

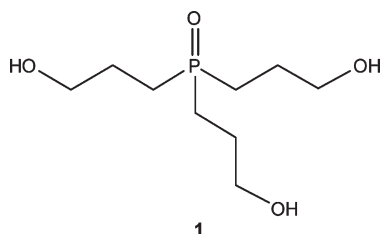
Tris(hydroxypropyl)phosphine Oxide: A Chiral Three-Dimensional Material with Nonlinear Optical Properties

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ABSTRACT: The achiral C_{3v} organic phosphine tris(hydroxypropyl)phosphine oxide (**1**) crystallizes in the unusual chiral hexagonal space group $P6_3$. The structure is highly ordered because each phosphine oxide moiety forms three hydrogen bonds with adjacent hydroxy groups from three different molecules. The properties of the crystals and the presence of hydrogen bonding interactions were investigated using single crystal Raman spectroscopy. The crystals show nonlinear optical properties and are capable of efficient second harmonic generation.

In recent years, there has been considerable interest in crystal engineering, the predictable design and synthesis of supramolecular materials with specific properties from molecular building blocks.¹ One of the main applications of crystal engineering is the design of compounds for second-order nonlinear optics, which play a crucial role in photonic technology.² In general, only non-centrosymmetric solids display nonlinear optical properties and the controlled synthesis of molecules of this type is often difficult. Here, we report that a simple nonchiral organic compound, tris(hydroxypropyl)phosphine oxide **1**, has an extremely unusual chiral three-dimensional (3D) supramolecular structure and displays nonlinear optical properties. In addition, we utilize single crystal Raman spectroscopy to probe the properties of the molecule.



Colorless crystals of **1** were grown from a saturated solution of acetone at room temperature.³ Even though **1** is an achiral molecule with C_{3v} symmetry, it crystallizes in the chiral hexagonal space group $P6_3$. This is an extremely unusual space group and a search of the Cambridge Structural Database reveals only 331 examples (currently, the total number of structures in the database is greater than 450 000) and less than 80 which involve simple organic molecules with no metals present.⁴ A number of symmetric amine,⁵ phosphine,⁶ arsine,^{6a,7} and phosphine oxide⁸ derivatives have molecular structures similar to **1** but very different 3D packing (Figure 1). In general, the observed bond lengths and angles in **1** are unremarkable, except the $P=O$ bond length (1.513(2) Å) is considerably lengthened in comparison to trimethylphosphine oxide (1.44 Å)⁹ or phosphorus pentoxide (1.43 Å).¹⁰ The $P=O$ bond is presumably elongated because each phosphine oxide unit is hydrogen bonded to three hydroxy groups from three different adjacent molecules, with a

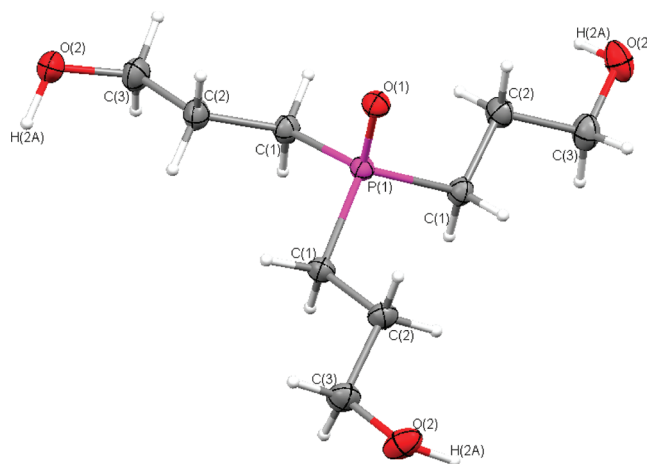


Figure 1. Solid-state structure of **1**. Selected bond distances (Å) and angles (°) of **1**: P(1)–O(1) 1.513(2), P(1)–C(1) 1.8003(15), O(2)–C(3) 1.413(3), C(1)–C(2) 1.529(3), C(2)–C(3) 1.514(2), O(1)–P(1)–C(1) 112.17(5), C(1)–P(1)–C(1) 106.65(8), P(1)–C(1)–C(2) 113.18(10), O(2)–C(3)–C(2) 112.15(15), C(1)–C(2)–C(3) 112.02(14).

