

Structure of 2-amino-5-nitropyridinium-dihydrogen phosphate (2A5NPDP)

Il-Hwan Suh, Sung-Su Lim, Jin-Ho Lee, Bo-Young Ryu,
Jeong-Ran Park, Moon-Jib Kim*, So-Ra Cho*,
Choon Sup Yoon**, SunKoo Lee** and Kwang sup Lee***

Department of Physics, Chungnam National University, Daejeon, 305-764

*Department of Physics, Soonchunhyang University, Onyang, 336-600

**Korea Advanced Institute of Science and Technology, Daejeon, 305-701

***Department of Macromolecular Science, Hannam University, Daejeon,
306-010

徐日煥, 林星秀, 李珍昊, 柳保盈, 朴晶蘭, 金文執*,
趙素羅*, 尹椿燮**, 李善求**, 李光燮***

忠南大學校 物理學科, 大田, 305-764

*順天鄉大學校 物理學科, 溫陽, 336-600

**韓國科學技術院 物理學科, 大田, 305-701

***韓南大學校 高分子工學科, 大田, 306-010

ABSTRACT

$C_5H_6N_3O_2^+ \cdot H_2PO_4^-$, $M_r = 221.693$, Orthorhombic,
 $Pna2_1$, $a=25.680(3) \text{ \AA}$, $b=6.234(1) \text{ \AA}$, $c=5.674(1) \text{ \AA}$, $V=908.35 \text{ \AA}^3$,
 $Z=4$, $D_x=1.734 \text{ Mg m}^{-3}$, $\lambda(\text{MoK}\alpha)=0.71069 \text{ \AA}$, $\mu=2.60^{-1} \text{ mm}^{-1}$,
 $F(000)=488$, $T=297\text{K}$, final $R=0.0328$ for 881 independent
reflections. The crystal contains planar layers of $H_2PO_4^-$
tetrahedra running parallel to the b - c plane (the cleavage
plane) and stacks of 2-amino-5-nitropyridinium
(2A5NP⁺) ions connecting the phosphate planes.

1. INTRODUCTION

Research on new materials with enhanced nonlinear optical properties has increased considerably over recent years as a result of potentially wide range of applications in optical communication and computation.^{1,2)}

Although nonlinear optical properties of organic materials may surpass by several orders of magnitude that of inorganic materials, they are often more fragile because of relatively weak van der Waals interactions which are mainly responsible

for molecular packing. In order to overcome the relatively poor mechanical properties of organic materials, new approach has been recently proposed³⁾, where the nonlinear optical properties mainly originates from the organic species^{4,5)} while the mineral anion provides a rigid structural skeleton compared to van der Waals or even hydrogen bonded organic molecular crystals.

2-Amino-5-nitrophenyridinium dihydrogen mono-phosphate(2A5NPDP) exemplifies such strategy.

Here the 2A5NPDP molecules are encapsulated in tartrate anionic chains and form herringbone packings. This leads to noncentrosymmetric structure which is essential for demonstrating the second order nonlinear optical effects.

The overall effects result in increasing the values of the second order nonlinear optical coefficients to the order of 10 pm/v which is an order of magnitude greater than that of KH_2PO_4 (KDP).

In this paper we carried out X-ray structure analysis of 2A5NPDP crystal in order to contribute to solving the relationship between the crystal structure and the basic characteristics in nonlinear optical material.

The Laue group was confirmed by X-ray photography⁶⁾.

The lattice parameters were determined from setting of 25 reflections in the range $11.43^\circ < \theta < 14.28^\circ$. Three standar

d reflections (-3 6 2), (-2 13 0) and (-2 -12 -1) were measured every 2 hours of X-ray exposure and showed maximum variation of 2.46%. One orientation reflection (-2 13 0) was monitored every 200 reflections. 881 independent reflections with $0 \leq h \leq 7$, $0 \leq k \leq 29$, $0 \leq l \leq 6$ ⁵⁾ were collected using graphite-monochromated $\text{MoK}\alpha$ radiation and $\omega/2\theta$ scan mode, ω -scan width = $(0.8 + 0.34 \tan \theta)^\circ$, $\theta_{\max} = 24^\circ$. Lorentz and polarization corrections were applied but no absorption correction.

