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One Pot Synthesis and X-ray Crystallographic Investigation of *p*-*t*-Butylcalix[4]arenes with Flexible Narrow Rim Dimethylphosphinoylpropoxy Ligating Groups

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A study on the synthesis and X-ray analysis of dimethylphosphinoylpropoxy ligated at the narrow rim 5,11,17,23-tetra-*tert*-butyl-calix[4]arenes are presented herein. It is found that the rate of substitution is rather slow and that the disubstituted product is the major one formed even after prolonged heating. Based on these observations and on the comparison with the rates of formation of similar products, known from literature, it is suggested that in the case of cyclic systems like calix[4]arenes at equal conditions the effective size of the substituents is crucial and that it controls the rate of *O*-alkylation due to steric reasons. The results are explained by the steric hindrance caused by the ligating groups combined with double intramolecular hydrogen bonding, clearly demonstrated by the X-ray structure of the disubstituted product. It is shown that the level of substitution for this class of compounds does not depend significantly on the reaction duration and on the quantity of the reagent used.

Keywords: Calix[4]arenes; Dimethylphosphinoylpropoxy groups; X-ray structure; Steric hindrance; Intramolecular hydrogen bonding

INTRODUCTION

Calixarenes are macrocyclic compounds which have received great attention during the last decades [1–5] due to their unique complexing abilities towards various metal ions, especially in view of their potential use as ligands for the recovery of actinides from nuclear waste. They are widely used in supramolecular chemistry as molecular capsules for the construction of various receptors for complexation of charged and neutral molecules [6–8]. The bowl-like structure of the molecules allows them to sequester a variety of other molecules, which is of great interest to host–guest chemistry, purification, chromatography, storage and slow release of drugs. Fine control of the size of the molecule by changing the number of the elementary units and the introduction of functional groups sets the pattern for a variety of chemical applications, such as catalysts, ligands and molecular hosts for neutral and charged inorganic and organic species. Their unique three-dimensional structures with almost unlimited derivatization abilities [9] offer versatility with respect to the number of podands to be deployed per molecule. The latter and the tunable shape of the molecules make calixarenes ideal candidates for building blocks and molecular scaffolds in the design of new and more sophisticated molecules.

Inter- and intra-group separation of lanthanides and actinides, among the most difficult of all metal ion separations, are important processes in the strategies for management and storage of high-level radioactive waste and clean-up of decommissioned nuclear facilities [10]. Of the various extractants used in actinide process chemistry, polyfunctional organophosphorus calixarenes have displayed interesting ionophoric properties [11,12] and have shown superiority over the bifunctional analogues carbamoylmethylphosphine oxides (CMPOs) [13]. Calix[4]arene derivatives with narrow rim phosphine oxide ligating groups are among the most useful due to their ability to complex a large number of metal ions with selectivity determined by

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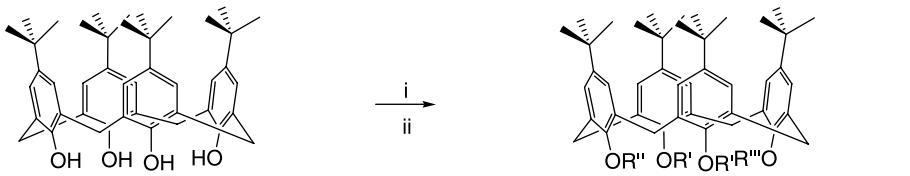


5,11,17,23-tetra-tert-butyl-calix[4]arene R', R'' , R''' = H or -$CH_2CH_2CH_2P(=O)(CH_3)_2$

SCHEME 1 (i) NaH, toluene, reflux, 5 h; (ii) $ClCH_2CH_2CH_2P(=O)(CH_3)_2$, reflux, 65 h.

the precise ligand structure, thus emphasizing the unique potential for selective ion separations and in ion sensor technology [14–21].

A study on the synthesis of 5,11,17,23-tetra-*tert*-butyl-calix[4]arenes with two, three and four dimethylphosphinoylpropoxy ligating groups at the narrow rim is presented herein as well as a report on the X-ray crystallographic investigation of these products.

