Supporting information

Pseudopolymorphism leading and two different supramolecular aggregations in a phosphate monoester: Role of a rare waterdimer

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Experimental

All reactions were carried out under fume hood by using Schlenk line technique in an inert atmosphere. Recrytstallization was done on bench top using beakers or round bottom flask. The melting points were measured in glass capillaries and are reported uncorrected. Infrared spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer as KBr diluted discs. NMR spectra were recorded on a Bruker Advance DPX-400 spectrometer using DMSO-d₆ solvent. The peaks which are not labelled are always solvent peaks, if not stated otherwise. Commercial grade solvents were purified by employing standard procedures. Chemicals such as 2,6-diisopropylphenol (Sigma Aldrich), LiCl catalyst (Sigma Aldrich), POCl₃ (Spectrochem), Pd/C catalyst (Sigma Aldrich), Hydrazine hydrate 80% (Spectrochem) were used as received.

2,6-diisopropyl-4-nitrophenylphosphate (1 g, 3.29 mmol) was dissolved in dry ethanol (25 mL). Pd/C (100 mg) was added to this solution and started to reflux in an inert atmosphere for 15 minutes. Hydrazine hydrate (15 mL) was added to the hot reaction mixture dropwise (Caution: exothermic reaction). The mixture was further heated under reflux for 24 h and cooled to room temperature under a stream of N₂. The reaction mixture was filtered to obtain colourless solution. The crude product was obtained as white solid after removal of solvent which was crystallized from methanol to yield single crystals of $[1.\frac{1}{3}H_2O.MeOH]$ (1a). First and repeated recrystallizations of 1a from methanol results in the crystals of second pseudopolymorph [1.MeOH] (1c). Yield for 1a 0.57 g (46 %). M.p. for 1a: 160 °C. EA for C₃₉H₇₄N₃O₁₆P₃ (**1a**) Calculated C, 50.16; H, 7.99; N, 4.50%; Found: C, 50.88; H, 7.56; N, 5.11%. EA for C₁₃H₂₄N₁O₅P₁ (**1c**) Calculated C, 51.14; H, 7.92; N, 4.59%; Found: C, 50.29; H, 7.58; N, 5.53%. IR (KBr, v_{max}/cm⁻¹): 3285, 2964, 1608, 1095. HRMS Calculated for C₁₂H₂₁NO₄P (M+1): m/z 274.1208; found m/z 274.1211. ¹H NMR (DMSO-d₆ 400 MHz, ppm) δ: 6.25 (s, Ar-CH, 1H), 3.43 (septet, ⁱPr-CH, 2H), 1.05 (d, CH₃, 12H). ³¹P NMR (DMSO-d₆, 160 MHz, ppm) δ: -4.24 ppm. ¹³C NMR (DMSO-d₆, 100.6 MHz, ppm) δ: 143.6 (C-NH₂), 140.7 (C), 138.6(C-O), 109.7(CH), 26.0 (CH-^{*i*}Pr) and 23(CH₃-^{*i*}Pr).

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Single crystal X-ray diffraction Studies

Intensity data was collected on a Rigaku Saturn724+ diffractometer. All calculations were carried out using the programs in WinGX module.¹ The structure was solved in each case by direct methods (SIR-92).² The final refinement of the structure was carried out using full least-squares methods on F^2 using SHELXL-97.³

Crystal structure determination of 1a:

Crystallization of the crude product of 2,6-diisopropyl-4-aminophenylphosphate (1) from methanol at room temperature yields crystals of polymorph of **1a** as block (light yellow). A suitable crystal of size 0.51 x 0.50 x 0.15 mm³ was mounted on a Rigaku saturm 724+ ccd diffractometer for unit cell determination and three dimensional intensity data collection. 800 frames in total were collected at 150 K with the exposure time of 16 s per frame. Unit cell determination using both high angle and low angle diffraction reveal that compound crystallizes with the trigonal P-31c space group (12 asymmetric parts). Data integration and indexing of **1a** using crystal clear followed by crystal structure resulted in the structure determination of 1a, which revealed that the asymmetric part contains one molecule of 2,6diisopropyl-4-aminophenylphosphate along with one solvent methanol molecule and one third of water molecule. One of the phosphonic acid proton has migrated to the amino group. The second P-OH proton as well as the proton of the one third of water could neither be located in the diffaction map nor be fixed geometrically in a meaningful position. Hence although the asymmetric part is supposed to have the formula of $C_{13}H_{24.66}N_1O_{5.33}P_1$, Hence of the 24.66 H-atoms are suppose to be present in the asymmetric part, only 23 is accounted for. Thus of the total contains of the unit cell C156H296N12O64P12, only 276 protons have been accounted for. The final refinement after accounting for all the rest of the atoms converge the R value of 0.0638 (I> 2σ (I)).

