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The first structural study on a cyclic tricoordinate phosphorochloridite and a pentacoordinate phosphorane based on 1,2,3,5-protected *myo*-inositol—a new conformation of 1,3,2-dioxaphosphorinane ring

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Abstract—Treatment of the phosphoramidite {*myo*-C_6H_6-2-[OC(O)Ph]-1,3,5-(O_3CH)-4,6-(O_2P-NH-*i*-Pr)} with *o*-chloranil affords the first example of inositol-based pentacoordinate phosphorane {*myo*-C_6H_6-2-[OC(O)Ph]-1,3,5-(O_3CH)-4,6-(O_2P-NH-*i*-Pr)(1,2-$O_2C_6Cl_4$)} (**9**) (X-ray structure) with a trigonal bipyramidal geometry at phosphorus. The six-membered 1,3,2-dioxaphosphorinane ring with the inositol residue has an unusual *boat* conformation in **9** which is quite different from that found in unrestrained rings investigated before, but is similar to that of its P^{III} chloro precursor {*myo*-C_6H_6-2-[OC(O)Ph]-1,3,5-(O_3CH)-4,6-(O_2PCl)} (X-ray structure). Also, a convenient and chromatography-free procedure for the protected *myo*-inositol derivative {*myo*-C_6H_6-2-[OC(O)Ph]-1,3,5-(O_3CH)-4,6-$(OH)_2$} is reported.

Keywords: *myo*-Inositol; Conformation; Phosphoranes; Pentacoordinate; X-ray structure

1. Introduction

Phosphorus, in the form of either a phosphate or a phosphonate is ubiquitous in nature, and *c*-AMP, inositol phosphates, RNA, and alkylphosphonic acids represent a few examples wherein it exhibits a significant role in metabolic processes.[1] Several partially substituted *myo*-inositol (**1**) phosphates with the phosphate at (1,3,4,5)-, (1,2,4,5,6)-, (1,2,3,5,6)-, (1,3,4)-positions occur in nature, in addition to 1D-*myo*-inositol 1,4,5-trisphosphate [Ins(1,4,5)P_3] (**2**) which acts as a second messenger in linking the spatially separated events of receptor simulation and release of intramolecular calcium from internal stores.[2–6] All these derivatives therefore have significant therapeutic potential and hence developing new synthetic routes to them may be beneficial. The proposed mechanism for the phosphatidylinositol cleavage catalyzed by phosphatidylinositol-specific phospholipase (PI-PLC) also takes place via a pentacoordinate transition state species (**3**, Chart 1).[7]

In the above context, the structural characterization of biologically relevant amino acid and thymidine based phosphoranes **4** and **5** are of some significance.[8,9] Also, in the metabolic reactions involving cyclic adenosine monophosphate (*c*-AMP), featuring a saturated 1,3,2-dioxaphosphorinane ring, it is not clearly known whether in the transition state the six-membered ring assumes a diequatorial e–e or a–e disposition or if the conformation is enzyme dependent.[10] Studies on a large number of neutral pentacoordinate compounds during 1990's revealed that in a majority of cases similar rings assume an a–e disposition with a *boat* conformation (**I**).[11–13] By contrast, such a ring in the precursor P(III) compounds adapts a *chair* conformation of type **II**.[13–16] Thus there is interest in pentacoordinate phosphorus compounds formed with biologically relevant molecules[17] and this

