

Supporting Information

Tris(hydroxypropyl)phosphine Oxide: A Chiral 3D Material with Non-linear Optical Properties

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I. Synthesis of **1**

Tris(hydroxypropyl)phosphine oxide (**1**) was prepared using literature methods.¹ The ¹H and ³¹P NMR chemical shifts were consistent with those previously reported.¹ Crystals were grown from a saturated solution in acetone at room temperature.

Reference

(1) Moiseev, Dmitry V. (2006), *Inorg. Chem.*, *45*, 10338-10346.

II. X-ray Crystallography of **1**

Data Collection

A colorless block crystal of C₉H₂₁O₄P having approximate dimensions of 0.39 x 0.12 x 0.11 mm was mounted in a loop. All measurements were made on a Rigaku Mercury2 CCD area detector with filtered Mo-K α radiation.

Indexing was performed from 6 images that were exposed for 20.0 seconds. The crystal-to-detector distance was 49.90 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive hexagonal cell (laue class: 6/m) with dimensions:

$$\begin{aligned} a &= 9.736(4) \text{ \AA} \\ c &= 7.223(3) \text{ \AA} \\ V &= 592.9(4) \text{ \AA}^3 \end{aligned}$$

For $Z = 2$ and F.W. = 224.24, the calculated density is 1.256 g/cm³. Based on the systematic absences of: 000l: $l \neq 2n$, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: P6₃ (#173).

The data were collected at a temperature of $-50 \pm 1^\circ\text{C}$ to a maximum 2θ value of 54.8° . A total of 330 oscillation images were collected. A sweep of data was done using ω scans from -120.0 to 60.0° in 1.0° step, at $\chi=54.0^\circ$ and $\phi = 0.0^\circ$. The exposure rate was 20.0 [sec./ $^\circ$]. The detector swing angle was -28.40° . A second sweep was performed using ω scans from -120.0 to 60.0° in 1.0° step, at $\chi=54.0^\circ$ and $\phi = 120.0^\circ$. The exposure rate was 20.0 [sec./ $^\circ$]. The detector swing angle was -28.40° . The crystal-to-detector distance was 49.90 mm. Readout was performed in the 0.146 mm pixel mode.

Data Reduction

Of the 3802 reflections that were collected, 908 were unique ($R_{\text{int}} = 0.026$). Data were collected and processed using CrystalClear (Rigaku). Net intensities and sigmas were derived as follows:

$$F^2 = [\Sigma(P_i - mB_{\text{ave}})] \cdot Lp^{-1}$$

where P_i is the value in counts of the i^{th} pixel
 m is the number of pixels in the integration area
 B_{ave} is the background average
 L_p is the Lorentz and polarization factor

$$B_{\text{ave}} = \Sigma(B_j)/n$$

where n is the number of pixels in the background area
 B_j is the value of the j^{th} pixel in counts

$$\sigma^2(F^2_{\text{hkl}}) = [(\Sigma P_i) + m((\Sigma(B_{\text{ave}} - B_j)^2)/(n-1))] \cdot L_p \cdot \text{errmul} + (\text{erradd} \cdot F^2)^2$$

where $\text{erradd} = 0.00$
 $\text{errmul} = 1.00$

The linear absorption coefficient, μ , for Mo-K α radiation is 2.213 cm⁻¹. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.860 to 0.976. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods² and expanded using Fourier techniques.³ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement⁴ on F^2 was based on 907 observed reflections and 48 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.0301$$

$$wR2 = [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2} = 0.0697$$

The standard deviation of an observation of unit weight⁵ was 1.04. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.23 and -0.15 e-/Å³, respectively. The absolute structure was deduced based on Flack parameter, 0.09(12), using 416 Friedel pairs.⁶

Neutral atom scattering factors were taken from Cromer and Waber.⁷ Anomalous dispersion effects were included in F_{calc} ; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.⁹ The values for the mass attenuation coefficients are those of Creagh and Hubbell.¹⁰ All calculations were performed using the CrystalStructure¹¹ crystallographic software package except for refinement, which was performed using SHELXL-97.¹²

References

(1) CrystalClear: Rigaku Corporation, 1999. CrystalClear Software User's Guide, Molecular Structure Corporation, (c) 2000. J.W. Pflugrath (1999) Acta Cryst. D55, 1718-1725.