RESULTS AND DISCUSSION

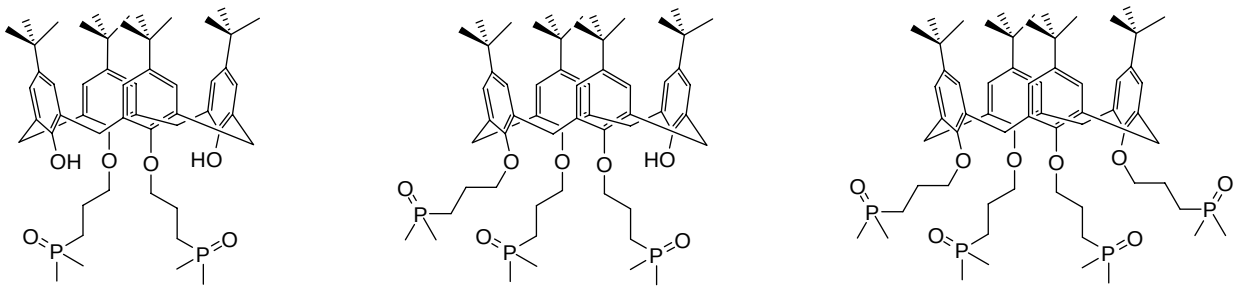
Synthesis of Dimethylphosphinoylpropoxy Ligated 5,11,17,23-Tetra-*tert*-butyl-calix[4]arenes

5,11,17,23-Tetra-*tert*-butyl-calix[4]arenes with two (**1**), three (**2**) and four (**3**) dimethylphosphinoylpropoxy ligating groups at the narrow rim, shown in Scheme 2, were obtained from 5,11,17,23-tetra-*tert*-butyl-calix[4]arene in a two-step one pot procedure, as shown on Scheme 1.

The starting calixarene was first metalated with NaH in refluxing toluene and then treated with dimethyl(3-chloropropyl)phosphine oxide to give the three phosphinoyl-containing calixarenes **1**, **2** and **3** (Scheme 2). The products differ substantially in their R_f-values and were isolated by column chromatography on silica gel. No 1,2-disubstituted and monosubstituted products were isolated nor detected by NMR spectra of the crude reaction mixtures at various stages of the transformation.

Matt *et al.* [16] have obtained diphenylphosphinoylmethoxy ligated 5,11,17,23-tetra-*tert*-butyl-calix[4]arenes and shown that the transformation is much slower and results in the alternately (1,3) disubstituted product when the iodide was used, while the corresponding tosylate led to the formation of the tetrasubstituted calixarene. However, Bünzli *et al.* [19] have prepared dimethylphosphinoylmethoxy ligated at the narrow rim calix[4]arenes by using dimethyl(chloromethyl)phosphine oxide as a reagent and have isolated the tetrasubstituted product in the moderate yield of 46% after 65 h. This result and the similarity in the type of the ligating groups, one vs three CH_2-groups, prompted us the idea to perform the transformation by using the chloride as a reagent in the same time scale. Surprisingly, the ^1H NMR spectrum of the crude reaction mixture showed the presence of the three phosphinoyl-containing calixarenes **1**, **2** and **3** in 64%, 21% and 15% conversion, respectively. The slow rate of the formation of the tetrasubstituted product **3** was additionally demonstrated by prolonging the reaction time to 130 h, when 22% conversion into **3** was observed and the disubstituted product (**1**) was still the major one.

The rate of tetrasubstitution in our case as compared with that obtained by Bünzli *et al.* [19] shows that the bigger dimethylphosphinoylpropoxy ligating group inserts much slower than the smaller dimethylphosphinoylmethoxy group, 15% of **3** vs 46% of the corresponding methoxy analogue were formed. Although bigger in the effective size, the dimethylphosphinoylpropoxy group behaves as less bulky than the dimethylphosphinoylmethoxy at open-chained compounds alkylation, as the bulky phosphinoyl moiety is more distant from the reactive



SCHEME 2 5,11,17,23-Tetra-*tert*-butyl-calix[4]arenes with two, three and four dimethylphosphinoylpropoxy ligating groups at the narrow rim.