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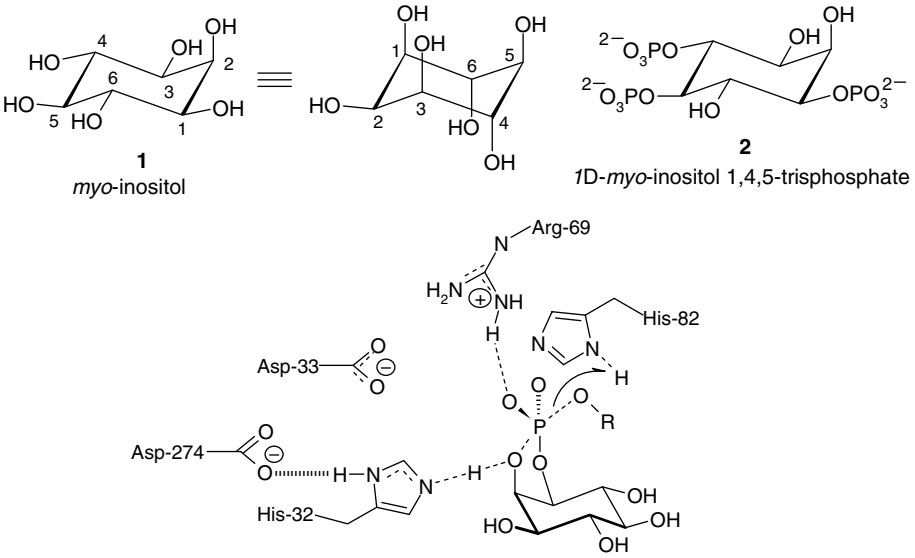
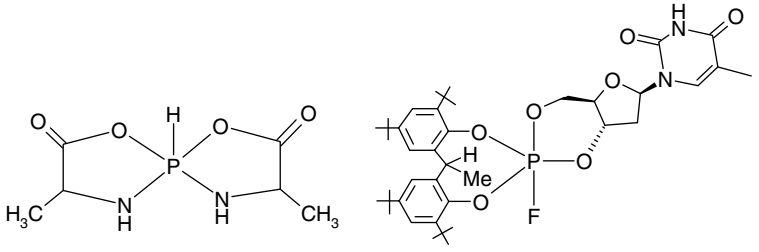


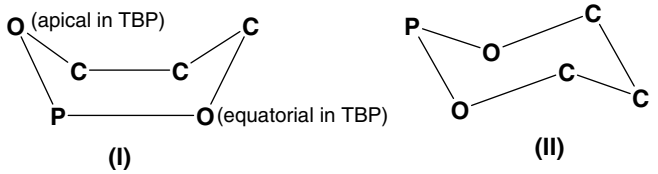
Chart 1.

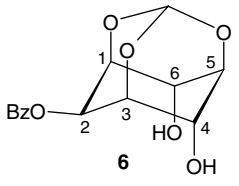
is a subject in which we have been interested.[18–20] We were interested in systems with the (1,3,5) positions blocked so that (4,6) positions can be effectively utilized for phosphorylation. In doing so, we were curious to see whether the generally observed structural features of 1,3,2-dioxaphosphorinane systems are seen in such compounds or not. Although we are not aware of reports on such cyclic inositol phosphates in biosystems, it is possible that they may have some role as transition state species in metabolic processes. Herein we report a *chromatography-free* synthesis of 2-benzoylated 1,3,5-protected inositol (**6**), and structural features of some of its phosphorus (tri- and penta-coordinate) derivatives.