$P=O \cdots HO$ distance of 1.886 Å (Figure 2). This distance is consistent with values observed for organic carbonyls multiply hydrogen bonded to amines or alcohols,¹¹ and lengthening of the $P=O$ bond due to hydrogen bonding has been observed in other systems.¹² Further confirmation of the presence of hydrogen bonding can be inferred from the melting point of **1** which is 88–90 °C and is significantly higher than those observed for the related compounds $(OHCH_2)_3P=O$ and $(OHCH_2CH_2)_3P=O$, which are both liquids at room temperature.¹³

Analysis of the crystal packing of **1** reveals that the hydrogen bonds create an unusual supramolecular structure which is highly ordered (Figure 3). The 3D arrangement of molecules in **1** is similar to the arrangement recently reported for $\{P(S)[N(CH_3)_2NH_2]_3\}$, in which the sulfur atom acts as a hydrogen bond acceptor and interacts with three amino groups from three different adjacent molecules.¹⁴ Looking down the crystallographic a - or b -axis of **1**, it can be seen that a layered structure is formed. Any given layer n is staggered with respect to an adjacent layer ($n + 1$ or $n - 1$) but is eclipsed with respect to a layer two units away ($n + 2$ or $n - 2$). The crystallographic c -axis shows that this gives rise to a structure which contains regular

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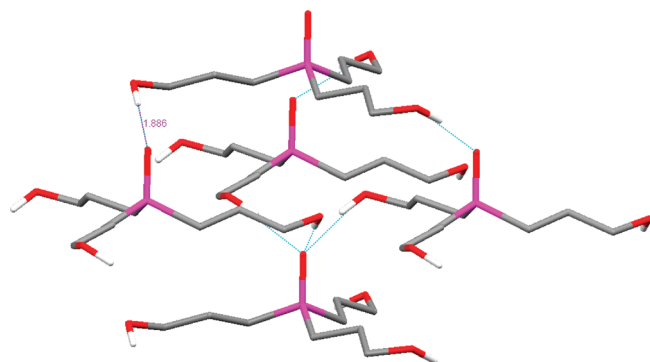


Figure 2. Hydrogen bonds between OH and P=O functional groups in **1**.

tubular channels, which are hydrophobic in nature because of the orientation of the CH₂ groups. The diameter of the pores is approximately 3.5 Å, which is presumably too small to trap solvent and explains why the channels are empty. **1** is a rare example of a structure with a tubular architecture which is built from a small molecule, as commonly larger molecules such as peptides, oligosaccharides, cyclodextrins, and calixarenes are used as the building blocks.¹⁴

In order to further investigate the highly ordered and anisotropic nature of the crystals, single crystal Raman spectroscopy was performed on **1**. Four different sets of data were collected, with the crystal oriented so that the crystallographic *c*-axis (coincident with the crystal *z*-axis in a hexagonal structure) was either perpendicular or parallel to the polarization of incident light and the detector set either perpendicular or parallel to the excitation plane.¹⁵ In addition, a control experiment was performed in which polarized light was used to excite the crystal, but an unpolarized Raman spectrum was recorded. With the exception of the regions containing the O–H stretch, the spectra were highly anisotropic.¹⁵ The O–H stretching frequency was approximately 3450 cm^{−1}, which is considerably lower than the expected value for a free hydroxy group and provides clear evidence that the hydroxy groups are involved in hydrogen bonding.¹⁶ Analysis of Figure 3 shows that there is an O–H bond approximately aligned with all three crystallographic axes, which explains why crystal orientation does not significantly affect the stretch at 3450 cm^{−1}.

The most complicated region of the spectrum is between 1000 and 1500 cm^{−1} (Figure 4). Comparison of the spectra with the crystallographic *c*-axis perpendicular and parallel to the polarization of incident light and the analyzer set parallel to the excitation plane reveals many more peaks in the perpendicular spectrum. This is not surprising as with the exception of the P=O bond and one C–H bond, the rest of the C–C and C–H bonds are at least partially normal to the crystallographic *c*-axis (the P=O stretch, C–C stretches, and C–H bending modes are expected to give bands between 1000 and 1500 cm^{−1}).^{16,17} We assign the bands above 1200 cm^{−1} in the perpendicular spectrum to linear combinations of C–C stretching modes, which is consistent with previous literature and also density functional theory (DFT) calculations.^{15,17} The four peaks below 1200 cm^{−1} are attributed to linear combinations of C–H bending modes.

The parallel spectrum only contains two major peaks at 1040 and 1085 cm^{−1} (Figure 4). The band at 1040 cm^{−1} is present in both the parallel and perpendicular spectrum and is therefore assigned as a C–H bending mode. In contrast, the peak at 1085 cm^{−1} is only present in the parallel spectrum and is attributed to the P=O stretch. A comparison of the spectra collected with the crystal parallel to the *c*-axis and the analyzer either parallel or perpendicular to the excitation plane (Figure 4) shows the band at 1085 cm^{−1} is highly polarized (the depolarization ratio is signi-

