

Supramolecular Structures by Hydrogen Bonding: The Solid-State Structure of Tris[3-(3-dimethylamino-1-oxoprop-2-enyl)phenyl]phosphane Oxide

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Tris[3-(3-dimethylamino-1-oxoprop-2-enyl)phenyl]phosphane oxide, which can be synthesized quantitatively by oxidation of the corresponding phosphane, crystallizes in the trigonal space group *R*3̄. Because of the four different strong proton accepting sites ($1 \times \text{P}=\text{O}$, $3 \times \text{C}=\text{O}$), this molecule can form $\text{P}=\text{O} \cdots \text{H}-\text{O}-\text{H} \cdots \text{O}=\text{P}$ and $\text{C}=\text{O} \cdots \text{H}-\text{C}$ hydrogen bonds in the

solid state, which results in the generation of two interpenetrating networks. In the cavities of the solid-state structure, water and acetone are enclosed.

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Introduction

Hydrogen bonds are of fundamental importance for the world we are living in. This fact is mainly related to the hydrogen bond strength (up to about 40 kJ/mol), which allows reversible bond formation and cleavage under ambient conditions.^[1] The resulting dynamics, especially in protic and/or polar solvents like water, enables a hydrogen bonding system, in contrast to a purely covalently bound structure, to adapt to the requirements of its environment.^[2] This reveals the relevance of hydrogen bonding in molecular biology and biochemistry.

The secondary structures of proteins, for example, are strongly determined by intramolecular hydrogen bonds mainly performed between the proton donating and accepting sites of the amide units $[-\text{C}(\text{O})-\text{NH}-]$. Here, the involvement of the N–H group as a proton donor in hydrogen bonding increases the hydrogen accepting feature of the carbonyl moiety and vice versa. Removal of the proton of the N–H group against a carbon substituent leaves a strong hydrogen acceptor, which manifests itself in polar compounds such as dmf, where the dimethylamino moiety enhances the electron density at the carbonyl oxygen atom. Introduction of a $-\text{CH}=\text{CH}-$ fragment into the C–N bond results in vinylogous 3-dimethylaminoprop-2-en-1-ones. Such molecules, which are accessible in high yields by reacting an aryl methyl ketone with an activated dmf analogue have recently attracted our interest as precursors for the synthesis of pyrazole- and pyrimidine-based ligands.^[3] Additionally, 3-dimethylaminoprop-2-en-1-ones are powerful proton accepting compounds, which we were able to prove spectroscopically and by quantum chemical calculations as well as

by the elucidation of several solid-state structures.^[4] The proton accepting power of the electron rich carbonyl group of such compounds enables intermolecular $\text{C}=\text{O} \cdots \text{H}-\text{C}$ hydrogen bonding with the protons of the $-\text{CH}=\text{CH}-$ fragment or the NMe_2 groups of a neighbouring molecule. In the present manuscript, we will show that the specific introduction of multiple 3-dimethylaminoprop-2-en-1-one units allows to design the solid-state structure of such systems.

The introduction of two 3-dimethylaminoprop-2-en-1-one side chains at one central unit leads to chain-type hydrogen bound aggregates, as realized, for example, in the solid-state structure of 2,6-bis(3-dimethylamino-1-oxoprop-2-enyl)pyridine.^[4b] By adding a third 3-dimethylaminoprop-2-en-1-one function to one planar central unit, as it is realized in 1,3,5-tris(3-dimethylamino-1-oxoprop-2-enyl)benzene, should thus make layer-type structures accessible. Crystallization from wet acetone gives the trihydrate of this compound wherein the water molecules act as proton donors and acceptors in the expected two-dimensional hydrogen bonded network. However, cocrystallization with larger proton donors like hydroquinone or 4,4'-dihydroxybiphenyl gives linear structures wherein only two of the three 3-dimethylaminoprop-2-en-1-one side chains are engaged in hydrogen bonding, presumably this is due to steric reasons.^[4a] By following something like a crystal engineering strategy, the steric problems can be overcome by changing the core from a planar 1,3,5-trisubstituted benzene into a pyramidal arrangement like it is, for example, realized in triarylphosphanes.