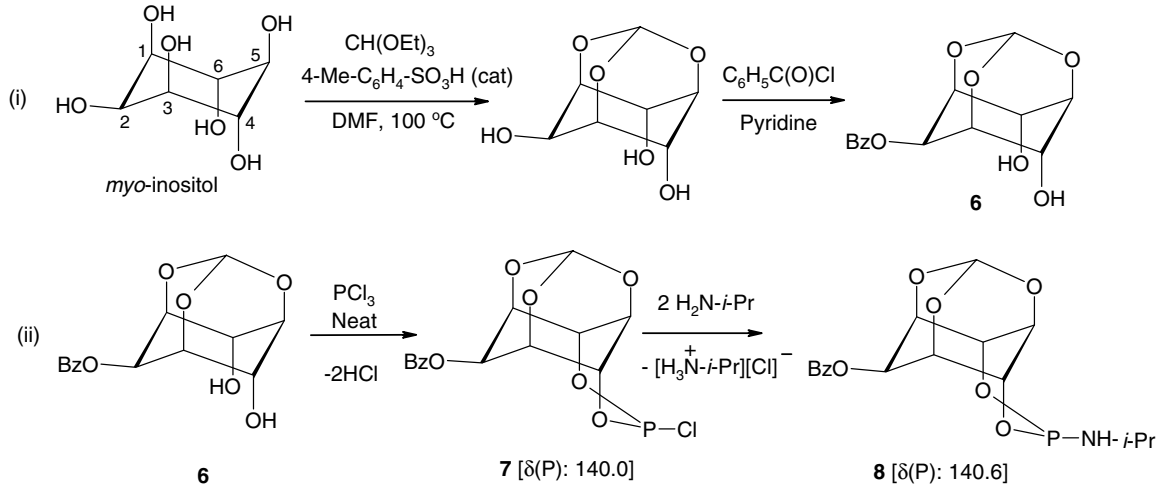
2. Results and discussion

The monobenzoylated inositol *diol* **6** was prepared by a modification of the literature procedure,[21] which used column chromatography for purification of the com-









Scheme 1.

pound. In our case, after removal of most of the pyridine [Scheme 1i], ethyl acetate was added; the organic layer was washed with dilute hydrochloric acid (to remove traces of pyridine) and solvent removed completely. Upon addition of dichloromethane, the monobenzoylated compound **6** crashed out, leaving behind the dibenzoylated derivative in soln. Thus the tedious column chromatography is avoided. This compound was then reacted with PCl_3 under neat condition to lead to the phosphorochloridite **7** in good yield. Further treatment of **7** with isopropylamine gave the corresponding phosphoramidite **8** [Scheme 1ii]. It is possible that the orientation of the NH-*i*-Pr group is opposite to that of chlorine in **7**, but we have not studied this aspect in the current study.

The ^{1}H, ^{13}C, and ^{31}P NMR spectra are consistent with the structure as written; in its ^{13}C NMR spectrum (1100 MHz), **7** exhibits a total of six peaks in the region δ 60–70 for the inositol ring carbons. Since these compounds constitute the first examples of inositol based cyclic phosphites, we were curious to look at the conformational features of this compound vis-a-vis the pentacoordinate derivatives (vide infra). Also, we have been interested in learning about the conformation of the six-membered 1,3,2-dioxaphosphorinane rings with phosphorus in tri-, tetra-, penta- or hexa-coordinate state.[13,22–26] We succeeded in getting the crystals of **7**, but not of **8**.

The X-ray structure of **7** (Fig. 1) clearly shows that the six membered 1,3,2-dioxaphosphorinane ring containing phosphorus adapts a *boat* conformation with the phosphorus and C(5) atoms above the mean plane containing the other four atoms in the ring by 0.391 and 0.695 Å, respectively. This is quite interesting because for the previously determined structures containing unconstrained phosphorinane rings, a *chair* conformation was found.[13–16,22–25] The unusual *boat* conformation found in **7** is probably formed because in the chair conformation the phosphorus (or chlorine) may have unfavorable steric interactions with O(7) or C(2)–H (see Fig. 1). Although not investigated herein, it is interesting to note that the molecule crystallizes in the chiral space group $P2_1$ and the structure determined shows C(1) and C(3) having the configuration (*S*) and (*R*), respectively. In soln, there was no observable optical rotation.

That the 1,3,2-dioxaphosphorinane ring system prepared from the protected inositol diol **6** has a different conformation compared to the unrestrained ones is also