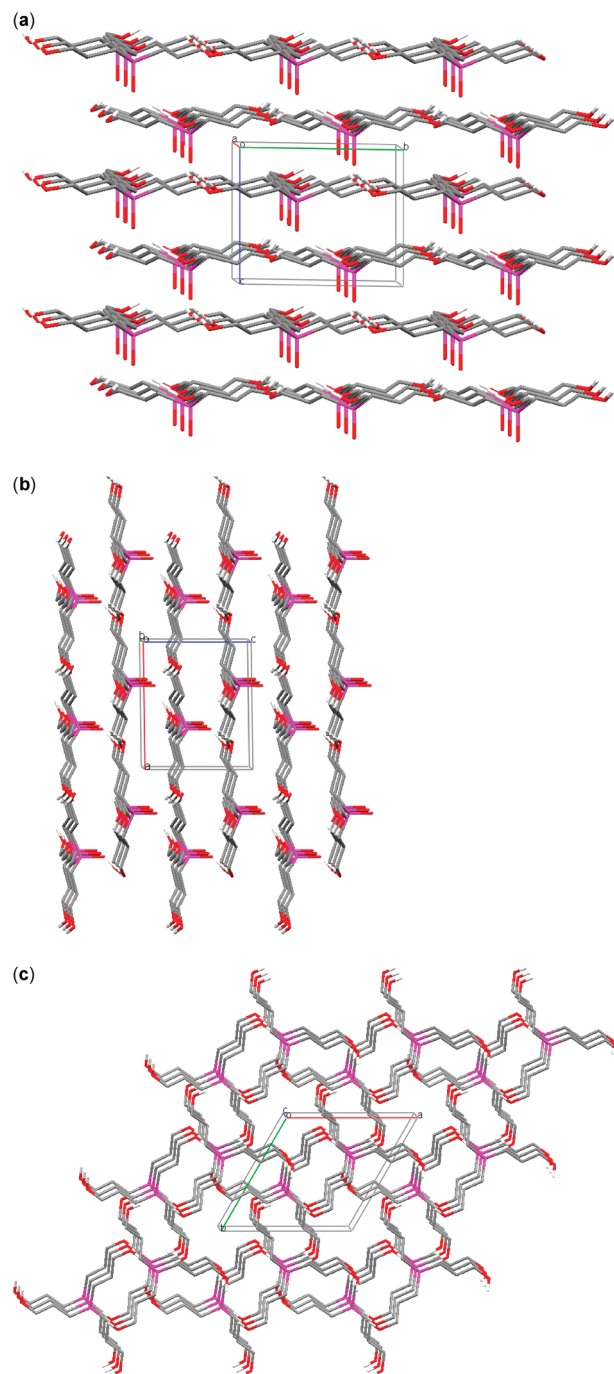


Figure 3. Packing diagram for **1** with H atoms attached to C omitted for clarity, (a) viewed down the crystallographic *a*-axis; (b) viewed down the crystallographic *b*-axis; and (c) viewed down the crystallographic *c*-axis.

ficantly less than 0.75). Further evidence to support our assignment comes from the absence of the peak at 1085 cm^{−1} in the Raman spectrum recorded with the crystal perpendicular to the *c*-axis and the analyzer set to record unpolarized light.¹⁵ A stretching frequency of 1085 cm^{−1} is unusually low for a P=O bond,¹⁷ but we believe that hydrogen bonding weakens the bond and as result lowers the vibrational frequency. DFT calculations predict a P=O stretching frequency of 1200 cm^{−1} when there are no hydrogen bonding interactions between the P=O bond and adjacent O–H groups, but as the number of hydrogen bonding interactions is increased, the calculated value becomes closer to the experimental value. If one hydrogen bonding interaction is

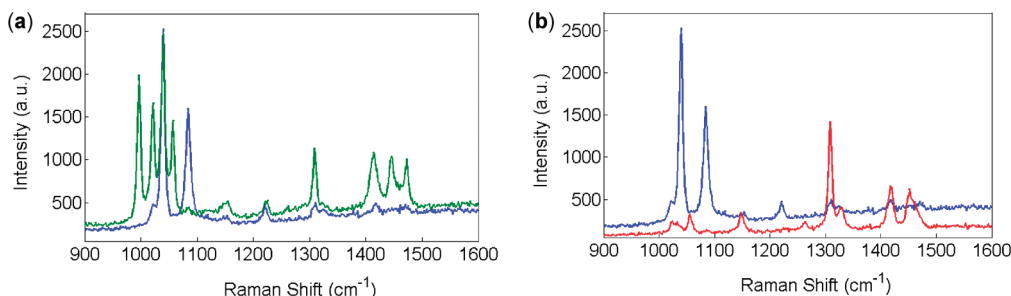


Figure 4. Single crystal Raman spectra of **1** between 900 and 1600 cm^{-1} , (a) comparison of spectra with the crystallographic c -axis parallel (blue) and perpendicular (green) to the polarization of incident light with the analyzer set parallel to the excitation plane, (b) comparison of spectra with the crystallographic c -axis parallel to the polarization of incident light source and the analyzer set parallel (blue) or perpendicular (red) to the excitation plane.