(2) SIR92: Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M., Polidori, G., and Camalli, M. (1994) J. Appl. Cryst., 27, 435.

(3) DIRDIF99: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M. (1999). The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

(4) Least Squares function minimized: (SHELXL97)

$$\sum w(F_o^2 - F_c^2)^2 \quad \text{where } w = \text{Least Squares weights.}$$

(5) Standard deviation of an observation of unit weight:

$$[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$$

where: N_o = number of observations

N_v = number of variables

(6) Flack, H. D. (1983), Acta Cryst. A39, 876-881.

(7) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(8) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(9) Creagh, D. C. & McAuley, W.J. ; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(10) Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

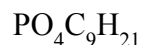
(11) CrystalStructure 3.8: Crystal Structure Analysis Package, Rigaku and Rigaku Americas (2000-2007). 9009 New Trails Dr. The Woodlands TX 77381 USA.

(12) SHELX97: Sheldrick, G.M. (1997).

Experimental Details

A. Crystal Data

Empirical Formula



Formula Weight

224.24

Crystal Color, Habit

colorless, block

Crystal Dimensions	0.39 X 0.12 X 0.11 mm
Crystal System	hexagonal
Lattice Type	Primitive
Indexing Images	6 images @ 20.0 seconds
Detector Position	49.90 mm
Pixel Size	0.146 mm
Lattice Parameters	a = 9.736(4) Å c = 7.223(3) Å V = 592.9(4) Å ³
Space Group	P6 ₃ (#173)
Z value	2
D _{calc}	1.256 g/cm ³
F ₀₀₀	244.00
μ(MoKα)	2.213 cm ⁻¹
B. Intensity Measurements	
Diffractometer	Rigaku SCXmini
Radiation	MoKα (λ = 0.71075 Å)
Detector Aperture	75 mm round
Data Images	330 exposures
ω oscillation Range (χ=54.0, φ=0.0)	-120.0 - 60.0°
Exposure Rate	20.0 sec./°
Detector Swing Angle	-28.40°
ω oscillation Range (χ=54.0, φ=120.0)	-120.0 - 60.0°
Exposure Rate	20.0 sec./°
Detector Swing Angle	-28.40°
Detector Position	49.90 mm
Pixel Size	0.146 mm
2θ _{max}	54.8°
No. of Reflections Measured	Total: 3802 Unique: 907 (R _{int} = 0.026) Friedel pairs: 416
Corrections	Lorentz-polarization Absorption (trans. factors: 0.860 - 0.976)
C. Structure Solution and Refinement	
Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F ²
Function Minimized	Σ w (F _o ² - F _c ²) ²
Least Squares Weights	w = 1 / [σ ² (F _o ²) + (0.0456 · P) ² + 0.0000 · P]

	where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	54.8°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	907
No. Variables	48
Reflection/Parameter Ratio	18.90
Residuals: R1 ($I > 2.00\sigma(I)$)	0.0301
Residuals: R (All reflections)	0.0319
Residuals: wR2 (All reflections)	0.0697
Goodness of Fit Indicator	1.041
Flack Parameter	0.09(12)
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.23 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.15 e ⁻ /Å ³

III. Experimental Procedure for Raman Spectroscopy

Raman spectra were recorded on a Renishaw M1000 MicroRaman spectrometer. Excitation was performed at 514.5 nm using an Ar ion laser operating at 5 mw at the sample. Spot size was reduced to approximately 4 μm using a 50x objective lens. The entrance slit was adjusted to provide 4 cm⁻¹ resolution. Polarized spectra were collected by aligning the c-axis of a single crystal either parallel or perpendicular to the E-vector of the laser. Rayleigh scattering was removed by passing Raman scattered light through a Semrock RazorEdge® long wave pass filter for the 514.5 nm laser before passing through a Polaroid film polarizer to select light oriented parallel to the original E-vector of the laser. A λ/2 plate was added to select perpendicular light. Unpolarized spectra were collected using a quartz wedge polarization scrambler. The signal was detected with a Peltier-cooled CCD detector. Peak positions were calibrated against a single crystal silicon standard.