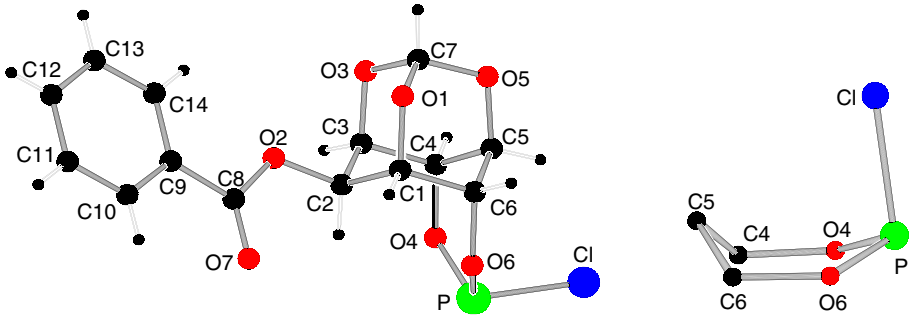
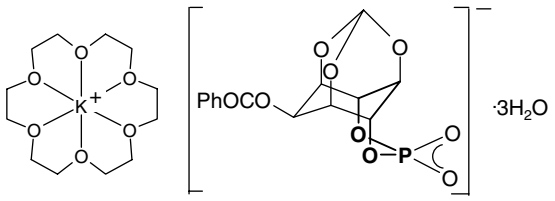


Figure 1. Left: Molecular structure of **7** showing the numbering scheme on selected atoms. Right: Drawing showing the conformation of the phosphorinane ring. Selected bond parameters: P–O(4) 1.6127(16), P–O(6) 1.6024(16), P–Cl 2.1227(9) Å, O(4)–P–O(6) 102.12(8), O(4)–P–Cl 100.72(7), O(6)–P–Cl 100.38(6)°.

shown by the structure of a cyclic inositol phosphate as a trihydrate of its potassium-18-crown-6 salt, viz. $[K\text{-}(18\text{-crown-6})]^{+}\{myo\text{-}C_6H_6\text{-}2\text{-}[OC(O)Ph]\text{-}1,3,5\text{-}(O_3CH)\text{-}[O_2P(O)O]\}^{-}\cdot 3H_2O$ (**10**) reported previously from our laboratory.[26]



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We treated the protected inositol phosphite **7** with diisopropyl azodicarboxylate (DIAD) as well as *o*-chloranil at room temperature, but there was no apparent reaction in either case [^{31}P NMR]. Then we reacted **8** with *o*-chloranil (which is more reactive) and obtained the pentacoordinate phosphorane **9** (Scheme 2). Compound **9** is the first example of a pentacoordinate phosphorus compound with the inositol residue. Its ^{31}P NMR spectrum shows a peak at δ −53.1 consistent with pentacoordination in soln.[13,19,20,27–32]

The molecular structure of $\mathbf{9}\cdot CH_2Cl_2$ along with the bond parameters is shown in Figure 2. The more electronegative oxygen atoms occupy the apical positions while the less electronegative nitrogen is equatorial in the trigonal bipyramidal (TBP) structure, as expected from Bent's rule.[33] The P–O bond distances for apical substituents in TBP structures are expected to be longer than the equatorial ones. In compound **9**, one of the P–O(apical) bonds [P–O(4) 1.6306(14) Å] is actually 0.02 Å *shorter* than P–O(equatorial) bonds [P–O(9) 1.6546(15) Å]. Although one can say that O(4) is connected to an aliphatic residue and O(9) belongs to a 5-membered catecholate residue, the fact remains that apical one is *shorter*. Why is it that apical P–O(4) bond is shorter than even the equatorial P–O(9) bond is not satisfactorily explained by the 3c–4e model for the apical