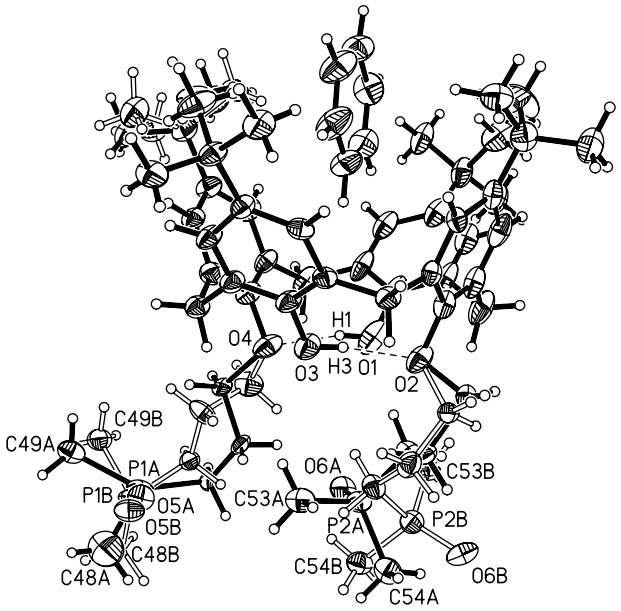


FIGURE 1 Diagram of **1** C_6H_6 in the crystal. Displacement ellipsoids are drawn at the 25% probability level, radii of hydrogen atoms are chosen arbitrarily, most of the carbon and hydrogen atom labels are omitted for clarity. Note the benzene guest molecule situated in the hydrophobic binding pocket of the calixarene, the rotational disorder of one of the upper rim *t*-butyl substituents and the different modes of disorder of the conformational flexible functional groups attached to O2 and O4. Dashed lines are indicating intramolecular hydrogen bonds. Selected geometric features [Å; °]: P—O 1.467 to 1.516 with e.s.ds. between 0.009 and 0.013, P—C 1.747 to 1.849 with e. s. ds. between 0.011 and 0.017, O1–H1 0.82, H1···O4 1.80, O1···O4 2.603(7), O3–H3 0.82, H3A···O2 1.84, O3···O2 2.648(6).

centre. It could be suggested that in the case of cyclic systems like the calix[4]arenes the effective size of the substituents is crucial and that at equal conditions it is the one that controls the rate of *O*-alkylation due to steric reasons.

When performing the reaction with a two times higher concentration of the phosphinoyl group introducing reagent the same relative degrees of conversion to the di-, tri- and tetrasubstituted products were obtained. This could be an indication that the level of the substitution for this class of compounds does not depend significantly on the reaction duration and on the quantity of the reagent used.

X-ray Crystallographic Investigations

Several attempts have been made to determine the molecular structures of **1**, **2** and **3** in the crystal by X-ray diffraction. Thin but well shaped 'crystals' grown from benzene solutions of **2** and **3** at room temperature are soft and easily deformed. Their wax-like behaviour combined with the diffraction property to give very few relatively intense reflections strongly reminds of the properties of so called plastic crystals [22], i.e. three dimensional ordered arrangements of freely rotating molecules of approximately globular shape. In the case of **2** only, this plastic phase behaviour could be overcome by cooling down to −50°C. As to be expected from group theoretical considerations the respective phase transformation resulted in the generation of poly-crystalline samples within the shapes of the starting single crystals. On focusing some bigger crystallites with the X-ray beam for each of them a monoclinic unit cell could be determined ($a = 12.090(2)$ Å, $b = 13.340(3)$ Å, $c = 20.060(4)$ Å, $\beta = 99.90(3)°$). Its volume ($V = 2776.5(10)$ Å^3) fits well to the requirements of 8 formula units of **2** C_6H_6. Due to the samples character it was impossible to collect diffraction data of sufficient quality and intensity for the determination of the structure.

In contrast to the samples derived from **2** and **3** the crystals grown from a benzene solution of **1** do not behave wax-like and show the usual diffraction properties of a crystalline organic substance even at room temperature. The results of the structure determination show them to be crystals of the calixarene benzene host–guest complex **1** C_6H_6. Crystal data and further information concerning the structure determination procedure of **1** C_6H_6 are given in the Experimental Section. Figure 1 shows the structure of the supramolecular complex. Taking into account the enhanced uncertainty of the refined structural parameters of the disordered fragments of the calixarene molecule all geometric features of the structure are as expected [19,23,24]. Some selected mean values concerning the bond lengths of the novel ligating groups at the narrow rim and hydrogen bonding parameters are given in the caption to Fig. 1.