2. EXPERIMENTAL

Crystals of 2A5NPDP suitable for X-ray analysis were obtained from an ethanol solution by slow evaporation at room temperature. A hexagon-columned bright yellow crystal of size $0.23 \times 0.23 \times 0.26 \text{ mm}$ was used for all X-ray measurements on an Enraf-Nonius CAD-4 diffractometer.

All of the experimental details of the X-Ray diffraction study of 2A5NPDP listed in Table 1.

3. STRUCTURE DETERMINATION AND REFINEMENTS

The structure was solved by direct methods using

Table 1. Experimental details of the X-Ray diffraction study of 2A5NPDP.

(A) Crystal data	
$\text{C}_5\text{H}_8\text{N}_3\text{O}_5\text{P}$	$\text{MoK}\alpha$
Orthorhombic	$\lambda = 0.71069$
$M_r = 237.11$	Cell parameters from
$\text{Pna}2_1$ (No. 33)	24 reflection
$a = 25.680(3) \text{ \AA}$	$\theta = 11.43 - 14.28$
$b = 6.234(1) \text{ \AA}$	$\mu = 2.60 \text{ mm}^{-1}$
$c = 5.674(1) \text{ \AA}$	$T = 297$
$V = 908.35 \text{ \AA}^3$	bright yellow
$Z = 4$	hexagoned column
$D_x = 1.73 \text{ Mg m}^{-3}$	$0.23 \times 0.23 \times 0.26 \text{ m}$
	Crystal source: synthesis
(B) Data collections	
Enraf-Nonius CAD-4 diffractometer	$\theta_{\max} = 24^\circ$
ω - 2θ scans	$h = 0 \rightarrow 7$
Absorption correction: none	$k = 0 \rightarrow 29$
913 measured reflections	$l = 0 \rightarrow 6$
881 independent reflections	3 standard reflections
744 observed reflections [$F > \sigma(F)$]	frequency: 7200 seconds
	intensity variation: 2.46 %
(C) Refinement	
Refinement on F	$\omega = \text{unit weights}$
Final R = 0.0328	$(\Delta/\sigma)_{\max} = 0.045$
$\omega R = 0.0328$	$\Delta\rho_{\max} = 0.223 \text{ e\AA}^{-3}$
$S = 0.7862$	$\Delta\rho_{\min} = -0.245 \text{ e\AA}^{-3}$
744 reflections [$F > \sigma(F)$]	Atomic scattering factors were
167 parameters	provided in SHELX76
Only coordinates of H-atoms were refined	

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with e. s. d. 's in parentheses.

	x	y	z	U_{eq}^*/U_{iso}
P	0.2866(0)	0.3583(2)	0.6126 ^a	28
O(1)	0.2358(2)	0.2363(8)	0.5453(8)	55
O(2)	0.3022(2)	0.2652(7)	0.8587(9)	43
O(3)	0.2746(1)	0.5950(5)	0.6333(9)	37
O(4)	0.3308(1)	0.3135(5)	0.4446(8)	38
O(1N2)	0.4507(2)	0.3944(8)	-0.4128(11)	59
O(2N2)	0.4864(2)	0.7084(8)	-0.4610(10)	69
N(1)	0.3527(2)	0.8664(8)	0.4299(10)	39
N(2)	0.4577(2)	0.5824(9)	-0.3544(11)	47
N(3)	0.3751(2)	0.5995(7)	0.1693(9)	30
C(1)	0.3787(2)	0.8064(9)	0.2419(11)	33
C(2)	0.4130(2)	0.9465(8)	0.1212(16)	43
C(3)	0.4391(2)	0.8764(9)	0.0767(13)	45
C(4)	0.4320(2)	0.6634(9)	-0.1461(11)	34
C(5)	0.4005(2)	0.5287(9)	-0.0240(11)	34
H(O2)	0.274(3)	0.215(12)	0.933(14)	81
H(O3)	0.277(4)	0.657(16)	0.794(21)	144
H(1N1)	0.347(2)	1.022(9)	0.456(12)	52
H(2N1)	0.323(2)	0.788(7)	0.506(9)	30
H(N3)	0.355(2)	0.506(10)	0.256(11)	54
H(C2)	0.411(2)	1.112(9)	0.189(10)	45
H(C3)	0.464(2)	0.998(10)	-0.188(13)	64
H(C5)	0.395(2)	0.377(9)	-0.065(11)	41