Crystal structure determination of 1b:

Methanol from the channels of **1a** can be fully removed through a SC-SC transformation under vacuum. Evacuating the crystals of **1a** for 3 hours (10^{-3} mmHg) leads to the formation of **1b**, with a new crystal system and space group (monoclinic C2/c). The crystal structure determination protocol, instruments used, and details of structure determination and refinement are same as that described for **1a** above. Structure determination from this data clearly established the chemical constitution of the

crystal to be $[1.\frac{1}{3}H_2O]_3$ (**1b**), a new structural form for adippH₂. It is instructive to note that the prolonged evacuation under high vacuum results only in the loss of methanol and not water. Crystal data for **1b**: $C_{36}H_{62}N_3O_{13}P_3$, M = 837.80, monoclinic, a = 19.394(2) Å, b = 35.680(3) Å, c = 15.180(1) Å, $\alpha = 90^\circ$, $\beta = 90.311(15)^\circ$, $\gamma = 90^\circ$, V = 10504(2) Å³, T = 150(2) K. Space group *C* 2/*c*, Z = 8, 38532 refl measured, 9210 indep refl [R(int) = 0.0748]. Final R1 (1.33). Hintel wR2 0.2882[I>2[I]; 0.2947 (all data).

Crystal structure determination of 1c:

Dissolution of crystals of 1a in CH₃OH followed by recrystallization at room temperature results in the second polymorph 1b as colourless hexagonal crystals in good yield. The suitable single crystal of 1b was used to determine its structure as above for 1a. Structure solution of 1b reveal that the asymmetric part of unit cell contains two molecule of 2,6diisopropyl-4-aminophenylphosphate and two solvent methanol molecules. In this case all the H-atoms on the aryl ring and isopropyl group were fixed in the constraint position while OH, NH and methanol CH₃ protons have been located for the diffraction map. The final refinement of this case converge the R value of 0.049 (I>2 σ (I)). The final coordinates along with the thermal parameter and other refinement details have been deposited as cif file in CCDC.

- 1. Farrugia, L. J. WinGX, Version 1.64.05 J. Appl. Crystallogr. 1999, 32, 837.
- Altomare, A.; Cascarano, G.; Giacovazzo, C.; Gualardi, A. J. Appl. Crystallogr. 1993, 26, 343.
- Sheldrick, G. M. SHELXL-97, Program for Structure Refinement, University of Göttingen: Germany, 1997.



Fig. S1. Aggregation of organosilanetriols (Ref. 2-5 in main text).



Fig. S2. IR spectrum of **1a** as KBr diluted disc.







Fig. S4. ¹H NMR spectrum of compound 1a in DMSO- d_6 .



Fig. S5. ³¹P NMR spectrum of compound 1a in DMSO- d_6 .

Elemental Composition Report

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Single Mass Analysis (displaying only valid results) Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons 382 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Micromass : Q-Tof micro (YA-105)			Dept. Of Chemistry I.I.T.(B)						25-Mar-201112:25:55			
C12H20O4P RM-AK-324 56	(0.553) AM (Cen,5, 80 274.1211	.00, Ar,5000.0),556.28,1.00)	; Sm (Mn, 3x6	.00); Cm (56:61)				т	OF MS ES- 7.49e	3	
%- 158.0	275. 268 232.0738 275	258 9.1545371	448.2270	547.2413	577.1992 672	2.3185 78	3.4836 8	48.3461	948.	5348 m/	z	
150	200 250 300	350 40	450 5	500 550	600 650 7	750 750	800	850	900 9	50		
Minimum: Maximum:		200.0	5.0	-1.5 50.0								
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula	ı					
274.1211	274.1208	0.2	0.9	3.5	1	C12 H2	21 N	04 P				

Fig. S6. ESI-HRMS (+ve ion polarity) of compound 1a in methanol.



Fig S7. TGA of **1a** and **1c** at heating rate of 10 °C/min under N₂ atm.



Fig. S8. ESI-Mass spectrum (-ve ion polarity) of compound 1a and DABCO mixture in methanol.



Fig. S9. ESI-Mass spectrum (-ve ion polarity) of compound **1a** and piperazine mixture in methanol.



Fig. S10. ¹³C NMR spectrum of compound 1a in DMSO- d_6 .