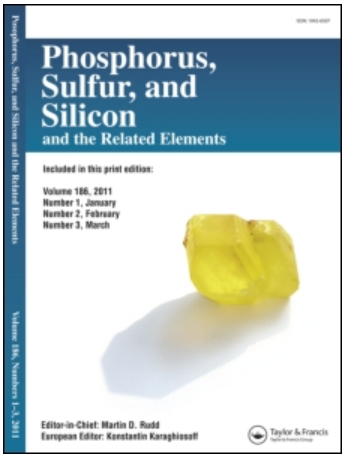

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Synthesis, Host Properties and Structure of Phosphorylated Cavitands

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New supramolecular phosphorus receptors with conformationally rigid structures were investigated. Tetraphosphonate-calix[4]resorcinarenes with long chain substituents on the resorcinolarene unit were synthesized in fairly good yields. The *all in (iiii)* stereoisomer was preferentially obtained. The phosphacavitands exhibit an extremely large affinity for metallic and ammonium cations, which is due to the complementary positioning of a "soft" lipophilic cavity and "hard" phosphorylated binding sites, leading to cooperative binding interactions. The formation of a thio-phosphorylated hemicryptophane, bearing a phosphotrihydrazone moiety, is also reported. It forms stable complexes with neutral aromatic guests and provides a novel synthetic approach to the design of new metallo-receptors.

Keywords: phosphorus ligands; cavitands; cation complexation; ditopic cavity

INTRODUCTION

The design of organized molecular architectures containing phosphorus moieties and exhibiting complexing properties is an area of considerable current interest. However, the introduction of phosphorus into supramolecular receptors with suitable binding properties still represents a synthetic challenge. Synthetic and structural restraints imposed by the phosphorus moieties need an improved control of the strategy used for the construction of these supramolecular receptors. Macrocyclic and polymacrocyclic phosphorus compounds have recently proved to be promising ligands for cationic species.[1] Further developments based on the chemistry of the calixarenes and cavitands, have led to the synthesis of rigid and highly preorganized phosphorus cavitands.[2] The cyclotriveratrylene and resorcarene (or resorcinolarene) units provided ideal starting material for the preparation of molecular cavities that

exhibited fascinating complexing properties.[3] Their use in the design of rigid phophorus ligands is the purpose of the work presented herein.

SYNTHESIS OF A THIOPHOSPHORYLATED HEMICRYPTOPHANE

Cryptophanes and hemicryptophanes represent a family of molecular receptors based on the cyclotriveratrylene (CTV) unit, and possess a quasi-spherical molecular cavity defined by aromatic rings.[4] The main features of these molecular containers are their exceptionnal complexing properties towards neutral and cationic guests. The phosphorylated hemicryptophane **3** was synthesized in two steps from the cyclotriguaiacylene **1** according to the strategy depicted in Fig. 1. **2** contains one CTV unit with three vanillyl pendent arms which are allowed to react with tris-hydrazinophosphine sulfide, following a method developped by Majoral *et al.*[5] This reaction led to the hemicryptophane **3** which possesses a large enforced ditopic cavity defined by the CTV unit on one side and by the phosphorus end on the other side.

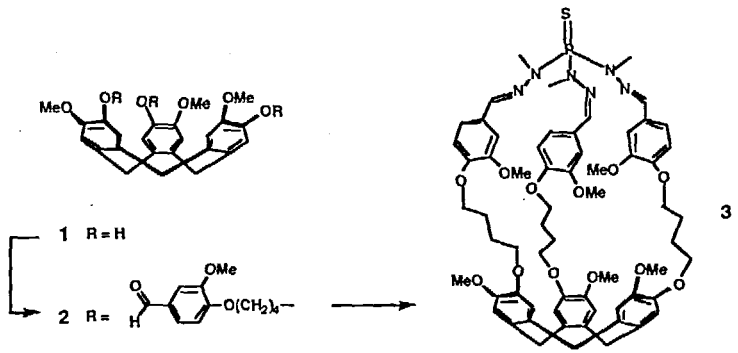

FIGURE 1 Synthesis of hemicryptophane **3**.

