

FACILE SYNTHESIS OF A NEW FAMILY OF CAGE MOLECULES

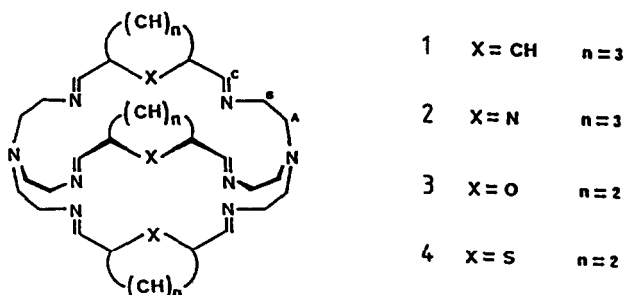
Debbie MacDowell and Jane Nelson*
The Open University, Milton Keynes, MK7 6AA.

Cyclic (2+3) Schiff-base condensation of the triamine tris(2-aminoethyl)amine with a range of dicarbonyls produces, in high yield, a new series of cage molecules.

Since their introduction by Lehn⁽¹⁾ in 1969, cryptating molecules have found many uses in the fields of molecular recognition, catalysis and transport. Thus, they may function as receptors capable of selective complexation of substrate species, as catalysts assisting a chemical transformation of bound substrates and as carriers allowing for passage of bound species through a membrane⁽²⁾. They show particular promise as enzyme models. The nature and disposition of donor atoms in the rigid cage may enhance the stability of unusual oxidation states in the coordinated transition metal ion⁽³⁾, while encapsulation may protect normally labile substrate species. It is hoped that this combination of circumstances may eventually lead to oxygen- and moisture-sensitive chemistry taking place in the protected cavity under ambient conditions⁽⁴⁾.

Normally, synthesis of the cryptating molecule presents a considerable challenge to the chemist. We have developed a simple one-pot synthesis which generates a new family of cryptands of considerable potential.

Treatment of the tripod amine tris(2-aminoethyl)amine in refluxing alcohol with the dicarbonyl compound isophthalaldehyde in stoichiometric ratio 2:3 resulted in the isolation of white crystals of product 1 in 47-56% yield.



This product analysed correctly for the cage molecule and exhibited no ν NH₂ or ν C=O frequencies in the infrared, but instead a medium strong ν C=N absorption showing

Schiff-base condensation to be complete. The base peak in the mass spectrum was the molecular ion at m/e 586. The ^{13}C spectrum in CDCl_3 was simple, with resonances at 56.1(t), 60.0(t), 127.5(d), 129.0(d), 132.3(d), 137.1(s) and 160.7(d) ppm from TMS. (Symbols in brackets referring to the multiplicity of the signal in the off-resonance spectrum: s = singlet, d = doublet, t = triplet.). These may be assigned to methylene carbons A and B, to the four phenyl carbons, and to the imino-carbon C, respectively. The ^1H nmr spectrum however, is complex and fluxional suggesting a fair degree of flexibility in the cage. An X-ray crystallographic structure determination of the compound is in progress(5).

Repetition of the reaction with 2,6-diformylpyridine or 2,5-diformylfuran in place of isophthalaldehyde gave, in \approx 60% yield, cage molecules 2 or 3 as characterised by ir, elemental analysis, and mass spectral molecular ion peaks. The thiophene-containing cryptand 4 was not obtained in the absence of metal, but formed easily by template synthesis on Ag(I) .

These syntheses clearly represent a valuable high-yield route to a new and adaptable family of cryptating molecules. They have the capacity to act as bi- or tri-nucleating ligands for transition metal ions, as well as receptors for polar or non-polar organic substrates, and in turn, possibly to promote reaction between these encapsulated reagents.

We are presently developing the range of cage molecules made available by this method: (a) by employing variously substituted aromatic dicarbonyls designed to influence polarity and water solubility and/or rigidity and hydrophobicity of the inner cavity, and (b) by hydrogenating the Schiff-base function to increase the chemical stability of the cage and alter the redox preferences of any coordinated metal ions.

The simple synthetic procedure described above thus promises to be of some importance in the developing field of supramolecular chemistry.

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References

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