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Guanylurea(1+) hydrogen phosphite: a novel promising phase-matchable material for second harmonic generation

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A novel and promising material, guanylurea(1+) hydrogen phosphite which belongs to the group of inorganic salts of polarisable organic molecules was prepared. Its real potential for optical applications is based on the simplicity of synthesis, good ability to crystallize, transparency, thermal stability and efficiency of the second harmonic generation comparable to urea.

Synthesis

GUHP was prepared in high yield (3.3g, 87%) by acid hydrolysis of saturated aqueous solution containing 2 g of cyanoguanidine (Fluka, 98%) with 12 ml of the solution (2 $mol.dm^{-3}$) of the phosphorous acid (Fluka, 97.5%). After few days of spontaneous crystallization in an open beaker at the laboratory temperature, small colourless crystals were obtained and purified by recrystallization from water. The substance is transparent, not hygroscopic, and stable on air up to its melting point (mp 179°C (from water)).

X-ray structure determination

Collection of X-ray structural data was performed on a Nonius Kappa CCD diffractometer (MoK_α radiation, graphite monochromator). The phase problem was solved by direct methods (SIR-92[1]) and the non-hydrogen atoms were refined anisotropically, using the full-matrix least-squares procedure (SHELXL-97[2]). The positions of the hydrogen atoms were localised on difference Fourier maps and refined isotropically. The basic crystallographic data, measurement and refinement details are summarised in Table 1. The crystallographic data were deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 752254. A copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CG21, EZ, UK (fax: +44 1223 336 033; e-mail:

deposit@ccdc.cam.ac.uk). Atom numbering and packing scheme are depicted in Fig. 1 and Fig. 2, respectively.

Table 1: Basic crystallographic data and structure refinement details of **GUHP.**

Identification code	GUHP
Empirical formula	C_2 H_9 N_4 O_4 P
Formula weight	184.10
Temperature (K)	293
a (Å)	6.6990(3)
b (Å)	6.8420(2)
c (Å)	16.354(1)
β (°)	96.514(3)
Volume (Å^3)	744.74(6)
Z	4
Calculated density (Mg/m^3)	1.642
Crystal system	monoclinic
Space group	*Cc*
absorption coefficient (mm^{-1})	0.348
F(000)	384
crystal size (mm)	0.15 x 0.20 x 0.47
Diffractometer and radiation	Nonius Kappa CCD, Mo λ = 0.71073 Å
Scan technique	ω and ψ scans to fill Ewald sphere
Completeness to θ	27.53, 99.5%
range of *h*, *k*, *l*	-8 $\rightarrow$ 8, -8 $\rightarrow$ 8, -21 $\rightarrow$ 21
θ range for data collection (°)	4.27 – 27.53
Reflection collected/unique (R_{int})	4256/ 1637 (0.026)
No. of reflections observed	1562
Absorption correction	none
Function minimised	$\Sigma w(F_o^2 - F_c^2)^2$
Weighting scheme	$w = [\sigma^2 (F_o^2)+(aP)^2+bP]^{-1}$ $P = (F_o^2+2F_c^2)/3$ a = 0.0318 b = 0.2284
Parameters refined	138
R,*wR* [$I > 2\sigma(I)$]	0.0276, 0.0660
R,*wR* (all data)	0.0301, 0.0679
Value of *S*	1.090
Maximum and minimum heights in final $\Delta\rho$ (eÅ^{-3})	0.172 and -0.182
Source of atomic scattering factors	SHELXL-97
Programmes used	SHELXL-97, PLATON, SIR92

