

## **Supplementary material to manuscript LC0047**

Miroslav Slouf, Antonin Holy, Vaclav Petricek & Ivana Cisarova: “Charge density study of hydrogen-[(2,4-diaminopyrimidin-1-yl)methyl]phosphonate monohydrate”

Supplementary table 1. Resolution versus numbers of reflections and agreement factors.  
 (Definition of agreement factor  $R_{\sigma}$  is given in the main article. Observed reflections have  $I > 3\sigma(I)$ ).

$\sin\theta/\lambda$ ( $\text{\AA}^{-1}$ )	$\theta$ ( $^{\circ}$ )	No. of all reflections	No. of obs. reflections	$R_{\sigma}(\text{all})$	$R_{\sigma}(\text{obs})$
0,20	8,2	59	59	1,16	1,16
0,40	16,52	486	478	1,13	1,13
0,60	25,22	1622	1540	1,33	1,32
0,80	34,7	3863	3382	1,89	1,81
1,00	45,3	7479	5508	3,13	2,57
1,08	50,1	9362	6082	3,79	2,80

Supplementary table 2. Anisotropic thermal displacement parameters of non-H atoms ( $\text{\AA}^2$ ).

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
P1	0.01082(5)	0.01008(5)	0.00995(5)	-0.00046(4)	-0.00014(3)	-0.00108(4)
O1	0.01614(18)	0.00995(15)	0.0200(2)	-0.00174(13)	0.00190(15)	-0.00286(14)
O2	0.01754(19)	0.01864(18)	0.00898(17)	0.00142(14)	-0.00175(14)	0.00006(14)
O3	0.01050(18)	0.01894(19)	0.01321(19)	-0.00094(14)	-0.00037(15)	0.00092(15)
N1	0.01043(17)	0.00935(15)	0.01357(15)	-0.00144(14)	0.00035(15)	-0.00062(13)
C2	0.01009(17)	0.00936(15)	0.01209(16)	-0.00090(13)	-0.00075(15)	-0.00011(13)
N2	0.01292(20)	0.01159(16)	0.0173(2)	-0.00210(15)	-0.00470(18)	0.00251(16)
N3	0.01123(17)	0.00949(15)	0.01319(15)	-0.00132(14)	-0.00150(16)	0.00083(13)
C4	0.01170(17)	0.01065(16)	0.01261(16)	-0.00030(15)	-0.00057(15)	0.00085(14)
N4	0.01500(19)	0.01264(17)	0.0194(2)	-0.00105(15)	-0.00227(17)	0.00470(15)
C5	0.01125(17)	0.01253(17)	0.01581(17)	-0.00080(15)	-0.00192(15)	0.00013(14)
C6	0.01047(17)	0.01171(16)	0.01547(17)	-0.00177(14)	-0.00102(16)	-0.00110(14)
C7	0.01423(18)	0.01000(15)	0.01208(18)	-0.00172(13)	0.00296(15)	-0.00068(13)
O4	0.01739(17)	0.0175(2)	0.01999(18)	-0.00082(15)	0.0010(2)	-0.00015(16)

Supplementary table 3. Charge density parameters of non-H atoms at the end of multipole refinement.

(Parameters  $\kappa'$  were not refined in the last step of refinement (see the main article); when they were refined, their maximum e.s.d.'s were  $\approx 0.01$ .)

Parameters marked with cross were not refined due to symmetry constraints.)