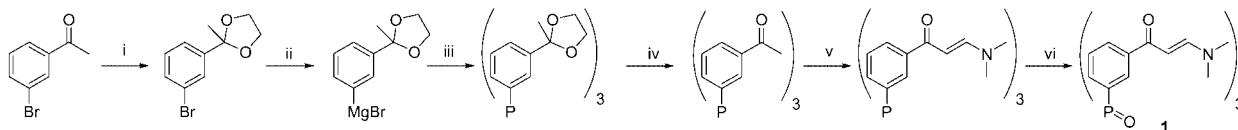
A similar strategy is realized in supramolecular coordination chemistry where the thermodynamically reversible coordination of transition metal building blocks to symmetrically substituted donor ligands is used to build up oligonuclear aggregates of nanometer dimension.^[5] M. Albrecht recently highlighted the supramolecular chemistry of C_3 -symmetric ligands leading to C_3 -symmetric structures.^[6]

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Results and Discussion

Our C_3 -symmetric target molecule tris[3-(3-dimethylamino-1-oxoprop-2-enyl)phenyl]phosphane oxide (**1**) can be syn-

thesized quantitatively by oxidation of the corresponding phosphane by air. The phosphane is accessible following a stepwise synthesis starting from 3-bromoacetophenone in about 50% overall yield (Scheme 1).^[3a]



Scheme 1. i) TsOH, HOCH₂CH₂OH, toluene, reflux; ii) Mg, thf, reflux; iii) PCl₃, thf, reflux; iv) TsOH, H₂O, thf, reflux; v) HC(OMe)₂-NMe₂, reflux; vi) air, acetone, room temp.