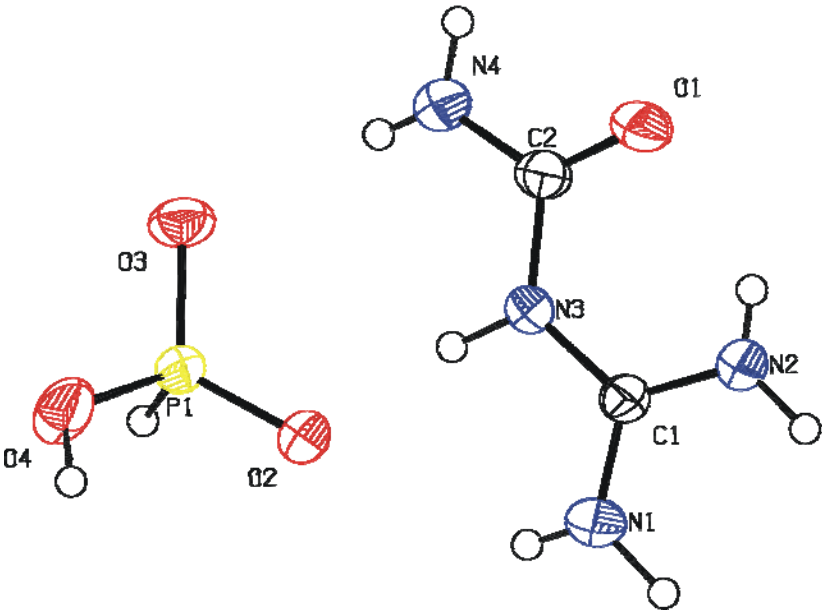

Fig. 1: Atom numbering of **GUHP**.

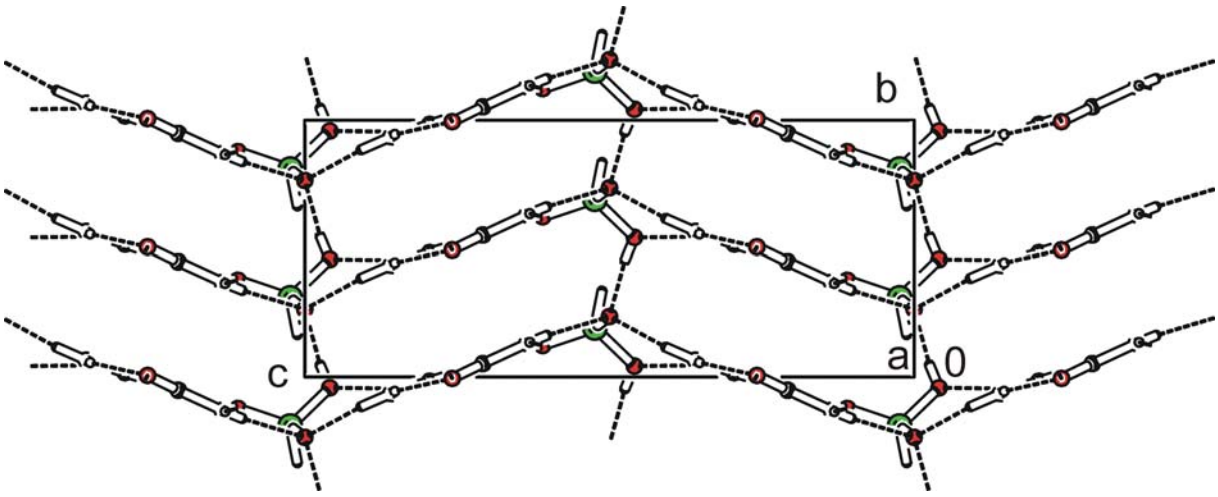

Fig. 2: Packing scheme of **GUHP** (view in *[1 0 0]* direction). Dashed lines indicate hydrogen bonds. Carbon atoms are shown in black, nitrogen atoms in blue, phosphorus atoms in green, oxygen atoms in red and hydrogen atoms are colourless.

Vibrational spectra

IR spectra were recorded using nujol and fluorolube mull (AgCl windows - MID, PE windows - FAR) techniques on a Nicolet Magna 760 FTIR spectrometer with 2 cm^{-1} resolution and Happ-Genzel apodization in the 50 - 4000 cm^{-1} region. The Raman spectra of polycrystalline samples were recorded on a Nicolet Magna 760 FTIR spectrometer equipped with the Nicolet Nexus FT Raman module (2 cm^{-1} resolution, Happ–Genzel apodization, 1064 nm Nd:YVO_4 laser excitation, 200 mW power at the sample) in the 100–3700 cm^{-1} region. Recorded vibrational spectra are presented in Figure 3. Observed peaks are listed below:

IR spectrum: ν_{max}/cm^{-1} 77w, 147m, 183w, 288w, 430s, 459w, 501w, 540m, 566m, 591m, 690w, 716w, 733w, 763w, 830w, 904s, 937 m, 1003s, 1029s, 1039sh, 1051m, 1101w, 1149m, 1216m, 1367m, 1456m, 1557m, 1600m, 1634m, 1692m, 1738m, 1750sh, 2310mb, 2418m, 2795mb, 3181mb, 3341mb, 3406mb.