Most interesting part of the structure with respect to the synthetic work is the O–H···O hydrogen bonding region at the narrow rim of the calixarene host molecule. The O···O distances of *ca.* 2.62 Å indicate relatively strong hydrogen bonding between O1 and O4 and O3 and O2. In context with the bulky substituents at O2 and O4 this double intramolecular hydrogen bonding gives an explanation of the pronounced stability of the disubstituted product and the reduced reaction rate concerning third and fourth substitution.

CONCLUSION

The substitution of calix[4]arene O–H protons with dimethylphosphinoylpropoxy groups was investigated and it is found that the reaction is rather slow and the disubstituted product is the major one formed even at prolonged heating in toluene. The results are in agreement with the observation of Matt *et al.* [16] that halides react much slower than tosylates in this transformation, leading to disubstituted product, but are in contradiction with those of Bünzli *et al.* [19], where the tetrasubstituted

product has been isolated as the sole product by using a chloride as a reagent. The results are explained by the ligating groups steric hindrance combined with double intramolecular hydrogen bonding, clearly demonstrated by the X-ray structure of the disubstituted product.

EXPERIMENTAL

Materials and Methods

The reagents were purchased from Aldrich, Merck and Fluka and were used without any further purification. Dimethyl(3-chloropropyl)phosphine oxide was a gift from Hoechst AG. Toluene was dried over sodium wire. Merck silica gel 60 (0.040–0.063 mm) was used for the column chromatography isolation of the products. The melting points were determined in capillary tubes without corrections. The IR spectra were taken on a Bruker IFS 113v as KBr discs and were quoted in cm^{-1}. The NMR spectra were recorded on a Bruker AVANCE DRX 250 spectrometer in deuterochloroform, the chemical shifts were quoted in ppm in δ-values against tetramethylsilane (TMS) as internal standard in ^1H and ^{13}C and against 85% H_3PO_4 as external standard in ^{31}P spectra; the coupling constants were calculated in Hz. The assignment of the signals was confirmed by DEPT and 2D experiments—COSY, HMQC and HMBC. The microanalyses were carried out by the microanalyses service of the Institute of Organic Chemistry, Bulgarian Academy of Sciences.

Synthesis of Dimethylphosphinoylpropoxy Substituted Calix[4]arenes 1, 2 And 3

General Procedure

To a stirred oil-free suspension of NaH (16 mmol, 640 mg 55–60% in oil) in dry toluene (20 ml) a solution of 5,11,17,23-tetra-*tert*-butyl-calix[4]arene (2 mmol, 1.30 g) in toluene (20 ml) was added and the mixture was refluxed for a period of 5 h. Dimethyl(3-chloropropyl)phosphine oxide (20 mmol, 3.08 g) was added and afterward the resulting solution was refluxed for additional 65 h. The solvent was removed *in vacuo* and the residue formed was partitioned between dichloromethane and 10% aq. HCl. The organic layer was washed with brine, dried over $MgSO_4$ and evaporated to dryness to afford the products **1**, **2** and **3** in 64%, 21% and 15% conversion, respectively, determined by ^1H NMR of the crude reaction mixture. The compounds were separated by column chromatography on silica gel, by using CH_2Cl_2/MeOH as a mobile phase with a gradient of polarity from 9:1 to 2:1, and were additionally purified by recrystallization from appropriate solvents. Crystals of **1**, **2** and **3** that seemed to be suitable for X-ray structure determination were obtained by slow diffusion of heptane into benzene solutions.

5,11,17,23-Tetra-tert-butyl-25,27-bis(dimethylphosphinoylpropoxy)-26,28-dihydroxy-calix[4]arene 1