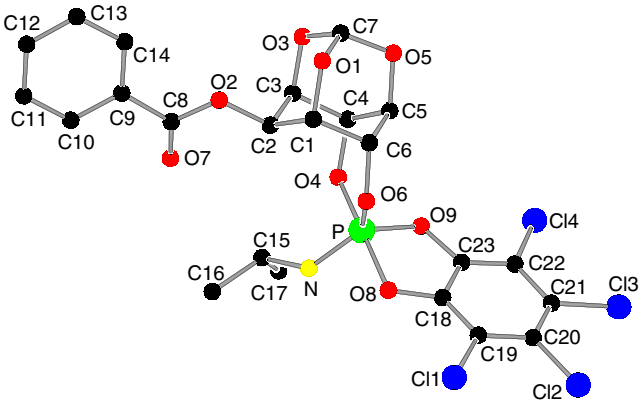
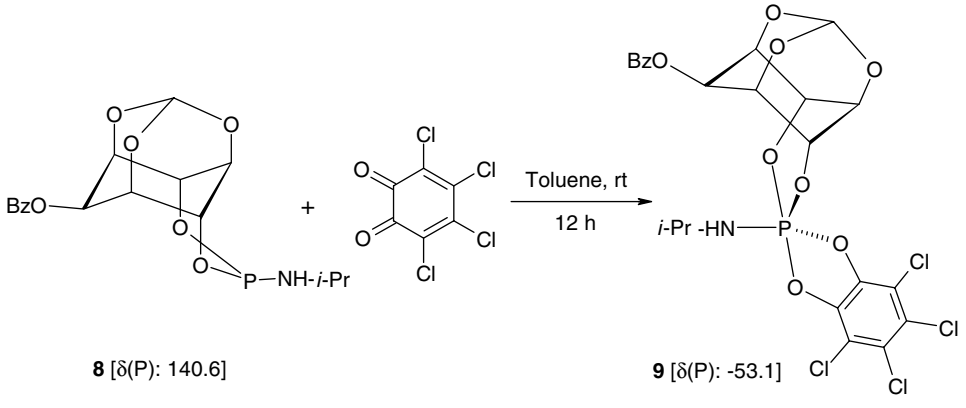


Figure 2. Molecular structure of $\mathbf{9}\cdot CH_2Cl_2$ showing all non-hydrogen atoms. The symmetry (inversion) related molecule in the unit cell is not shown. Solvent molecule is also not shown. Selected bond parameters (Å, °): P–O(4) 1.6306(14), P–O(6) 1.5985(15), P–O(8) 1.7907(15), P–O(9) 1.6546(15), P–N 1.616(2); O(4)–P–O(6) 98.84(7), O(4)–P–O(8) 176.50(8), O(4)–P–O(9) 89.44(7), O(4)–P–N 92.27(9), O(6)–P–O(8) 84.64(8), O(6)–P–O(9) 112.46(8), O(6)–P–N 121.18(9), O(8)–P–O(9) 88.87(7), O(8)–P–N 86.20(9), O(9)–P–N 125.30(10).

bonds in pentacoordinate phosphorus.[34] Although this feature has been observed before, a satisfactory bonding model has not emerged so far. The sum of the bond angles at nitrogen is 357.6°, suggesting that it is essentially planar.

The six-membered ring in **9**, which is more rigid because of the adamantane moiety of the inositol residue, has a *boat* conformation [Fig. 3a] slightly flattened at the phosphorus end. This is in line with that observed for several other pentacoordinate compounds with 1,3,2-dioxaphosphorinane ring (Fig. 3b).[13] However, it should be noted that in those cases, the precursor P^{III} compound had a *chair* conformation (e.g., **11**[13]) while our inositol derived P^{III} compound **7** has a *boat* conformation (discussed above). A more important point of interest is that the observed *boat* conformation in **9** [Fig. 3a] is actually different from that observed in other pentacoordinate compounds in that for the latter, one oxygen and a CH_2 carbon are above the mean plane of the other four atoms (e.g., **12**;[13] Fig. 3b). In **9**, the phosphorus and



8 [δ(P): 140.6] **9** [δ(P): -53.1]

Scheme 2.