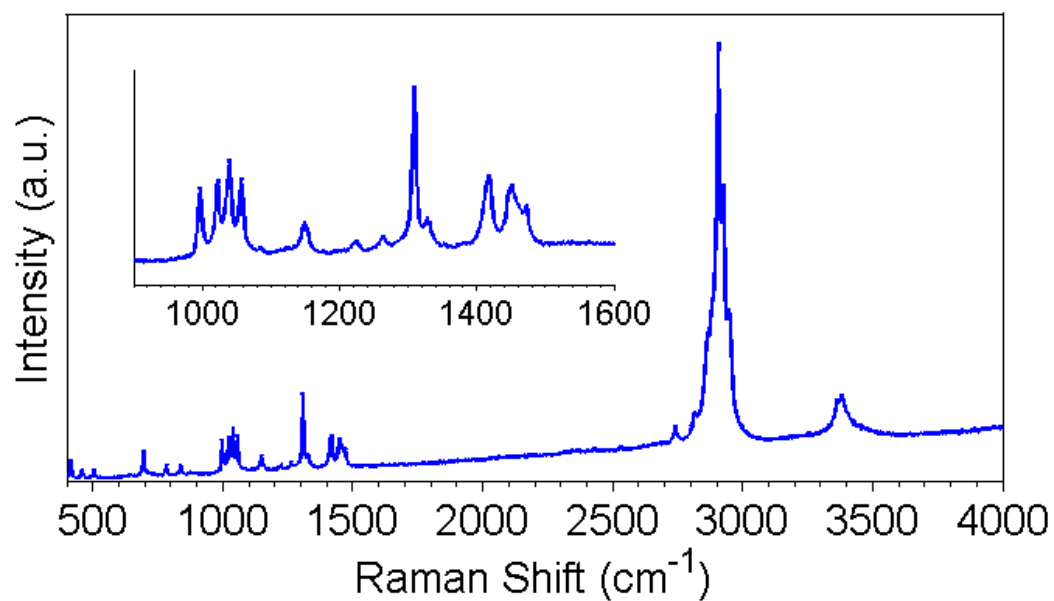


Figure S1: Raman spectrum of **1** with crystallographic c-axis perpendicular to the polarized light source and the analyzer set to record unpolarized light.

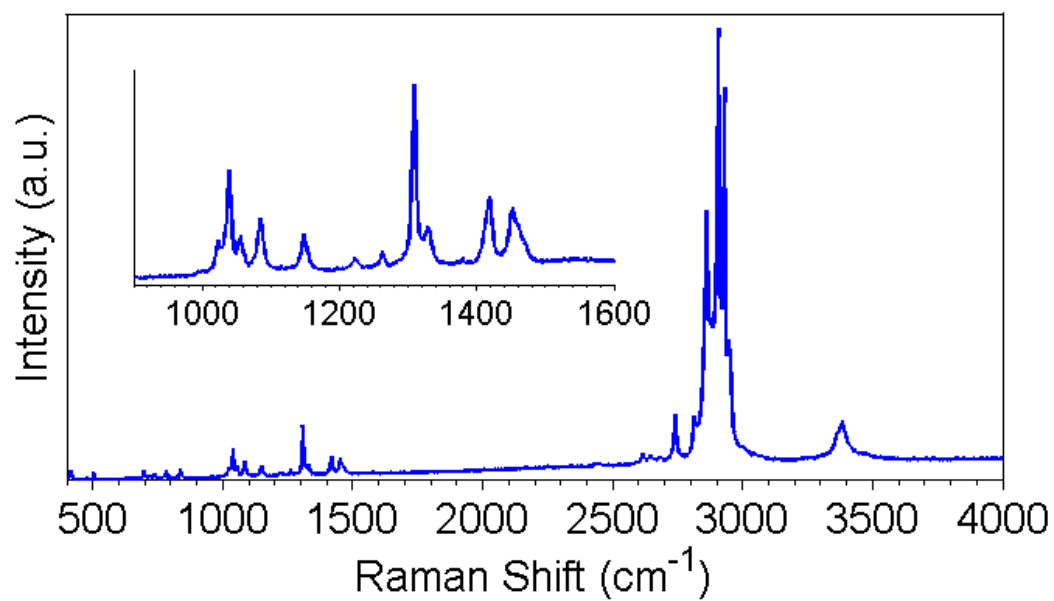


Figure S2: Raman spectrum of **1** with crystallographic c-axis parallel to the polarized light source and the analyzer set to record unpolarized light.

