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The first example of the supramolecular regulation of amidophosphite reactivity

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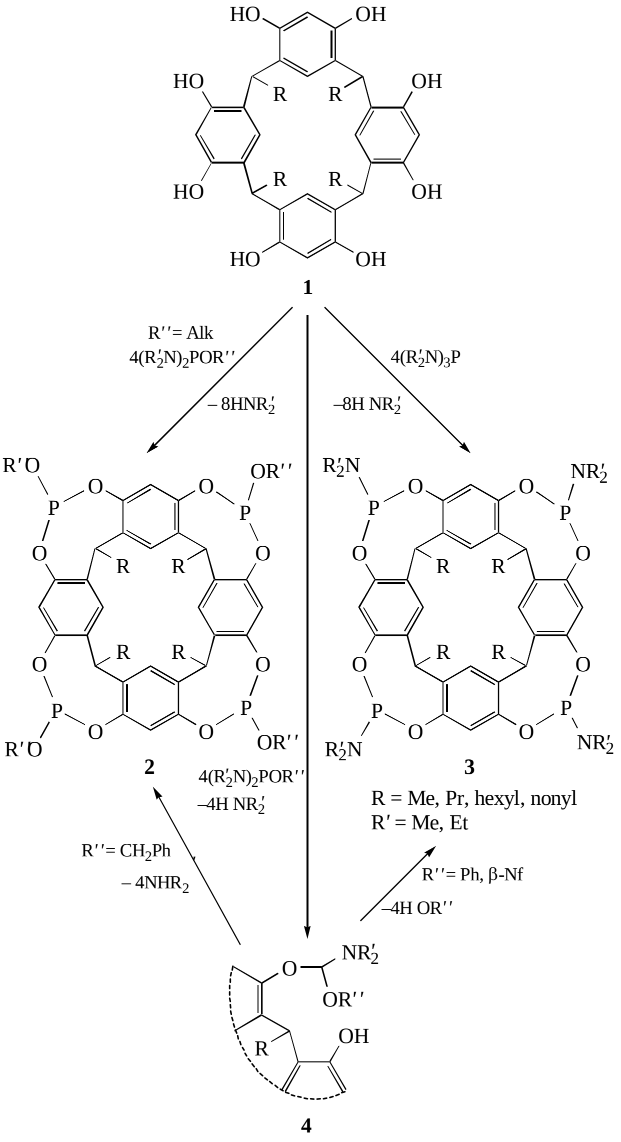
The cyclophosphorylation of calix[4]resorcinolarenes by aromatic diamides of phosphorous acid follows an anomalous pathway with opening of the P–O bond and preservation of one of the P–N bonds due to the interaction between the aromatic nuclei of the phosphorus-containing fragment and the calixarene matrix of the intermediate phosphorylated calixarene.

The interaction between phosphorous acid amidoesters and alcohols primarily results in the alcoholysis of the amido bond.[1] This is also true for the phosphorylation of complex polyol systems. In particular, the use of alkyldiamidophosphites for the cyclophosphorylation of tetraalkylcalix[4]resorcinolarenes **1** always yielded cavitands **2** containing triarylphosphite nodes in the second deck of the macrocycle.[2,3]

In this work, a formally analogous interaction between calix[4]resorcinolarenes **1** and aryldiamidophosphites was examined. Reactions were conducted at room temperature (18–22 °C). Phenyl- and β-naphthyltetraalkyldiamidophosphites were used as phosphorylating agents.