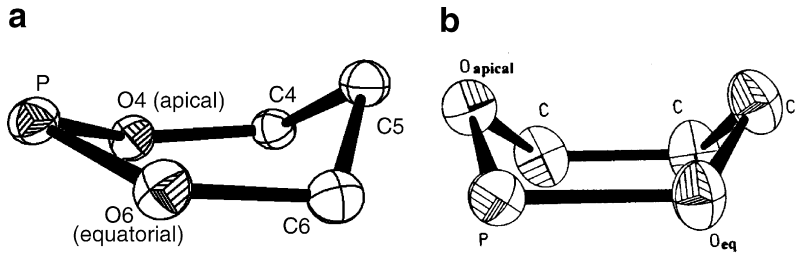
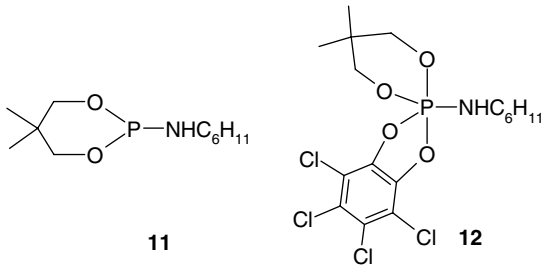


Figure 3. Plots showing the conformation of the six-membered ring in (a) compound **9** and (b) other pentacoordinate compounds (e.g., **12**) with apical–equatorial disposition of the ring.

a carbon atom of the inositol residue are above the mean plane of the remaining four atoms.



The extent of distortion from TBP to square pyramidal (SQP) or tetragonal pyramidal (RP) geometry in **9** is calculated by the dihedral angle method of Holmes[35] and this value is 15.4% TBP→SQP (RP). Thus, for all practical purposes, phosphorus in compound **9** can be considered to be having trigonal bipyramidal geometry.

2.1. Summary

To summarize, we have provided a convenient chromatography-free synthesis of the 1,2,3,5-protected inositol that could be utilized as a convenient 4,6-diol. X-ray structures of the first examples of a cyclic phosphite (**7**) and a pentacoordinate phosphorane (**9**) based on this protected inositol are reported. The 1,3,2-dioxaphosphorinane ring in these compounds adopts a *boat* conformation, which is different from those normally observed for other analogous dioxaphosphorinane rings that exhibit either a *chair* conformation or a *boat* form different from that observed here.

3. Experimental

Chemicals were purchased from Aldrich or local manufacturers; they were purified when required according to standard procedures.[36] All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. ^{1}H, ^{13}C, and $^{31}P\{H\}$ NMR spectra were recorded using a 200 or a 400 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85% H_3PO_4 ($\delta = 0$). Infrared spectra were recorded on a JASCO FT/IR 5300 FT-IR spectrometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Microanalyses were performed using a Thermo Finnigan EA1112 analyzer.

3.1. Preparation of 8,9-dihydroxy-6-phenylcarbonyloxy-2,4,10-trioxa-tricyclo[3.3.1.1^{3,7}]decane (6): modified procedure

Myo-inositol (2.70 g, 15.0 mmol), triethylorthoformate (2.40 g, 22.5 mmol), *p*-toluenesulfonic acid monohydrate (0.25 g, 1.31 mmol) and dry DMF (20 mL) were mixed and heated at 100 °C with stirring for 3 h. The clear soln was cooled to room temperature. Then triethylamine (1.0 mL) was added to the mixture and low boiling components were removed under diminished pressure. Dry toluene was added and the solvent again removed under diminished pressure (2 × 5 mL). This operation was useful in removing traces of DMF. The residue was cooled to 0 °C and then pyridine (10 mL) followed by benzoyl chloride (2.20 g, 15.0 mmol) were added drop-wise over a period of 30 min. The reaction mixture was brought to room temperature and stirred for 8 h. After removal of most of the pyridine, ethyl acetate was added; the organic layer was washed with dil HCl (to remove traces of pyridine) and solvent removed completely. Upon addition of dichloromethane, the monobenzoylated compound **6** precipitated out. Yield: 0.22 g (50%). [Mp: 206–208 °C; lit. 209 °C;[21] ^{1}H NMR (Me_2SO-d_6 (0.3 mL)-CD_3OD (0.1 mL), 400 MHz): δ 7.46–8.05 (m, 5H, Ar-*H*), 5.69 (br s, 2H, –O*H*), 5.49 and 5.52 (2 br s, 2H, inositol-*H*), 4.41 (br s, 2H, inositol-*H*), 4.28 (br s, 1H, inositol-*H*), 4.19 (br s, 1H, inositol-*H*)]. We did not observe any optical rotation for this compound in soln.