An X-ray study revealed that in the solid, the molecule formed a 1:1 toluene complex; the guest molecule being totally encapsulated into the cavity.[6] This compound represents the first of a new family of large molecular cavities based on the CTV building block. The possibility of differenciating the two parts of the cavity opens the route to new ditopic cavitands which are particularly attractive for the design of supramolecular metallo-receptors with possible catalytic activities.

PHOSPHORYLATED CAVITANDS

Cavitands are "funnel like" aromatic cavities which can be suitably substituted at their upper or lower rim to give a still increasing family of molecular containers.[7] The combined effect of the preorganization of the structurally rigid aromatic

framework and of the binding power of phosphorylated groups should result in high performance complexing agents. Therefore we designed new phosphacavitands for which some specific properties (lipophily and complexation), and even the amphiphilic character, can be achieved through their upper and lower rim substitution patterns. The preparation of the phosphorylated cavitands is depicted in Fig. 2. The molecules are mainly obtained as their *iiii* stereoisomer with the four P=O oxygen atoms directed toward the center of the aromatic cavity. The quasi exclusive formation of this isomer is attributed to the template effect of the amine used during the reaction.

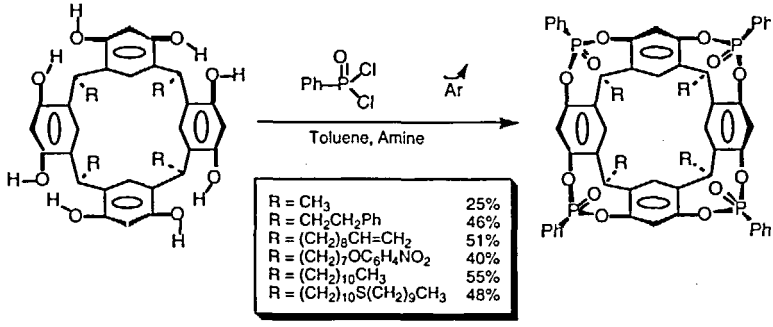

FIGURE 2 Synthesis of phosphacavitands.

The in situ formation of HCl leads to the formation of the ammonium salt which acts as a guest towards the P=O groups and favours the formation of the *all in* (*iiii*) structrure. An average yield of 50% is obtained whatever are the R substituents at the lower rim of the cavitand.

AMMONIUM CATIONS COMPLEXATION BY PHOSPHACAVITANDS

The combination of the deep aromatic cavity and the crown defined by the four phosphoryl groups creates a tailored environment for the complexation of cations. NMR investigations and solid state structure determinations demonstrated that alkali and alkaline earth cations are readily encapsulated into the cavity.[8] Similarly we examined the complexing properties of the ligands towards ammonium salts using extraction experiments. For instance the $[C_{11}]_4$-phosphacavitand bearing four C_{11} alkyl chains extracted very efficiently various methyl ammonium picrates as shown in Fig. 3. The extracted percentage depends on the lipophily of the guest molecule and on the presence of stabilizing H-bonds between the N-H and the phosphoryl groups. NMR studies in solution of $Me_xN^+H_{4-x}$ guests (x = 1 - 4), corroborate these data.

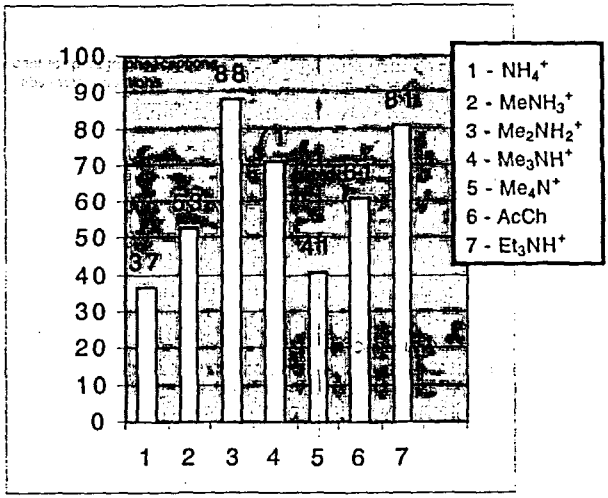

FIGURE 3 Extraction (%) of ammonium picrate salts by $[C_{11}]_4$-phosphacavitand