* $U_{eq} = \frac{1}{3} (U_{11} + U_{22} + U_{33})$

^a Fixed coordinate to define the origin

SHELXS86⁹⁾, and refined by full-matrix least squares using SHELX76¹⁰⁾. Function minimized was $\sum \omega (|F_o| - |F_c|)^2$, where ω is unit weight. 744 reflections with $F_o > \sigma(F_o)$ were used in refinement.

All of the non-H atoms were refined with anisotropic temperature factors. All of the H atoms were located on a difference map and refined with isotropic temperature factors. Number of parameters refined was 167.

Final reliability factors were $R=0.0328$, $\omega R=0.0328$ and $S=0.7862$ with $(\Delta/\sigma)_{max}=0.045$ and $\Delta\rho_{max}/\Delta\rho_{min}=0.2231/-0.2446 \text{ e}\text{\AA}^{-3}$ in final difference map. Atomic scattering factors were provided in SHELX76. Final atomic coordinates are listed in Table 2. Geometric calculations on the molecular structure were done using GEOM program¹⁰⁾. All computations were performed using the Micro VAX/VMS 3400 computer at Chungnam National University.

4. RESULTS AND DISCUSSION

Bond lengths, angles and hydrogen bonds are listed in Table 3. The molecule of stereoscopic view with atom labelling drawn by ORTEP¹¹⁾ is shown in Figure 1.

Table 3. Interatomic distances (\AA), angles ($^\circ$) and hydrogen bonds ($\text{\AA}, ^\circ$) with e. s. d. 's in parentheses.

The PO ₄ tetrahedron in H ₂ PO ₄ ⁻ anion						
P	O(1)	O(2)	O(3)	O(4)		
O(1)	1.557(4)	2.470(7)	2.498(6)	2.551(6)		
O(2)	104.6(2)	1.564(5)	2.523(6)	2.480(7)		
O(3)	109.0(2)	110.2(3)	1.512(4)	2.512(5)		
O(4)	112.6(2)	107.6(2)	112.5(2)	1.509(4)		
P-O(2)-H(O2) = 109.9(47)						
P-O(3)-H(O3) = 116.1(58)						
The 2-amino-5-nitropyridinium ion						
N(3)-C(1)	1.357(7)	N(3)-C(5)-C(4)	120.1(5)			
N(3)-C(5)	1.350(7)	C(5)-C(4)-N(2)	118.3(5)			
N(2)-O(1N2)	1.231(6)	C(3)-C(4)-N(2)	120.2(5)			
N(2)-O(2N2)	1.235(6)	C(5)-C(4)-C(3)	121.5(5)			
N(1)-C(1)	1.313(8)	C(4)-C(3)-C(2)	117.9(5)			
C(4)-N(2)	1.445(8)	C(3)-C(2)-C(1)	120.0(5)			
C(4)-C(5)	1.357(8)	C(2)-C(1)-N(3)	118.8(5)			
C(3)-C(4)	1.397(8)	C(2)-C(1)-N(1)	122.2(6)			
C(2)-C(3)	1.379(10)	N(3)-C(1)-N(1)	118.9(5)			
C(1)-C(2)	1.417(8)	C(5)-N(3)-H(N3)	120(4)			
N(3)-H(N3)	0.92(6)	C(1)-N(3)-H(N3)	118(4)			
N(1)-H(2N1)	1.00(5)	C(1)-N(1)-H(2N1)	127(3)			
N(1)-H(1N1)	0.99(6)	C(1)-N(1)-H(1N1)	118(4)			
C(5)-H(C5)	0.98(5)	H(1N1)-N(1)-H(2N1)	108(4)			
C(3)-H(C3)	1.17(7)	N(3)-C(5)-H(C5)	115(4)			
C(2)-H(C2)	1.10(5)	C(4)-C(5)-H(C5)	125(4)			
		C(4)-C(3)-H(C3)	122(3)			
C(1)-N(3)-C(5)	121.6(5)	C(2)-C(3)-H(C3)	120(3)			
C(4)-N(2)-O(1N2)	119.0(6)	C(3)-C(2)-H(C2)	127(3)			
C(4)-N(2)-O(2N2)	116.8(5)	C(1)-C(2)-H(C2)	113(3)			
O(1N2)-N(2)-O(2N2)	124.2(6)					
Hydrogen bonds						
D	— H	····· A	D—H	D···A	D···A	∠D—H···A
N(1)-H(2N1)	···	O(3)	1.00(5)	1.88(5)	2.867(6)	169(4)
N(3)-H(N3)	···	O(4)	0.92(6)	1.72(6)	2.629(6)	167(5)
N(1)-H(1N1)	···	O(4)	0.99(6)	1.87(6)	2.845(6)	168(6)
O(1)-H(O3)	···	O(3) ^b	0.99(12)	1.54(12)	2.512(7)	165(10)
O(2)-H(O2)	···	O(3) ^c	0.90(8)	1.85(8)	2.728(6)	168(7)
O(3)-H(O3)	···	O(1) ^d	0.99(6)	1.54(12)	2.512(7)	165(10)
Symmetry code					(a)x, 1+y, z	(b)0.5-x, -0.5+y, -0.5+z
					(c)0.5-x, -0.5+y, 0.5+z	(d)0.5-x, 0.5+y, 0.5+z