61% isolated yield; R_f 0.40 (CH_2Cl_2/MeOH, 9:1); m.p. 188–189°C; IR ν_{max} 871, 943, 1011, 1124, 1144, 1209, 1299, 1362, 1393, 1485, 2867, 2912, 2961, 3431; ^1H NMR 0.928 (s, 18H, $\frac{1}{2}$ of C*H*$_3$ of *t*-Bu), 1.299 (s, 18H, $\frac{1}{2}$ of C*H*$_3$ of *t*-Bu), 1.590 (d, 12H, $J_{CH3,P} = 12.6$, C*H*$_3$–P), 2.117 (m, 4H, C–C*H*$_2$–C), 2.267 (m, 4H, C*H*$_2$–P), 3.327 (d, 4H, $^2J = 13.0$, $\frac{1}{2}$ of Ar—C*H*$_2$—Ar), 4.064 (t, 4H, $J = 6.1$, C*H*$_2$—O), 4.234 (d, 4H, $^2J = 13.0$, $\frac{1}{2}$ of Ar—C*H*$_2$—Ar), 5.175 (s, 2H, O*H*, exchangeable), 6.760 (s, 4H, $\frac{1}{2}$ of C*H* of Ar), 7.071 (s, 4H, $\frac{1}{2}$ of C*H* of Ar); ^{13}C NMR 15.740 ($\frac{1}{2}$ of *C*H$_3$—P), 16.828 ($\frac{1}{2}$ of *C*H$_3$—P), 22.726 (*C*H$_2$—P), 27.568 (C–*C*H$_2$—C), 28.677 (Ar—*C*H$_2$—Ar), 30.905 (*C*H$_3$ of *t*-Bu), 33.851 (C_{quat} of *t*-Bu), 76.131 ($\frac{1}{2}$ of *C*H$_2$—O), 76.372 ($\frac{1}{2}$ of *C*H$_2$—O), 125.102 ($\frac{1}{2}$ of *C*H of Ar), 125.506 ($\frac{1}{2}$ of *C*H of Ar), 127.718 ($\frac{1}{2}$ of C_{quat}—CH$_2$ of Ar), 132.165 ($\frac{1}{2}$ of C_{quat}—CH$_2$ of Ar), 141.731 ($\frac{1}{2}$ of C_{quat}-Bu-*t* of Ar), 147.034 ($\frac{1}{2}$ of C_{quat}-Bu-*t* of Ar), 149.434 ($\frac{1}{2}$ of C_{quat}—O of Ar), 150.391 ($\frac{1}{2}$ of C_{quat}—O of Ar); ^{31}P NMR 43.832; ESI MS *m/z* 885 $(M + 1)^+$, 907 $(M + Na)^+$; Anal. calc. C, 73.27, H, 8.88, for $C_{54}H_{78}O_6P_2$, found C, 73.36, H, 8.72.

5,11,17,23-Tetra-tert-butyl-25,26,27-tris(dimethylphosphinoylpropoxy)-28-hydroxy-calix[4]arene 2