References

[1] Allan C. B., Spreer L. O., *J. Org. Chem.*, 1994, *59*, 7695; P. Delangle, J.-P. Dutasta, L. Van Oostenryck, B. Tinant, J.-P. Declercq, *J. Org. Chem.*, 1996, *61*, 8904. P. Delangle, J.-P. Dutasta, J.-P. Declercq and B. Tinant, 1998, *Chem. Eur. J.*, 1998, *4*, 100.

[2] W. Xu, J.J. Vittal, R..J. Puddephatt, *J. Am. Chem. Soc.*, 1993, *115*, 6456; W. Xu, J.P. Rourke, J.J. Vittal, R..J. Puddephatt, *J. Chem. Soc. Chem. Commun.*, 1993, 145; W. Xu, J.J. Vittal, R..J. Puddephatt, *J. Am. Chem. Soc.*, 1995, *117*, 8362; W. Xu, J.P. Rourke, J.J. Vittal, R..J. Puddephatt, *Inorg. Chem.*, 1995, *34*, 323; T. Lipmann, E. Dalcanale, G. Mann, *Tetrahedron Lett.*, 1994, *35*, 1685; T. Lipmann, H. Wilde, E. Dalcanale, L. Mavilla, G. Mann, U. Heyer, S. Spera, *J. Org. Chem.*, 1995, *60*, 235; V.I. Maslennikova, E.V. Panina, A.R. Bekker, L.K. Vasyanina, E.E. Nifant'ev, *Phosphorus, Sulfur, and Silicon*, 1996, *113*, 219; E.E Nifant'ev, V.I. Maslennikova, E.V. Panina, A.R. Bekker, L.K. Vasyanina, K.A. Lysenko, M.Y. Antipin., Y.T. Stuchkov, *Mendeleev Commun.*, 1995, 131; P. Delangle, J.-P. Dutasta, *Tet. Lett.*, 1995, *36*, 9325.

[3] A. Collet, in *Comprehensive supramolecular chemistry*, vol. 6, p. 281, F. Toda Ed. (Pergamon, New york, 1996); A. Collet, *Tetrahedron*, 1987, *43*, 5725; P. Timmerman, W. Verboom, D.N. Reinhoudt, *Tetrahedron*, 1996, *52*, 2663.

[4] A. Collet, in *Comprehensive supramolecular chemistry*, vol 2, p. 325, F. Vögtle Ed. (Pergamon, New york, 1996).

[5] A.-M. Caminade, J.-P. Majoral, *Synlett*, 1996, 1019; J. Mitjaville, A.-M. Caminade, J.-C. Daran, B. Donndieu, J.-P. Majoral, *J. Am. Chem. Soc.*, 1995, *117*, 1712.

[6] The X-ray structure was solved by M. Perrin and A. Thozet, University of Lyon: to be published.

[7] E. Maverick and D.J. Cram, in *Comprehensive supramolecular chemistry*, vol 2, p. 367, F. Vögtle Ed. (Pergamon, New york, 1996). D.J. Cram and J.M. Cram, in *Container Molecules and their guests*, J.F. Stoddart Ed. (The Royal Society of Chemistry, 1994).

[8] J.-P. Declercq, B. Tinant, J.-P. Dutasta, B. Bibal, P. Delangle, J.-C. Mulatier, unpublished results; P. Delangle, J.-C. Mulatier J.-P. Dutasta, *Proceedings of the ISMRI9* (Kluwer Academic Press), under the press.