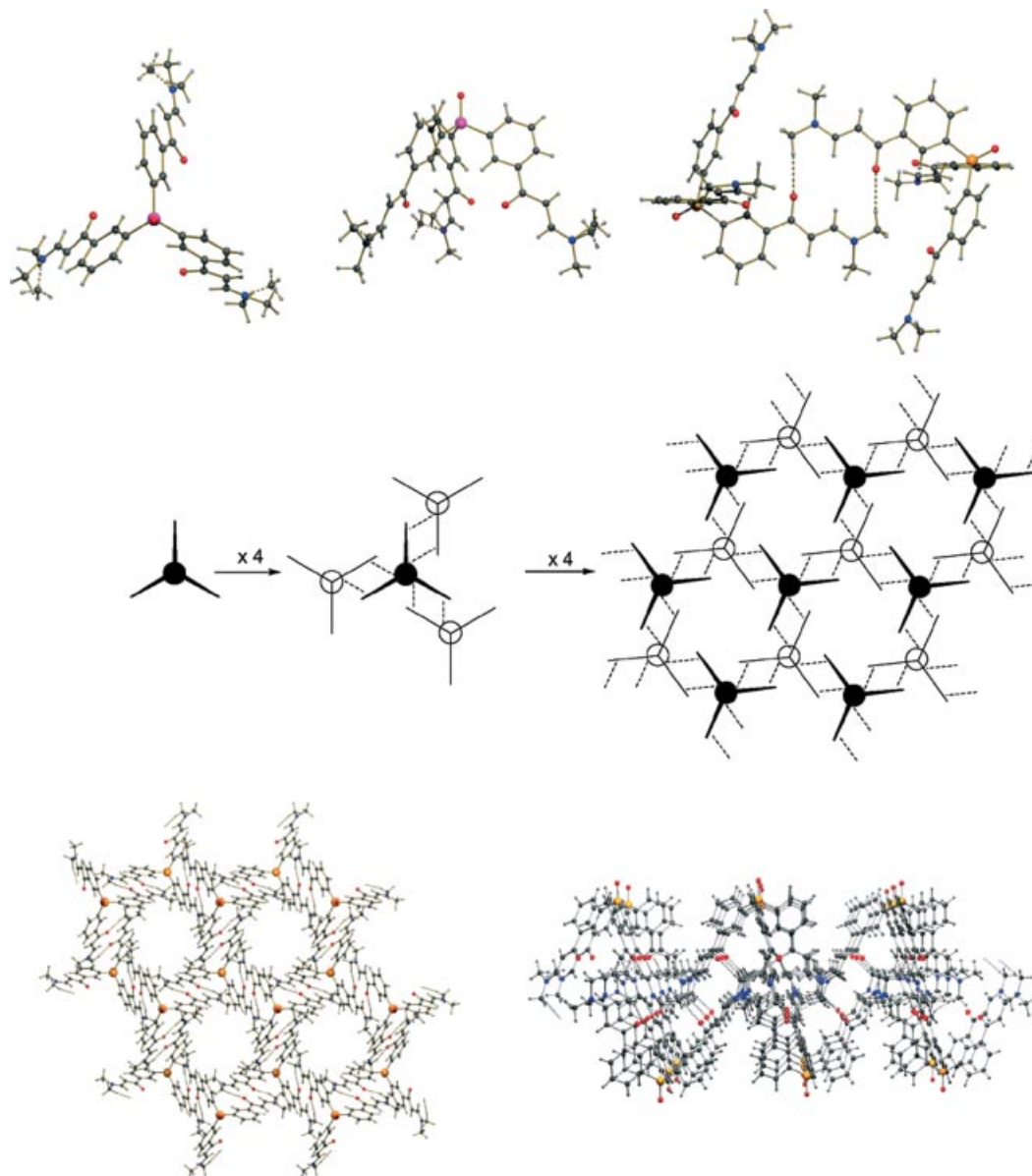


Figure 1. P: orange, O: red, N: blue. Top: Molecular views of single molecules of **1** in the solid state (left, middle); hydrogen bonds between two 3-dimethylamino-1-oxoprop-2-enyl side chains (right: disordered CH₃ groups omitted for clarity). Selected bond lengths [Å] and torsion angles [°]: P–O1 1.480(3), O2–C7 1.234(3), C7–C8 1.420(3), C8–C9 1.351(4), N–C9 1.320(3), O1–P–C1–C2 154.68(18), O2–C7–C8–C9 –0.8(4), C7–C8–C9–N –179.6(3), C10–N–C9–C8 –178.0(3), C9–N–C10–H10A 0.00. Hydrogen bond parameters [Å] and [°]: C10–H10A 0.96, H10A...O2 2.35, C10...O2 3.277(4), C10–H10A...O2 161.00. Middle: Sketch of the two dimensional supramolecular arrangement of **1** by hydrogen bonding; filled circles: P=O pointing up; open circles: P=O pointing down; dashed lines: hydrogen bonds. Bottom: The two dimensional arrangement of **1** that results from intermolecular hydrogen bonding; views along the crystallographic *c*- (left) and *a* axis (right).

Compound **1** crystallizes under “transfer” of the symmetry of the molecule into the solid state in the trigonal space group $R\bar{3}$ (No.148)^[7] by slow diffusion of diethyl ether into a concentrated solution of the compound in wet acetone.^[8] Figure 1 shows different aspects of the solid-state structure of **1**. Up to now, crystallization of **1** could only be performed successfully in this combination of solvents because of the inclusion of water and acetone in its solid-state structure (see below).

The aryl substituents of the triarylphosphane oxide cores are arranged in a paddle wheel type structure (torsion angle $O1-P-C1-C2$ 154.68°), with the 3-dimethylamino-1-oxo-prop-2-enyl chains almost oriented to the interior of the molecule's cone (Figure 1, top, left and middle).^[9] Looking along the P–O axis of **1**, which is one of the threefold axes of symmetry in the solid-state structure (Figure 1, top, left), makes clear that the orientation of the carbonyl groups determines the docking of the neighbouring molecules. Because of steric reasons, there is only one proton donor site that is able to undergo $C=O\cdots H-C$ hydrogen bonding: a

CH-unit of one of the terminal CH_3 groups. Figure 1, top right, gives a view on the 14-membered ring generated by twofold $C=O\cdots H-C$ hydrogen bonding. These interactions enforce coplanarity of all atoms of the $(O)C-C=C-N-CH$ moieties ($O2-C7-C8-C9-N-C10-H10A$). However, because the nitrogen atom of the dimethylamino group is found in a slightly pyramidal environment, the terminal CH_3 groups, which are not included in hydrogen bonding, are found disordered in two positions (Figure 1, top, left and middle).

Hydrogen bonding under perpetuation of the C_3 symmetry of the $P(Ar)_3$ cores generates in the first step a two-dimensional network, wherein the $P=O$ units, which are oriented parallel to the crystallographic c axis, are alternately pointing up and down (Figure 1, middle, bottom). As shown, the resulting two-dimensional network contains hexagonal pores along a crystallographic S_6 axis. The layers above and below (layer 1 and -1) are linked through these pores by hydrogen bonding between one $P=O$ unit from those layers and one molecule of water (half a molecule