The N(2) - O(1N2) and N(2) - O(2N2) interatomic distances are 1.231 and 1.235 \AA , respectively and show their bond order of 1.5. These values are comparable with those found for 3 - Methyl - 4 - Methoxy - 4' - Nitrostilbene(MMONS)¹²⁾, meta-nitroaniline¹³⁾ and N,N-Dimethyl-p-nitroaniline¹⁴⁾. The oxygen atoms as expected show a higher degree of thermal motion than the other atoms.

The 2-amino-5-nitro-pyridinium (2A5NP⁺) cation group of the molecule is essentially planar within 0.057 \AA with a mean C-C bond length of 1.388 \AA , which is slightly shorter than the mean value of 1.395¹⁵⁾.

The C-N(amino) distance of 1.313 and C-N(nitro) of 1.445 \AA may be compared with 1.371 and 1.460 \AA in

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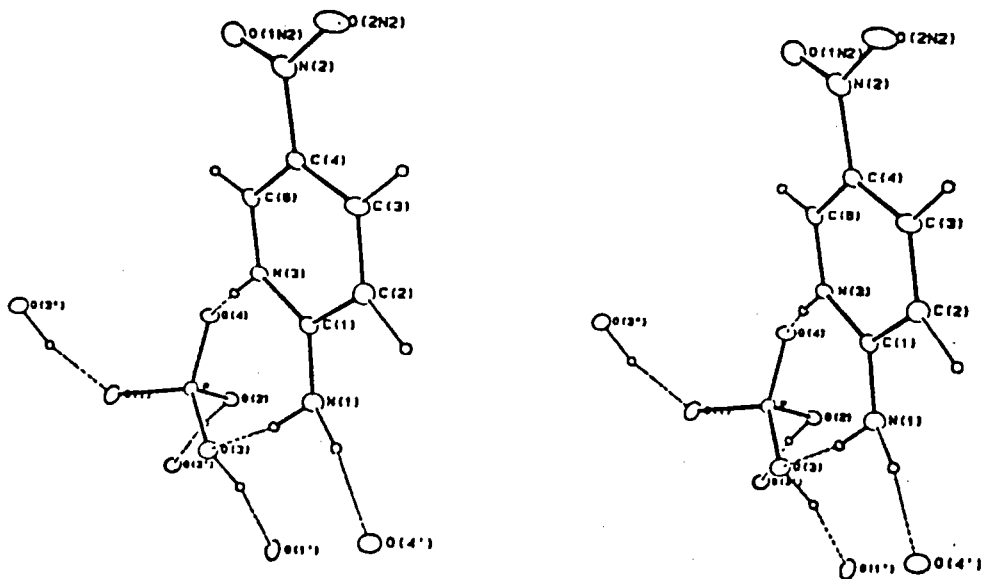


Figure 1. Stereoscopic view of atomic numbering scheme and molecular conformation. Primed atoms indicate the atoms of another molecule and hydrogen bonds are dotted lines.