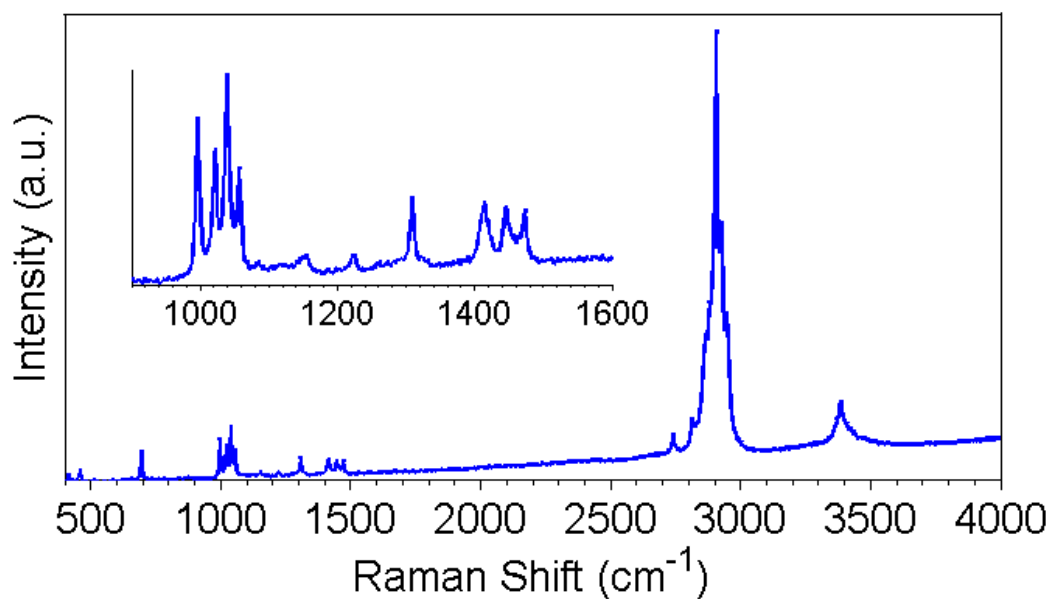


Figure S3: Raman spectrum of **1** with crystallographic c-axis perpendicular to the polarized light source and the analyzer set to record light parallel to the excitation plane.