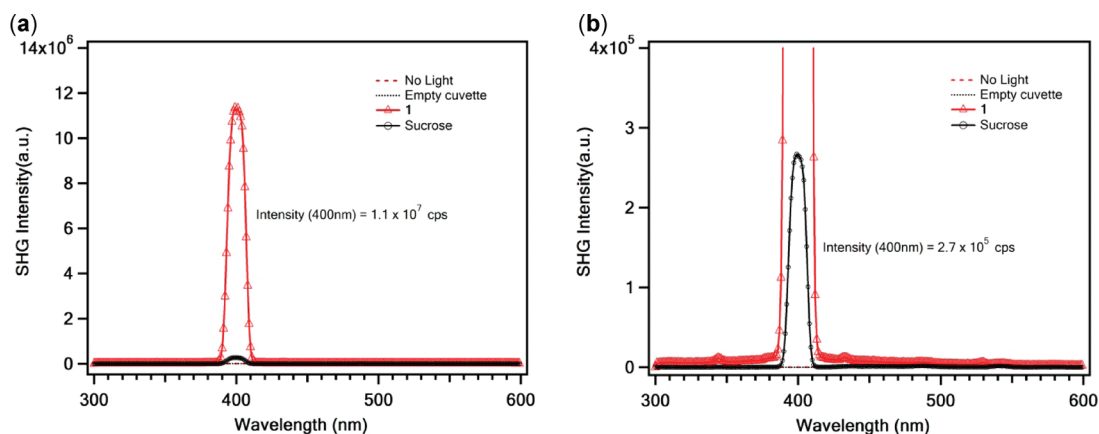


Figure 5. SHG spectra for sucrose and **1**, (a) full spectrum; (b) expansion of sucrose peak.

included, calculations predict a $\text{P}=\text{O}$ stretching frequency of 1165 cm^{-1} and if two are included the stretch is lowered even further to 1140 cm^{-1} (unfortunately, a calculation with three hydrogen bonding interactions could not be performed due to computational limitations).¹⁵

The Raman spectra of single crystals of **1** confirm the anisotropic nature of the material and highly ordered non-centrosymmetric crystals have been shown to have interesting nonlinear optical properties.² One of the most well studied nonlinear optical properties is second harmonic generation (SHG), in which photons at frequency ω interact with a nonlinear bulk material to generate second-harmonic photons with twice the energy at frequency 2ω . Ammonium dihydrogenphosphate (ADP) is a common material used to demonstrate nonlinear optical and electro-optic properties, and it is known that sucrose crystals possess approximately 20% of the efficiency of ADP for SHG.¹⁸ In our study, sucrose crystals were used as a reference. Crystals of sucrose or **1** were placed into a 1 mm transparent cuvette and the fundamental light at 800 nm from a Ti:sapphire oscillator was focused onto the samples.¹⁵ The scattered photons were collected with a 100-mm lens, focused onto the slit of a monochromator for spectral dispersion, and then detected by a photomultiplier tube. The SHG spectra were recorded and a well-defined peak was observed at 400 nm for both sucrose and **1** (Figure 5). The 400 nm signal was not detected when an empty cuvette was used or there was no input light, confirming that the 400 nm peak in the spectra originated from either the sucrose crystals or **1**.

Even though the second harmonic intensity of crystals of **1** is approximately 50 times greater than that of sucrose, it is difficult to compare the two compounds because the packing of the crystals in the cuvette and the size of the crystals are different. Although we believe that the nonlinearity of **1** is likely to be bigger

than sucrose, more quantitative measurements are needed in order to confirm this conclusion. At this stage, we believe that **1** can be classified as either a Class A or B material for SHG using the classification system described by Kurtz and Perry¹⁹ and to the best of our knowledge is the first example of a simple organic phosphine displaying nonlinear optical properties.

In conclusion, we have reported the crystal structure of a simple organic molecule, tris(hydroxypropyl)phosphine oxide, which is highly ordered due to hydrogen bonding between adjacent molecules and displays second-order nonlinear optical properties. Future work will look to understand how modifying the substituents on the phosphine change the packing of the molecules and affect SHG. Variations to the substituents may also create larger channels in the structure, making the materials suitable for use in hydrogen or carbon dioxide storage.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **1**, details of DFT calculations, and the experimental protocol for Raman and SHG measurements are available free of charge via the Internet at <http://pubs.acs.org>.

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