3.2. 4-Chloro-12-phenylcarbonyloxy-3,5,8,10,13-penta-oxa-4-phosphatetracyclo[7.3.1.0^{2,7}.0^{6,11}]tridecane (7)

An excess of phosphorus trichloride (20 mL) was added to **6** (1.20 g, 4.08 mmol) and the mixture heated under reflux for 1 d. Unreacted phosphorus trichloride was removed by distillation to obtain a white solid. This was crystallized from toluene to give **7**. Yield 1.16 g (80%).

Mp: 130–132 °C. IR (KBr): 1726, 1603, 1454, 1408, 1277, 1165 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.45–8.18 (m, 5H, Ar-*H*), 5.75 (s, 1H, O_3CH), 5.62 (m, 1H, inositol-*H*), 5.46 (m, 1H, inositol-*H*), 5.23 (m, 2H, inositol-*H*), 4.61 (m, 2H, inositol-*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.8 (Ph–*C*(O)O–), 133.7, 130.0, 129.2, 129.0, 128.6, 128.2, 102.2, 69.0, 68.9, 68.8, 63.3, 61.1, 60.9; ^{31}P NMR ($CDCl_3$, 160 MHz): δ 140.0. Anal. calcd for $C_{14}H_{12}ClO_7P$: C, 46.88; H, 3.37. Found: C, 46.79; H, 3.37. We did not observe any optical rotation for this compound in soln.

3.3. 4-Isopropylamino-12-phenylcarbonyloxy-3,5,8,10,13-pentaoxa-4-phosphatetracyclo[7.3.1.$0^{2,7}$.$0^{6,11}$]tridecane (8)

To a stirred soln of **7** (0.60 g, 1.60 mmol) in toluene (20 mL) at room temperature (25 °C) was added isopropylamine (0.20 g, 3.30 mmol) drop-wise over a period of 10 min. After stirring for 12 h, filtration followed by the removal of solvent afforded **8** as a white solid. Yield: 0.52 g (82%); mp: 114–116 °C; IR (KBr): 3414, 1620, 1408, 1167 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.48–8.20 (m, 5H, Ar-*H*), 5.93 (m, 1H, O_3CH), 5.56 (m, 1H, inositol-*H*), 5.18 (m, 1H, inositol-*H*), 5.07 (m, 2H, inositol-*H*), 4.50 (m, 2H, inositol-*H*), 3.79 (br s, 1H, N*H*), 2.87 (m, 1H, NHC*H*$(CH_3)_2$), 1.22 (d, 6H, $^3J_{H-H} = 6.2$ Hz, NHCH(CH_3)$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.0 (Ph–*C*(O)O–), 133.4, 130.0, 129.6, 129.0, 128.5, 128.2, 102.6 (O_3CH), 70.0, 68.9, 64.8, 64.4, 64.1, 42.0 (d, $^2J_{P-C} = 12.0$ Hz, PNH*C*$(CH_3)_2$), 26.7 (d, $^3J_{P-C} = 4.0$ Hz, PNCH(CH_3)$_2$); ^{31}P NMR ($CDCl_3$, 160 MHz): δ 140.6; Anal. calcd for $C_{17}H_{20}NO_7P$: C, 53.55; H, 5.29; N, 3.67. Found: C, 53.59; H, 5.28; N, 3.75. We did not observe any optical rotation for this compound in soln.