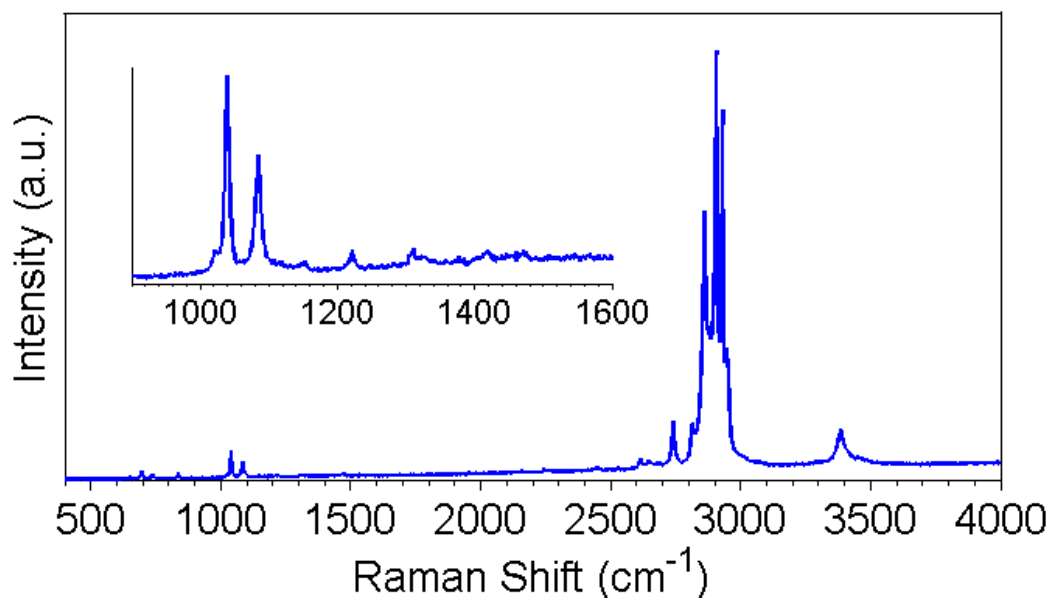


Figure S4: Raman spectrum of **1** with crystallographic c-axis parallel to the polarized light source and the analyzer set to record light parallel to the excitation plane.

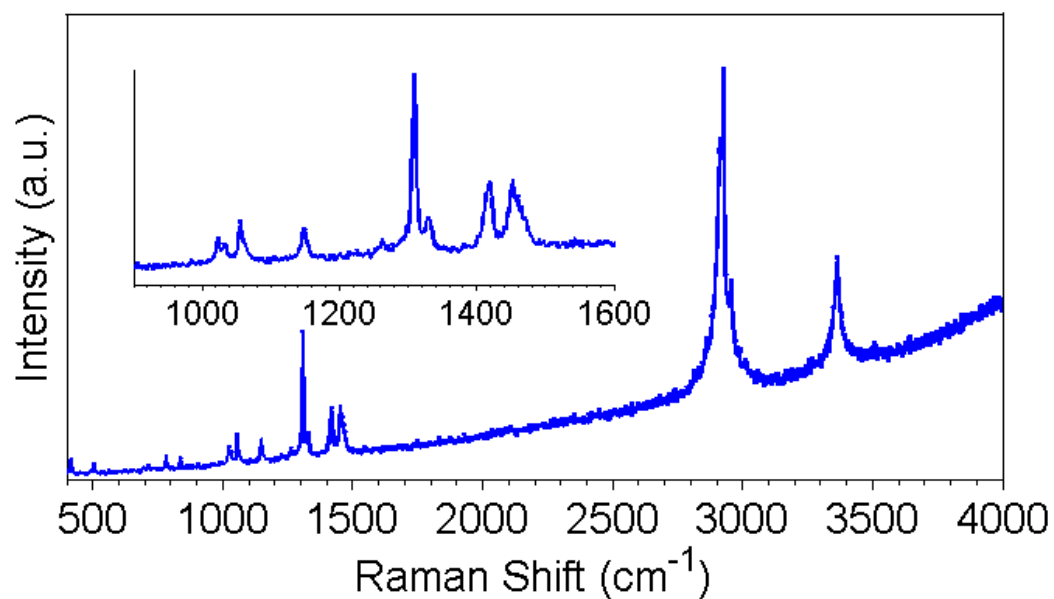


Figure S5: Raman spectrum of **1** with crystallographic c-axis perpendicular to the polarized light source and the analyzer set to record light perpendicular to the excitation plane.