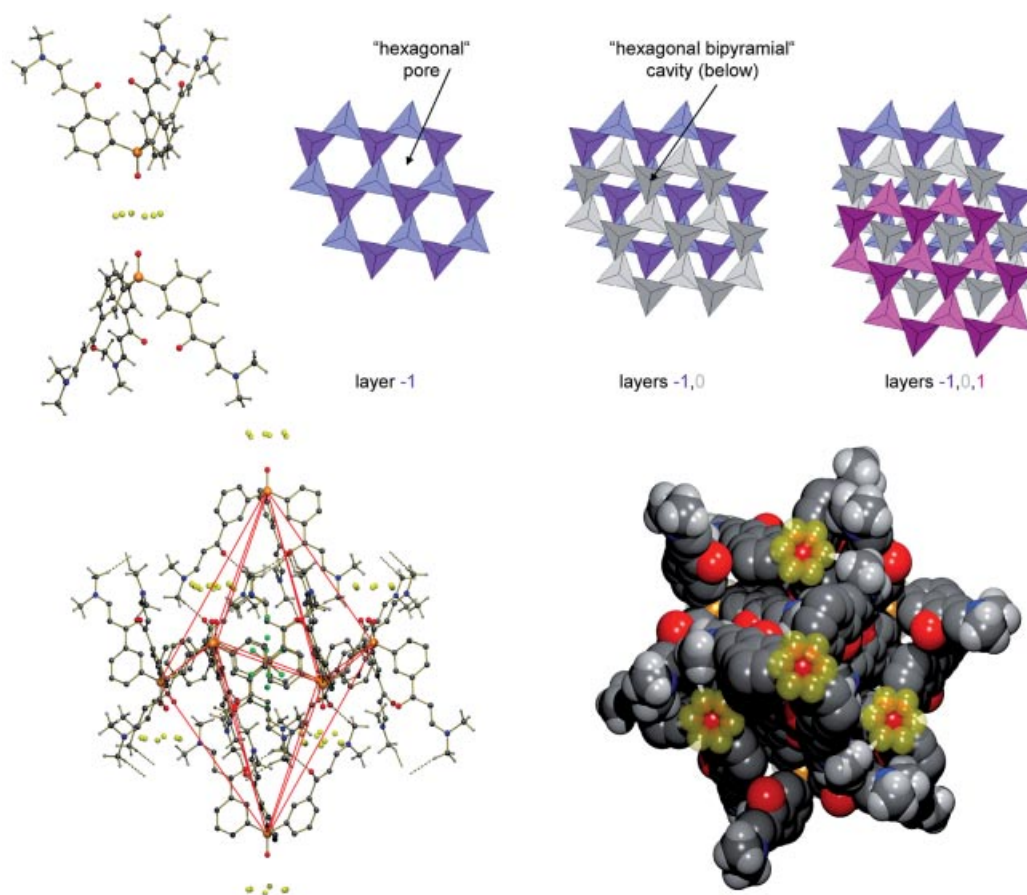


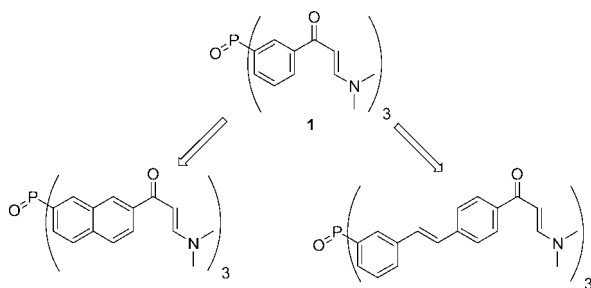
Figure 2. P: orange, O: red, N: blue, water positions: yellow. Top left: molecular view of the linkage between layer 1 and layer -1 by hydrogen bonding to disordered water molecules (yellow) through the pores of layer 0 (not shown); distances $P=O\cdots O_{H_2O}$: 2.95(2) and 2.83(2) [Å]. Top right: layer stacking that results in interconnection through "hexagonal" pores and formation of distorted hexagonal bipyramidal cavities. Bottom left: side view of the distorted hexagonal bipyramidal cavity containing one molecule of acetone on disordered positions (green: observed spots of enhanced electron density). Bottom right: top view (space filling) on one of those cavities including disordered water positions (yellow, translucent).

per formula unit of **1**), which results in two interpenetrating hydrogen bond networks (network 1: odd numbered layers; network 2: even numbered layers, Figure 2, top right). The water molecule is found disordered in six positions in a chair like structure due to the symmetry of the location (Figure 2, top left). The distance between the two water-linked oxygen atoms of the phosphane oxides is 4.895 Å.

Additionally, neighbouring layers form a second, less polar type of cavity, established by six [3-(3-dimethylamino-1-oxoprop-2-enyl)phenyl] side chains. In this cavity, which can be described by a distorted hexagonal bipyramid, one disordered molecule of acetone is enclosed (half a molecule per formula unit of **1**, Figure 2, bottom). The P–P distance between the phosphorus centres on top and on bottom of these cavities is 2.387 nm.