3.4. Synthesis of dichloromethane solvate of the *o*-chloranil adduct of 4-isopropylamino-12-phenylcarbonyloxy-3,5,8,10,13-pentaoxa-4-phosphatetracyclo-[7.3.1.$0^{2,7}$.$0^{6,11}$]tridecane {*myo*-C_6H_6-2-[OC(O)Ph]-1,3,5-(O_3CH)-4,6-{O_2P[NHCH(CH_3)$_2$][1,2-$O_2C_6Cl_4$]}·CH_2Cl_2} (9)

To a soln of **8** (0.40 g, 1.04 mmol) in toluene (10 mL), *o*-chloranil (0.25 g, 1.04 mmol) was added and the soln heated at 50–60 °C for 10 min. Later the reaction mixture was allowed to come to room temperature and stirred overnight. The solvent was removed and the residue crystallized from dichloromethane and traces of hexane. Yield: 0.46 g (70%); mp: 150–152 °C; IR (KBr): 3383, 1726, 1232, 1107 cm^{-1}; ^1H NMR (after drying for 2 h in vacuum) ($CDCl_3$, 400 MHz): δ 7.50–8.19 (m, 5H, Ar-*H*), 5.71 (br s, 1H, O_3CH), 5.58 (br s, 1H, inositol-*H*), 5.30 (s, CH_2Cl_2), 5.03 (br s, 2H, inositol-*H*), 4.82 (br s, 1 H, inositol-*H*), 4.63 (br s, 2H, inositol-*H*), 3.84 (br s, 1H, N*H*), 3.21 (m, 1H, NHC*H*$(CH_3)_2$), 1.23 (br s, 6H, NHCH(CH_3)$_2$); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.7 (s, Ph–*C*(O)O–),133.5, 129.9, 129.2, 128.9, 128.4, 128.1, 127.9, 127.8, 127.4, 125.2, 101.9 (s, O_3CH), 70.0, 63.4, 61.7, 61.5, 47.3 (s, N*C*H$(CH_3)_2$), 20.8 and 21.3 (2 s, NCH(CH_3)$_2$); ^{31}P NMR ($CDCl_3$, 160 MHz): δ −53.1; Anal. calcd for $C_{23}H_{20}Cl_4NO_9P$: C, 44.05; H, 3.21; N, 2.23. Found: C, 44.09; H, 3.25; N, 2.38. We did not observe any optical rotation for this compound in soln.

X-ray crystallography: Single crystal X-ray data were collected on a Bruker AXS-SMART diffractometer, using Mo-Kα ($\lambda = 0.71073$ Å) radiation. The structures were solved by direct methods and refined by full-matrix least squares method using standard procedures.[37] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed by geometry using a riding model.

Crystal data for **7**: $C_{14}H_{12}ClO_7P$, $M_r = 358.66$, monoclinic, space group $P2_1$, $a = 7.4207(8)$ Å, $b = 10.9150(12)$ Å, $c = 9.2807(10)$ Å, $\beta = 100.854(2)$, $V = 738.26(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.613$ Mg m^{-3}, $\mu = 0.402$ mm^{-1}, $F(000) = 368$, data/restraints/parameters = 3393/1/208. Flack parameter = −0.01(6) [absolute configuration at C(1) is *S* and at C(3) is *R*], *R* indices ($I > 2\sigma(I)$): $R_1 = 0.0326$, $wR_2 = 0.0819$, GOF = 1.046, max./min. residual electron density 0.284/−0.222 eÅ^{-3}.

Crystal data for **9**·CH_2Cl_2: $C_{24}H_{22}Cl_6NO_9P$, $M_r = 712.10$, triclinic, space group $P\bar{1}$, $a = 9.8167(8)$ Å, $b = 10.2887(9)$ Å, $c = 15.3489(13)$ Å, $\alpha = 89.190(1)$, $\beta = 83.788(1)$, $\gamma = 72.999(1)°$, $V = 1473.6(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.605$ Mg m^{-3}, $\mu = 0.689$ mm^{-1}, $F(000) = 724$, data/restraints/parameters = 6868/0/376, *R* indices ($I > 2\sigma(I)$): $R_1 = 0.0432$, $wR_2 = 0.1230$, GOF = 1.054, max./min. residual electron density 0.408/−0.300 e Å^{-3}.

4. Supplementary data

Complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 629164 and 629165. Copies of this information may be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk).

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