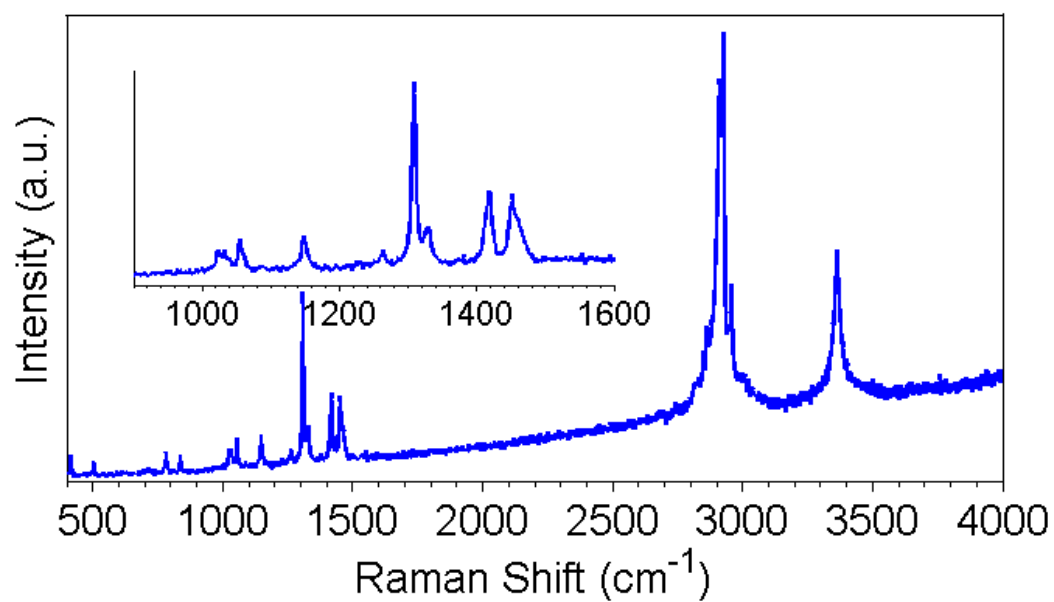


Figure S6: Raman spectrum of **1** with crystallographic c-axis parallel to the polarized light source and the analyzer set to record light perpendicular to the excitation plane.

IV. Computational Details

Density functional calculations were carried out using Gaussian 09 Revision A.02.¹ Calculations were performed using the B3LYP functional and the 6-31G** basis set was used for all atoms. Initial geometries were obtained using the coordinates from X-ray structures and all optimized structures were verified using frequency calculations to check that they did not contain any imaginary frequencies.

The following table compares experimental and calculated bond distances and angles and shows that there was excellent agreement.

Table S1: Comparison of experimental and calculated bond lengths (Å) and angles (°) for **1**.

	Experimental	Calculated
P(1)-O(1)	1.513(2)	1.507
P(1)-C(1)	1.8003(15)	1.848
O(2)-C(3)	1.413(3)	1.425
C(1)-C(2)	1.529(3)	1.538
C(2)-C(3)	1.514(2)	1.533
O(1)-P(1)-C(1)	112.17(5)	113.78
C(1)-P(1)-C(1)	106.65(8)	104.85
P(1)-C(1)-C(2)	113.18(10)	113.31
O(2)-C(3)-C(2)	112.15(15)	113.04
C(1)-C(2)-C(3)	112.02(14)	111.84

In order to reproduce the observed hydrogen bonding, calculations were also performed with both one and two additional molecule of tris(hydroxypropyl)phosphine oxide forming a hydrogen bond with the central P=O double bond of **1**. Due to restrictions related to the number of atoms present, a calculation could not be performed with three additional molecules of tris(hydroxypropyl)phosphine forming hydrogen bonds to **1**. For the calculations with two additional molecules of tris(hydroxypropyl)phosphine oxide, a QMMM model was utilized using ONIOM(b3lyp:UFF) as implemented in Gaussian 09. In this calculation the only the propyl arms of the two additional molecules of tris(hydroxypropyl)phosphine oxide involved in hydrogen bonding were treated using DFT (along with all of **1**) and the remainder of these two molecules was treated at the UFF level.

The xyz coordinates for all the optimized structures are given below.

1

P 0.000 0.000 0.258
O 0.000 0.000 1.765
O 0.089 5.297 0.164

C 0.623 1.572 -0.487
C 0.000 2.831 0.139
C 0.593 4.115 -0.452
H 1.710 1.586 -0.333
H 0.454 1.543 -1.573
H -1.088 2.834 -0.022
H 0.160 2.824 1.222
H 1.674 4.145 -0.280
H 0.430 4.146 -1.542
H -0.869 5.348 0.016
O -4.632 -2.572 0.164
C -1.673 -0.247 -0.487
C -2.452 -1.416 0.139
C -3.860 -1.544 -0.452
H -2.229 0.688 -0.333
H -1.563 -0.378 -1.573
H -1.910 -2.360 -0.022
H -2.525 -1.273 1.222
H -4.426 -0.623 -0.280
H -3.805 -1.701 -1.542
H -4.197 -3.426 0.016
O 4.543 -2.725 0.164
C 1.050 -1.326 -0.487
C 2.452 -1.416 0.139
C 3.267 -2.571 -0.452
H 0.519 -2.274 -0.333
H 1.109 -1.165 -1.573
H 2.999 -0.474 -0.022
H 2.365 -1.550 1.222
H 2.752 -3.522 -0.280
H 3.376 -2.445 -1.542
H 5.066 -1.921 0.016

