub>6</sub>H<sub>6</sub>·½H<sub>2</sub>O.



**Scheme 1.** 300 MHz  $^1\text{H}$  N.m.r. chemical shifts in  $[\text{}^2\text{H}_5]\text{pyridine}$  (chemical shifts in  $[\text{}^2\text{H}_6]\text{dimethyl sulphoxide}$  given in parentheses).

depicted in Figure 1. There is a striking contrast between the roughly circular macrocycle conformation observed in complexes of (2)<sup>6</sup> and the approximately elliptical conformation of the free ligand. The plane projections in Scheme 1 demonstrate that these two conformations are interconverted by nearly 180° rotations (flipping) of two opposite imine groups. Coplanarity of these imine groups with the adjacent aromatic rings is opposed by repulsion between the imine methine hydrogen atoms and two nitrogen atoms (H...N distance, 2.1 Å, using calculated H position). One of these contacts is indicated in a space-filling representation (Figure 1b), using reduced van der Waals radii.

The conformational situation in (2) is strikingly similar to that observed in 18-crown-6. Both in nonpolar solvents<sup>7</sup> and in the solid state,<sup>8</sup> 18-crown-6 exhibits a  $C_2$  conformation in which two oxygen dipoles are directed away from the molecular centre and two hydrogen atoms fill the 'cavity'. Complexation with potassium ion is accompanied by C—O and C—C bond rotation, resulting in  $D_{3d}$  symmetry.<sup>9</sup> In the crystal structure of (2), the cavity volume and dipole-dipole repulsions are similarly reduced by a flipping motion of two ligand groups. In this case, however, the deviation from planarity



**Figure 1.** (a) Ball-and-stick representation of crystal conformation of (2) (all imine hydrogen atoms below best plane); (b) space-filling representation of (2) (imine hydrogens above best plane; H...N contact indicated; radii: H 0.9, N 1.2 Å).

results in approximate  $C_2$  symmetry. Despite expected non-bonded repulsions, we believe the crystal conformation of (2) to be a reasonable energy minimum because it should be stabilized by extensive conjugation (ring/imine dihedral angles: 11–33°).

Evidence for a conformational change between free and complexed (2) is provided by proton n.m.r. data summarized in Scheme 1. The n.m.r. resonance of a proton bonded to C-4 of a pyridine ring is known to be a sensitive probe of electron density in pyridine salts and complexes with Lewis acids.<sup>10</sup> Relative to the model compound (3), the  $\text{K}^+$  and  $\text{Sr}^{2+}$  complexes of (2) display the expected downfield shift of H-4 as a function of decreasing electron density. The imine methine (H-m) chemical shifts display this same trend. Metal-free (2) is the anomalous member of this series, since H-4 resonates at even higher field than in n.m.r. model (3) and H-m resonates at even lower field than in (2)· $\text{Sr}^{2+}$ . If the conformation of (2) were identical in free and complexed forms, both H-4 and H-m would resonate at higher field in (2) than in (2)· $\text{K}^+$  and (2)· $\text{Sr}^{2+}$ . The results are consistent with a rapid equilibration between degenerate, unsymmetrical conformers resembling the solid-state conformer, since only one H-m resonance is observed for solutions of (2).§

We have shown that conformationally flexible (2) is not an ideal model for more rigid analogues, such as hexazacukelene (1), which would not have to pay the enthalpic cost of conformational reorganization during complexation. The poor solubility of (2) also suggests that if derivatives of (1) are to serve as functional hosts, then suitable substituents (R) must be present to solubilize the free ligand and its complexes.

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§ Solubility limitations determined the n.m.r. solvents (*cf.* Scheme 1) and hindered observation of low temperature  $^1\text{H}$  n.m.r. spectra of (2).

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*Added in proof:* An approach to unsubstituted hexazakekulene derivatives has appeared recently.<sup>11</sup>

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