Scheme 1

We found that the reaction proceeded unusually in all cases: the rupture of P–N and P–O bonds with formation of amidophosphitocavitands **3** took place rather than the traditional phenolysis of two P–N bonds (Scheme 1). The composition and structure of the resulting products were supported by elemental analysis, ^{1}H and ^{31}P NMR spectroscopy and an independent synthesis. The X-ray diffraction study of tetrahexylphosphocavitand **3** (R = C_6H_{13}, R′ = Et) was also performed.†

The physicochemical characteristics of the synthesised compounds are consistent with those of amidophosphitocavitands **3** obtained by the cyclophosphorylation of calix[4]resorcinolarene **1** with triamidophosphites.[3]

An X-ray diffraction study of tetrahexylphosphocavitand **3** showed that the main geometry parameters of the macrocycle are similar to those in amidophosphitocavitands studied previously[4,5] (Figure 1). All phosphocine cycles have chair–bath conformations with equatorial amino groups at the phosphorus atoms. The 'cover' and 'bottom' diameters of tetrahexylphosphocavitand **3** are 5.23 and 8.21 Å respectively. In the crystal of **3**, molecules are packed as centrosymmetrical dimerised conglomerations separated by a solvent dioxane molecule.

We believe that the anomalous reaction pathway is due to the molecular recognition effect manifested in the stacking interaction between two aromatic rings of intermediate **4**: its *P*-phenoxyl moiety and the adjacent fragment of the calixarene system. This interaction brings the benzene rings together (Figure 2) and thus removes the amido group from the phosphorylation sphere, *i.e.*, practically passivates the P–N bond. At the same time, the closing of the rings is responsible for the cyclophosphorylation through the rupture of the P–O bond (transesterification). Thus, we first found the supramolecular stipulation of changes in the O–P–N fragment reactivity in the reaction with phenols.

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† *Crystallographic data for* **3**: at 110 K crystals of $C_{72}H_{112}N_4O_{10}P_4$ are triclinic, space group $P\bar{1}$, a = 13.709(5), b = 16.343(4), c = 18.189(5) Å, α = 74.14(2), β = 68.76(3), γ = 83.88(2)°, V = 3653.6(2) Å^3, Z = 2, M = = 1317.54, d_{calc} = 1.198 g cm^{-3}, μ(MoKα) = 0.161 mm^{-1}, F(000) = 1424. Intensities of 30515 reflections were measured with a Smart 1000 CCD diffractometer at 110 K [λ(MoKα) = 0.71072 Å, ω-scans with a 0.3° step in ω and 10 s per frame exposure, 2θ < 60°], and 20978 independent reflections (R_{int} = 0.0241) were used in further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The analysis of electron density synthesis revealed that the dioxane solvate molecules, Et groups of the NEt_2 units at N(1) and N(2) atoms and the terminal parts of hexyl groups [C(46)–C(50) and C(59)–C(61)] are disordered over two positions each. The refinement of the s.o.f. revealed that they are equally occupied. Hydrogen atoms for non-disordered groups were located from the Fourier synthesis and refined in the isotropic approximation, while for all other positions were calculated from the geometrical point of view and refined in a riding model. The refinement converged to wR_2 = 0.2092 and GOF = 1.013 for all independent reflections [R_1 = 0.0737 was calculated against F for 10671 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0 on IBM PC AT. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2000. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/69.

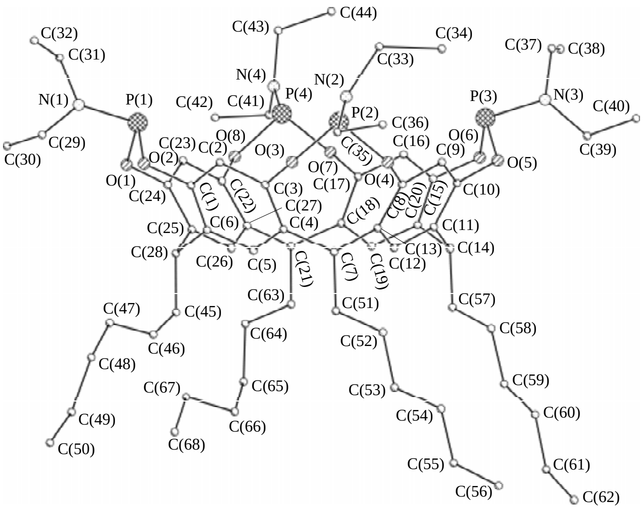
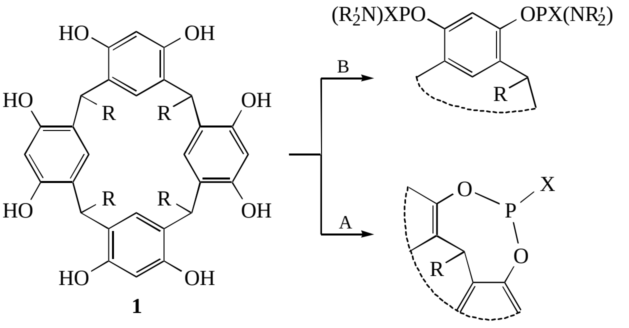