18% isolated yield; R_f 0.32 (CH_2Cl_2/MeOH, 9:1); m.p. 171–172°C; IR ν_{max} 872, 944, 1008, 1123, 1143, 1203, 1298, 1362, 1392, 1483, 2865, 2909, 2960, 3443; ^1H NMR 0.808 (s, 18H, $\frac{1}{2}$ of C*H*$_3$ of *t*-Bu), 1.335 (s, 9H, $\frac{1}{4}$ of C*H*$_3$ of *t*-Bu), 1.346 (s, 9H, $\frac{1}{4}$ of C*H*$_3$ of *t*-Bu), 1.524 (d, 6H, $J_{CH3,P} = 12.7$, $\frac{1}{3}$ of C*H*$_3$—P), 1.539 (d, 6H, $J_{CH3,P}$ 12.7, $\frac{1}{3}$ of C*H*$_3$—P), 1.612 (d, 6H, $J_{CH3,P}$ 12.7, $\frac{1}{3}$ of C*H*$_3$—P), 1.835 (m, 4H, ? of C–C*H*$_2$—C), 1.980 (m, 2H, $\frac{1}{3}$ of C–C*H*$_2$—C), 2.157 (m, 4H, $\frac{2}{3}$ of C*H*$_2$—P), 2.499 (m, 2H, $\frac{1}{3}$ of C*H*$_2$—P), 3.214 (d, 2H, $^2J = 12.1$, $\frac{1}{4}$ of Ar—C*H*$_2$—Ar), 3.263 (d, 2H, $^2J = 12.6$, $\frac{1}{4}$ of Ar—C*H*$_2$—Ar), 3.934 (t, 4H, $J = 7.3$, $\frac{2}{3}$ of C*H*$_2$—O), 3.993 (t, 4H, $J = 6.8$, $\frac{1}{3}$ of C*H*$_2$—O), 4.267 (d, 2H, $^2J = 12.6$, $\frac{1}{4}$ of Ar-C*H*$_2$-Ar), 4.301 (d, 2H, $^2J = 12.1$, $\frac{1}{4}$ of Ar—C*H*$_2$—Ar), 5.324 (s, 1H, O*H*, exchangeable), 6.478 (s, 2H, $\frac{1}{4}$ of C*H* of Ar), 6.500 (s, 2H, $\frac{1}{4}$ of C*H* of Ar), 7.081 (s, 2H, $\frac{1}{4}$ of C*H* of Ar), 7.151 (s, 2H, $\frac{1}{4}$ of C*H* of Ar); ^{13}C NMR 15.520 ($\frac{1}{3}$ of *C*H$_3$—P), 15.593 ($\frac{1}{6}$ of *C*H$_3$—P), 16.610 ($\frac{1}{3}$ of *C*H$_3$—P), 16.668 ($\frac{1}{6}$ of *C*H$_3$—P), 22.290 ($\frac{1}{3}$ of *C*H$_2$—P), 22.348 ($\frac{2}{3}$ of *C*H$_2$—P), 27.331 ($\frac{1}{6}$ of C–*C*H$_2$—C), 27.534 ($\frac{1}{3}$ of C–*C*H$_2$—C), 28.435 ($\frac{1}{6}$ of C–*C*H$_2$—C), 28.638 ($\frac{1}{3}$ of C–*C*H$_2$—C), 30.847 ($\frac{1}{2}$ of *C*H$_3$ of *t*-Bu), 31.123 ($\frac{1}{2}$ of Ar—*C*H$_2$—Ar), 31.253 ($\frac{1}{2}$ of Ar—*C*H$_2$—Ar), 31.515 ($\frac{1}{4}$ of *C*H$_3$ of *t*-Bu), 31.588 ($\frac{1}{4}$ of *C*H$_3$ of *t*-Bu), 33.520 ($\frac{1}{2}$ of C_{quat} of *t*-Bu), 33.752 ($\frac{1}{4}$ of C_{quat} of *t*-Bu), 34.028 ($\frac{1}{4}$ of C_{quat} of *t*-Bu), 124.766 ($\frac{1}{4}$ of *C*H of Ar), 124.824 ($\frac{1}{4}$ of *C*H of Ar), 125.027 ($\frac{1}{4}$ of *C*H of Ar),

125.783 ($\frac{1}{4}$ of *C*H of Ar), 129.473 ($\frac{1}{4}$ of C_{quat}—CH_2 of Ar), 131.230 ($\frac{1}{4}$ of C_{quat}—CH_2 of Ar), 131.724 ($\frac{1}{4}$ of C_{quat}—CH_2 of Ar), 135.531 ($\frac{1}{4}$ of C_{quat}—CH_2 of Ar), 142.010 ($\frac{1}{4}$ of C_{quat}-Bu-*t* of Ar), 145.438 ($\frac{1}{2}$ of C_{quat}-Bu-*t* of Ar), 146.019 ($\frac{1}{4}$ of C_{quat}-Bu-*t* of Ar), 150.174 ($\frac{1}{4}$ of C_{quat}—O of Ar), 150.901 ($\frac{1}{2}$ of C_{quat}—O of Ar), 153.080 ($\frac{1}{4}$ of C_{quat}—O of Ar); ^{31}P NMR 43.840 ($\frac{2}{3}$ of P), 45.054 ($\frac{1}{3}$ of P); ESI MS *m/z* 1003 $(M + 1)^+$, 1025 $(M + Na)^+$, 502 $(M + 2)^{++}/2$; Anal. calc. C, 70.63, H, 8.94, for $C_{59}H_{89}O_7P_3$, found C, 70.54, H, 8.98.