The space group $R\bar{3}$ is known from a series of solid-state structures of simple inorganic systems like dolomite,^[10] perovskites,^[11] silicates,^[12] metal halides and sulfates,^[13] as well as hexafluorometallates.^[14] Additionally, a variety molecular inorganic and organic compounds crystallize in this space group. Some of them, like $\text{TiCl}_3(\text{NPPH}_3)$,^[15] $(\text{PPh}_3)_3\text{Co}-\text{N}\equiv\text{N}-\text{Li}(\text{OEt})_3$ ^[16] or some spherands,^[17] exhibit C_3 symmetry in the single molecules as it is the case for **1**. However, they do not form hydrogen bond networks. On the other hand, there is a series of nonsymmetrical compounds or compounds with lower symmetry than C_3 , which also crystallize in the space group $R\bar{3}$. In those cases, the solid states structures are mainly determined by hydrogen bonding. Among them we have found two systems with interpenetrating hydrogen bond networks: 1,4-(dihydroxymethyl)cubane^[18] and the α -form of hydroquinone.^[19] However, these compounds are too small and are not pre-orientated to build up cavities for the inclusion of guest molecules.

We are now able to start systematic crystal engineering by the synthesis of a series of novel derivatives possessing analogue structural motifs such as **1**: replacement of the phosphane oxide $\text{O}=\text{P}$ group with another group that is unable to undergo hydrogen bonding (e.g. $\text{R}-\text{Si}$) should lead to systems without interpenetrating networks but still with cavities for the inclusion of guest molecules. On the other hand, we will extend the distance between the hydrogen bonding site and the central atom (here: P) to enlarge the cavities for guest inclusion. Scheme 2 shows two examples.



Scheme 2.

Conclusions

In the solid-state structure of **1**, four different strong proton accepting sites are engaged in the formation of hydrogen bonds. The tetrahedral phosphane oxide centre generates an arrangement of the proton accepting sites, which is comparable to certain building blocks frequently used in supramolecular coordination chemistry. However, in our case, the proton accepting sites are due to steric requirements oriented to the “outer” side of the molecule, which results in the formation of a three dimensional hydrogen bond based arrangement in the solid state.

Experimental Section

Tris[3-(3-dimethylamino-1-oxoprop-2-enyl)phenyl]phosphane^[3a] (5.76 g, 10.4 mmol) was dissolved in acetone (100 mL) and oxidized by stirring the solution for 12 h under ambient conditions in the air. The solvent was removed in vacuo to leave **1** as an orange-red microcrystalline solid in almost quantitative yield (5.90 g). Product **1** was recrystallized by slow diffusion of diethyl ether into a saturated solution of acetone. ^1H NMR (400.13 MHz, CDCl_3 , 25 °C): δ = 2.17 (s, 3 H, acetone), 2.44 (br., 1 H, H_2O), 2.91, 3.16 (2 × s, 18 H, NMe_2), 5.66 (d, $^3J_{\text{HH}} = 11.9$ Hz, 3 H, $=\text{CHNMe}_2$), 7.52 (dt, $^4J_{\text{PHm}} = 3.1$ Hz, $^3J_{\text{HmHo}} = ^3J_{\text{HmHp}} = 7.8$ Hz, 3 H, H-*meta*), 7.65 (dd, $^3J_{\text{PHo}} = 11.9$ Hz, 3 H, H-*ortho*), 7.93 [d, 3 H, C(O)CH=], 8.13 (d, 3 H, H-*para*), 8.23 (d, $^3J_{\text{PHo}'} = 12.6$ Hz, 3 H, H-*ortho'*) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, CDCl_3 , 25 °C): δ = 30.3 ppm. $\text{C}_{33}\text{H}_{36}\text{N}_3\text{O}_4\text{P}\cdot(\text{H}_2\text{O})_{0.5}\cdot(\text{C}_3\text{H}_6\text{O})_{0.5}$ (607.68): calcd. C 68.18, H 6.63, N 6.91; found C 68.08, H 6.64, N 6.59.

Acknowledgments

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- S: 0.851; min. and max. resd. density: $-0.12, 0.16$ [$\text{e} \text{ \AA}^{-3}$]. All crystals investigated were twinned. The crystals used for structure determination was largely cleaned from grown up species. The data were obtained with an IPDS diffractometer. The hydrogen atoms were localized geometrically, a riding model was taken for refinement. IPDS software: IPDS Operating, System Version 2.8., Stoe & Cie. GmbH, Darmstadt (Germany) **1997**. Software used for structure solution: A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, SIR92, *J. Appl. Crystallogr.* **1994**, 27, 435–436. Software used for structure refinement: G. M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen (Germany), **1998**. CCDC-628298 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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