Raman spectrum: ν_{max}/cm^{-1} 130s, 141s, 174m, 289w, 355w, 430m, 440s, 456s, 543w, 567m, 633w, 715m, 763w, 905m, 938m, 1004s, 1029s, 1039s, 1052s, 1095w, 1140w, 1217w, 1382w, 1463w, 1546w, 1605w, 1637w, 1688w, 1738w, 1745w, 2418s, 2467w, 3189wb, 3236wb, 3315wb.

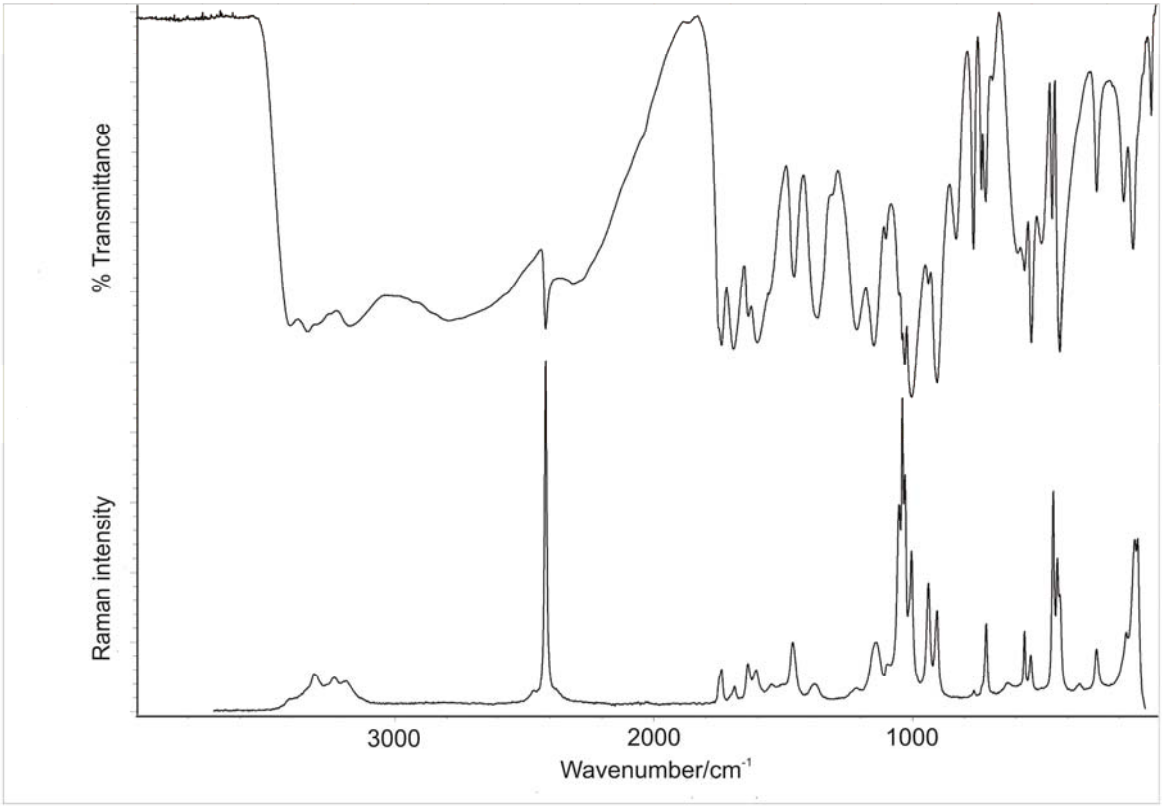

Fig 3: IR (compilation of nujol and fluorolube mulls) and Raman spectra of **GUHP**.

References

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