5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis (dimethylphosphinoylpropoxy)-calix[4]arene 3

11% isolated yield; R_f 0.16 (CH_2Cl_2/MeOH, 9:1); m.p. 145–146°C; IR ν_{max} 871, 943, 1031, 1073, 1119, 1145, 1209, 1264, 1300, 1362, 1376, 1400, 1466, 2866, 2913, 2961; ^{1}H NMR 1.076 (s, 36H, CH_3 of *t*-Bu), 1.534 (d, 24H, $J_{CH3,P} = 12.6$, CH_3—P), 1.781 (m, 8H, C–CH_2—C), 2.263 (m, 8H, CH_2—P), 3.153 (d, 4H, $^2J = 12.5$, $\frac{1}{2}$ of Ar-CH_2-Ar), 3.989 (t, 8H, $J = 7.7$, CH_2—O), 4.347 (d, 4H, $^2J = 12.5$, $\frac{1}{2}$ of Ar-CH_2-Ar), 6.776 (s, 8H, C*H* of Ar); ^{13}C NMR 15.751 ($\frac{1}{2}$ of *C*H$_3$—P), 16.833 ($\frac{1}{2}$ of *C*H$_3$—P), 22.261 ($\frac{1}{2}$ of *C*H$_2$—P), 22.317 ($\frac{1}{2}$ of *C*H$_2$—P), 27.426 (C–*C*H$_2$—C), 28.537 (Ar—*C*H$_2$—Ar), 31.292 (*C*H$_3$of *t*-Bu), 33.730 (C_{quat} of *t*-Bu), 75.009 ($\frac{1}{2}$ of *C*H$_2$—O), 75.292 ($\frac{1}{2}$ of *C*H$_2$—O), 125.021 (*C*H of Ar), 133.397 (C_{quat}—CH_2 of Ar), 144.722 (C_{quat}-Bu-*t* of Ar), 152.757 (C_{quat}—O of Ar); ESI MS *m/z* 1121 $(M + 1)^+$, 1143 $(M + Na)^+$; 561 $(M + 2)^{++}/2$; Anal. calc. C, 68.55, H, 8.99, for $C_{64}H_{100}O_8P$, found C, 68.62, H, 8.89.

Crystal Structure Determination of Compound 1 C_6H_6 [25]

Only weak diffracting crystals of limited quality were available. Some were selected by means of a polarization microscope and investigated on a Stoe Imaging Plate Diffraction System, using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by a least-squares refinement on the positions of 8000 strong reflections distributed equally in reciprocal space. An anorthic lattice was found, compatible with space groups *P*1 and ^{P1}. The latter was chosen with respect to the distribution of intensities in the reciprocal space and was also confirmed in the course of concurrent structure refinements. Crystal data: $M_r(C_{60}H_{84}O_{16}P_2) = 1107.08$, $a = 12.090(2)$ Å, $b = 13.340(3)$ Å, $c = 20.060(4)$ Å, $\alpha = 96.50(3)°$, $\beta = 99.90(3)°$, $\gamma = 116.82(3)$, $V = 2776.5(14)$ Å^3, $Z = 2$, $D_x = 1.152$ g cm^{-3}, $\mu = 0.127$ mm^{-1}, $T = 291$ K, colourless crystal of dimensions 0.5 mm × 0.45 mm × 0.3 mm. 14393 intensity data ($\Theta_{min} = 2.22°$, $\Theta_{max} = 26.20°$) were collected and Lp corrections were applied. Primary structure solution was achieved by direct methods [26]. In the course of secondary structure solution three regions of disorder of **1** became obvious: (i) rotational disorder of one of the tertiary butyl groups, (ii) conformational disorder of the PO-containing group attached to O4, and (iii) conformational *and* rotational disorder of the PO-containing group attaches to O2, with refined occupation of 0.61:0.39, 0.54:0.46 and 0.53:0.47, respectively. Approximate positions of all hydrogen atoms not suffering from any kind of disorder and also of some of those suffering from disorder of their parent carbon atoms were found via difference Fourier-synthesis. Refinement (770 parameters, all of 9655 unique reflections used, 182 appropriate same distance and isotropic displacement restraints concerning the disordered groups) by full-matrix least-squares calculations on F^2[26] converged to the following final indicators: $R_1[F_o^2 > 2\sigma(F_o^2)] = 0.076$, $wR_2 = 0.132$ (all data), $w = 1/[\sigma^2(F_o^2)]$, $S = 0.76$ [27], largest peak and hole in the final difference map are 0.230 e/Å^3 and −0.212 e/Å^3, respectively. Anisotropic displacement parameters were used for all non-hydrogen atoms. The H atoms were allowed to ride on their parent carbon atom in idealized positions. Their isotropic displacement parameters were kept equal 150% and 120% of the equivalent isotropic displacement parameters of the parent oxygen and primary carbon and of the parent secondary and 'aromatic' carbon atom, respectively.

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