1 with one hydrogen bond

P -3.061 -0.043 -0.377
O -2.507 -0.455 0.972
O -7.410 -2.944 0.461
C -4.891 -0.241 -0.495
C -5.387 -1.604 0.016
C -6.909 -1.733 -0.099
H -5.344 0.564 0.099
H -5.188 -0.076 -1.541
H -4.913 -2.417 -0.553
H -5.090 -1.738 1.062
H -7.400 -0.935 0.468
H -7.223 -1.633 -1.151
H -7.027 -3.697 -0.016
O 1.115 -2.382 -2.549
C -2.353 -0.964 -1.813
C -0.879 -1.336 -1.584
C -0.178 -1.880 -2.834
H -2.950 -1.870 -1.977
H -2.477 -0.336 -2.707
H -0.312 -0.468 -1.226
H -0.824 -2.090 -0.793

H -0.744 -2.721 -3.254
H -0.137 -1.094 -3.609
H 1.631 -1.705 -2.062
O -2.783 4.997 1.220
C -2.729 1.732 -0.756
C -3.006 2.674 0.426
C -2.642 4.126 0.100
H -1.670 1.797 -1.044
H -3.315 2.017 -1.641
H -4.069 2.625 0.708
H -2.435 2.348 1.302
H -1.587 4.197 -0.184
H -3.236 4.490 -0.753
H -3.718 5.038 1.474
P 3.061 -0.044 0.377
O 2.506 -0.456 -0.972
O 7.409 -2.946 -0.460
C 4.890 -0.241 0.495
C 5.387 -1.605 -0.016
C 6.909 -1.734 0.099
H 5.344 0.563 -0.100
H 5.188 -0.076 1.540
H 4.913 -2.418 0.554
H 5.089 -1.739 -1.062
H 7.400 -0.936 -0.468
H 7.223 -1.634 1.151
H 7.026 -3.698 0.017
O -1.115 -2.381 2.550
C 2.353 -0.964 1.813
C 0.879 -1.336 1.584
C 0.178 -1.879 2.835
H 2.950 -1.870 1.977
H 2.477 -0.335 2.707
H 0.312 -0.467 1.227
H 0.823 -2.089 0.793
H 0.744 -2.720 3.254
H 0.137 -1.093 3.609

1 with two hydrogen bonds

P 4.593 -1.523 -0.866
O 4.073 -1.824 -2.254
O 7.373 -5.891 -0.599
C 6.224 -2.316 -0.647
C 6.111 -3.843 -0.640
C 7.495 -4.495 -0.590
H 6.882 -1.998 -1.483
H 6.667 -1.965 0.309
H 5.533 -4.169 0.251
H 5.582 -4.185 -1.556
H 8.082 -4.189 -1.483
H 8.048 -4.161 0.317
H 7.096 -6.158 0.316
O -0.212 -1.263 1.166
C 3.416 -2.141 0.369
C 2.007 -1.565 0.154