Figure 1 The general view of a molecule of **3**. The principal bond lengths (Å): P(1)–N(1) 1.641(4), P(1)–O(2) 1.664(3), P(1)–O(1) 1.667(4), P(2)–N(2) 1.648(4), P(2)–O(3) 1.658(3), P(2)–O(4) 1.665(3), P(3)–N(3) 1.650(3), P(3)–O(5) 1.665(3), P(3)–O(6) 1.665(3), P(4)–N(4) 1.640(3), P(4)–O(8) 1.671(3), P(4)–O(7) 1.674(3) and bond angles (°): N(1)–P(1)–O(2) 97.5(2), N(1)–P(1)–O(1) 99.8(3), O(2)–P(1)–O(1) 98.3(2), N(2)–P(2)–O(3) 99.0(2), N(2)–P(2)–O(4) 99.6(2), O(3)–P(2)–O(4) 99.3(2), N(3)–P(3)–O(5) 96.3(2), N(3)–P(3)–O(6) 99.4(2), O(5)–P(3)–O(6) 99.5(1), N(4)–P(4)–O(8) 99.0(1), N(4)–P(4)–O(7) 98.7(2), O(8)–P(4)–O(7) 97.9(1), C(24)–O(1)–P(1) 119.5(3), C(1)–O(2)–P(1) 121.5(3), C(3)–O(3)–P(2) 118.9(3), C(8)–O(4)–P(2) 118.2(2), C(10)–O(5)–P(3) 118.9(2), C(15)–O(6)–P(3) 121.4(2), C(17)–O(7)–P(4) 120.5(2), C(22)–O(8)–P(4) 116.7(2).



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X = NR′$_2$; OAlk

Scheme 2

Note that the geometry factor (the high complementarity of the approached aromatic systems) is essential for this effect. The substitution of the benzoxyl group for a phenoxyl group in the phosphorylating agent does not longer provide an adequate complementarity of benzene rings. Therefore, the cyclophosphorylation of tetramethylcalixarene **1** (R = Me) by benzyldiamidophosphite proceeds through the rupture of only P–N bonds, *i.e.*, it follows a classical mechanism with the formation of phosphitocavitand **2** (R$''$ = CH$_2$Ph) (Scheme 1).

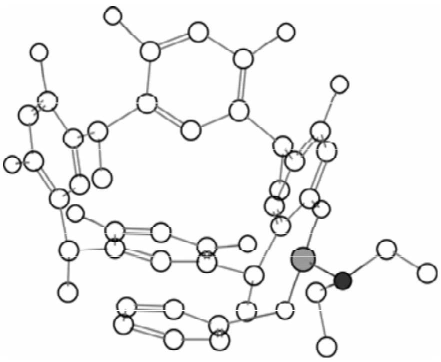

Figure 2 Intramolecular contacts of benzene rings in intermediate **4**.

It should be noted that the use of aromatic diamidophosphites was fruitful in synthetic terms. We found that phosphocavitands can be obtained under milder conditions than in the use of aliphatic diamidoesters and phosphorous acid triamides. In particular, the cyclophosphorylation of tetraphenylcalixarene **1** by aryldiamidophosphites (Scheme 2, A) proceeds at 20 °C, while only direction B takes place when triamido- and alkyldiamidophosphites are used.[4]

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