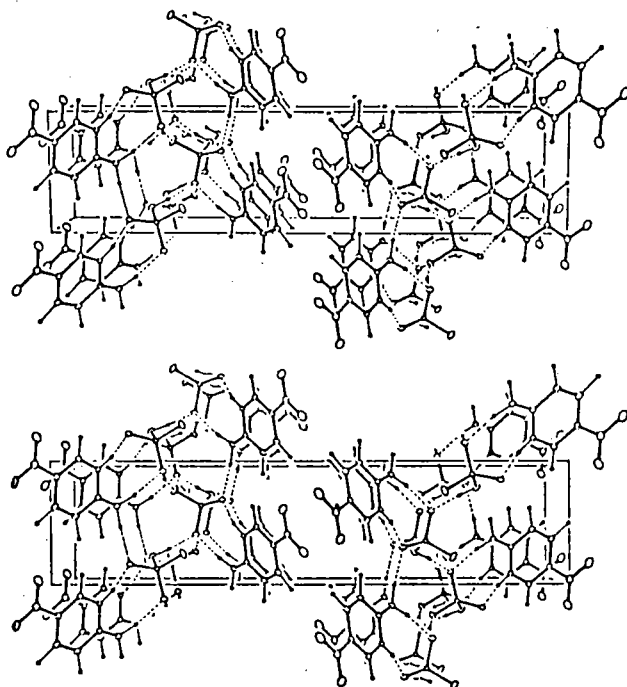


Figure 2. Stereoscopic view of molecular packing in the unit cell. Hydrogen bonds are dotted lines. (*a* vertical, *b* horizontal).

N,N-Dimethyl-*p*-nitroaniline¹⁴⁾ and 4-nitroaniline¹⁶⁾, 1.377 and 1.474 Å in *p*-methyl-*m*-nitro-*N*-methylaniline¹⁷⁾, respectively.

O(1N2), O(2N2) and N(2) atoms are deviated by 0.067, 0.045 and 0.051 Å respectively from the best plane of the pyridine ring such that the dihedral angle between the NO₂ group and the pyridine ring plane is 0.797°. The similar situation had been found in MMONS¹²⁾.

The axis connecting the C(1) and C(4) carbons of the pyridine ring is inclined by 36.7° with respect to the crystallographic *c*-axis and corresponds approximately to the charge-transfer axis⁵⁾.

The mean values of P-O distance 1.536 Å and of O-P-O angle 109.4° of tetrahedral H₂PO₄⁻ anion group (refer to Table 3) are in good agreement with the 1.531 Å and 109.3° in glycine monophosphate¹⁸⁾ respectively.

As shown in Figure 1 and Table 3, two intramolecular hydrogen bonds exist between 2A5NP⁺ and H₂PO₄⁻ groups: one of them is between N(1) atom of amino group and O(3) atom of H₂PO₄⁻ group and the other between N(3) of pyridinium ring and O(4) atom of H₂PO₄⁻ group, while N(1) in amino group and O(1), O(2), O(3) in H₂PO₄⁻ group are associated with intermolecular hydrogen bonds.

The packing diagram of the molecules in a unit cell viewed down *c*-axis (Figure 2) shows that the organic-inorganic salt 2A5NPDP contains planar layer of H₂PO₄⁻ tetrahedra running parallel to the *b*-*c* plane (the cleavage plane) and stacks of 2A5NP⁺ ions connecting the phosphate planes in a sort of herringbone structure⁵⁾.

The detailed structure elucidation of this compound gives good correlation between the structure and the effect of the non linear optical properties^{5,19)}.

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