C 1.067 -1.865 1.321
H 3.384 -3.232 0.314
H 3.799 -1.874 1.359
H 2.035 -0.477 0.041
H 1.565 -1.957 -0.767
H 0.896 -2.941 1.421
H 1.539 -1.526 2.259
H -0.089 -0.369 0.799
O 6.874 2.894 -2.337
C 4.762 0.283 -0.660
C 5.834 0.857 -1.589
C 5.920 2.379 -1.449
H 3.786 0.762 -0.886
H 5.027 0.495 0.397
H 6.822 0.418 -1.336
H 5.589 0.602 -2.643
H 4.935 2.832 -1.689
H 6.180 2.656 -0.401
H 7.764 2.694 -1.946
P -4.534 -1.693 -1.089
O -4.296 -2.867 -2.012
O -3.820 -4.308 3.334
C -3.569 -1.931 0.442
C -4.163 -3.031 1.323
C -3.265 -3.301 2.534
H -2.532 -2.204 0.158
H -3.551 -0.972 1.001
H -5.167 -2.718 1.682
H -4.268 -3.968 0.734
H -2.265 -3.639 2.186
H -3.124 -2.370 3.129
H -4.562 -3.889 3.844
O -9.369 -0.910 -2.773
C -6.313 -1.585 -0.696
C -7.135 -1.231 -1.938
C -8.632 -1.215 -1.620
H -6.647 -2.567 -0.298
H -6.459 -0.813 0.088
H -6.836 -0.227 -2.309
H -6.942 -1.978 -2.739
H -8.945 -2.217 -1.258
H -8.849 -0.474 -0.817
H -9.277 0.068 -2.919
O -0.594 1.443 -2.546
C -3.995 -0.168 -1.911
C -2.464 -0.052 -1.971
C -2.003 1.263 -2.600
H -4.421 -0.151 -2.920
H -4.424 0.681 -1.367
H -2.032 -0.098 -0.967
H -2.031 -0.885 -2.535
H -2.278 1.308 -3.658
H -2.520 2.101 -2.101
H -0.313 1.353 -1.619
P -0.091 2.583 1.229
O 0.018 1.418 0.261

O 4.967 2.052 2.710
 C 1.546 3.322 1.616
 C 2.588 2.319 2.133
 C 3.969 2.965 2.273
 H 1.898 3.768 0.680
 H 1.397 4.143 2.328
 H 2.280 1.921 3.107
 H 2.662 1.470 1.449
 H 4.311 3.325 1.299
 H 3.915 3.834 2.944
 H 4.754 1.755 3.601
 O -3.958 0.191 3.939
 C -0.852 2.104 2.832
 C -2.125 1.252 2.685
 C -2.818 1.036 4.032
 H -0.098 1.541 3.391
 H -1.049 3.024 3.396
 H -2.832 1.735 1.998
 H -1.864 0.281 2.258
 H -2.141 0.533 4.726
 H -3.089 2.005 4.478
 H -4.574 0.563 3.300
 O -1.266 6.217 -2.473
 C -1.123 3.963 0.592
 C -0.666 4.562 -0.748
 C -1.621 5.665 -1.212
 H -2.136 3.559 0.494
 H -1.162 4.733 1.373
 H 0.339 4.988 -0.645
 H -0.610 3.787 -1.517
 H -2.626 5.257 -1.348
 H -1.688 6.454 -0.447
 H -0.387 6.604 -2.411

References

(1) Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, Jr., J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, Millam, N. J., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R. E., Stratmann, O., Yazyev, A. J., Austin, R., Cammi, C., Pomelli, J. W., Ochterski, R., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J., and Fox, D. J., Gaussian 09, revision A.02, Gaussian, Inc., Wallingford CT, 2004.

V. *Experimental Procedure for Second Harmonic Generation*

A Ti:sapphire (Mai Tai, Spectra-Physics) laser provided 100 fs pulses with an energy of 7 nJ at 800 nm with a repetition rate of 80 MHz. The femtosecond laser pulse train passed through a half wave plate, a polarizer and a color filter, used to block all the stray light at twice the frequency of the laser light. The laser was then focused into the sample in a 1 mm UV cuvette (Precision Cells Inc.) by a lens with a focal length of 10 cm. The generated SHG signal was collected in the forward direction and sent through a lens pair and a filter, which block the 800 nm beam, into a monochromator. Spectra were recorded from 300-600 nm with a 1 nm interval. The exit of the monochromator was connected to a photomultiplier tube (PMT, Hamamatsu). The data acquisition system included a PC connected to a single photon counter (SR400, Stanford Research System). The size of the sucrose crystals used as the control was 1.25 mm x 0.77 mm x 0.44 mm, while the sample of **1** contained crystals of several different sizes.