	P1	O1	O2	O3	N1	C2	N2	N3	C4	N4	C5	C6	C7	O4
<b>P<sub>c</sub></b>	10.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
<b>P<sub>v</sub></b>	4.38(0)	6.72(3)	6.66(3)	6.42(3)	5.11(6)	3.59(6)	5.74(6)	5.39(5)	3.72(7)	5.54(5)	4.31(6)	4.03(6)	4.24(6)	6.68(4)
<b><math>\kappa</math></b>	0.982(6)	0.948(2)	0.955(2)	0.977(3)	1.005(5)	1.046(7)	0.963(4)	0.982(3)	1.033(7)	0.980(4)	0.995(5)	1.009(5)	0.993(5)	0.952(3)
<b><math>\kappa'</math></b>	1.14	0.73	0.73	0.82	0.98	1.01	0.93	1.04	1.02	0.82	0.97	0.96	0.91	0.90
<b>P<sub>10</sub></b>	0.064(11)	-0.007(10)	-0.054(11)	0.054(12)	x	x	-0.007(9)	x	x	0.006(10)	x	x	-0.007(10)	0.000(0)
<b>P<sub>11+</sub></b>	0.029(11)	0.085(15)	0.049(15)	0.023(12)	0.019(12)	0.076(15)	-0.008(16)	-0.077(11)	0.064(16)	-0.022(19)	-0.005(16)	-0.016(15)	-0.100(13)	-0.007(9)
<b>P<sub>11-</sub></b>	0.025(13)	-0.034(10)	0.058(10)	0.032(10)	0.009(13)	0.032(13)	0.012(10)	0.023(13)	0.037(14)	0.022(11)	0.020(17)	-0.085(18)	0.035(13)	0.059(15)
<b>P<sub>20</sub></b>	0.030(13)	-0.031(11)	-0.061(11)	0.038(11)	-0.035(13)	-0.197(14)	-0.059(14)	-0.096(11)	-0.229(15)	-0.082(15)	-0.160(14)	-0.215(14)	0.020(12)	0.030(12)
<b>P<sub>21+</sub></b>	0.035(11)	-0.019(11)	0.054(11)	-0.041(11)	x	x	-0.010(9)	x	x	-0.030(9)	x	x	0.009(10)	0.000(0)
<b>P<sub>21-</sub></b>	0.057(13)	-0.010(10)	0.020(10)	-0.001(11)	x	x	0.013(9)	x	x	0.004(9)	x	x	0.003(10)	0.000(0)
<b>P<sub>22+</sub></b>	-0.005(12)	-0.020(12)	0.044(12)	0.031(11)	-0.022(12)	0.019(14)	0.003(12)	0.015(11)	0.003(14)	-0.008(14)	0.027(15)	0.014(15)	-0.125(11)	0.019(12)
<b>P<sub>22-</sub></b>	-0.025(12)	0.035(11)	-0.001(11)	-0.025(10)	0.006(13)	0.046(13)	-0.027(11)	0.020(12)	-0.005(14)	0.007(12)	0.010(15)	-0.071(14)	-0.009(10)	-0.005(10)
<b>P<sub>30</sub></b>	0.081(15)	0.009(10)	0.018(10)	0.028(9)	x	x	0.029(9)	x	x	0.002(9)	x	x	0.044(10)	0.000(0)
<b>P<sub>31+</sub></b>	-0.198(13)	-0.052(10)	-0.060(10)	-0.088(8)	0.020(9)	0.006(10)	0.002(9)	0.004(8)	0.012(10)	0.013(11)	0.022(10)	0.001(10)	-0.150(11)	0.020(8)
<b>P<sub>31-</sub></b>	-0.299(16)	0.032(8)	0.013(9)	0.053(8)	0.015(8)	-0.002(10)	-0.036(9)	-0.010(8)	-0.019(10)	0.003(9)	0.022(11)	-0.027(11)	-0.211(11)	0.110(10)
<b>P<sub>32+</sub></b>	0.005(13)	0.010(10)	-0.024(10)	-0.031(9)	x	x	0.009(8)	x	x	0.010(9)	x	x	-0.021(10)	0.000(0)
<b>P<sub>32-</sub></b>	-0.038(13)	0.001(9)	-0.013(10)	-0.054(8)	x	x	-0.034(8)	x	x	0.032(8)	x	x	-0.014(10)	0.000(0)
<b>P<sub>33+</sub></b>	0.254(14)	0.002(9)	0.026(10)	0.045(8)	-0.201(12)	-0.246(17)	0.251(12)	-0.134(9)	-0.228(16)	0.256(14)	-0.244(15)	-0.256(16)	0.197(11)	0.005(7)
<b>P<sub>33-</sub></b>	-0.052(14)	0.041(9)	-0.012(10)	-0.017(8)	-0.023(11)	-0.008(14)	-0.024(9)	-0.015(9)	0.018(14)	0.016(10)	-0.021(13)	0.031(13)	-0.022(10)	-0.008(8)

Supplementary table 4. Charge density parameters of H atoms at the end of multipole refinement.

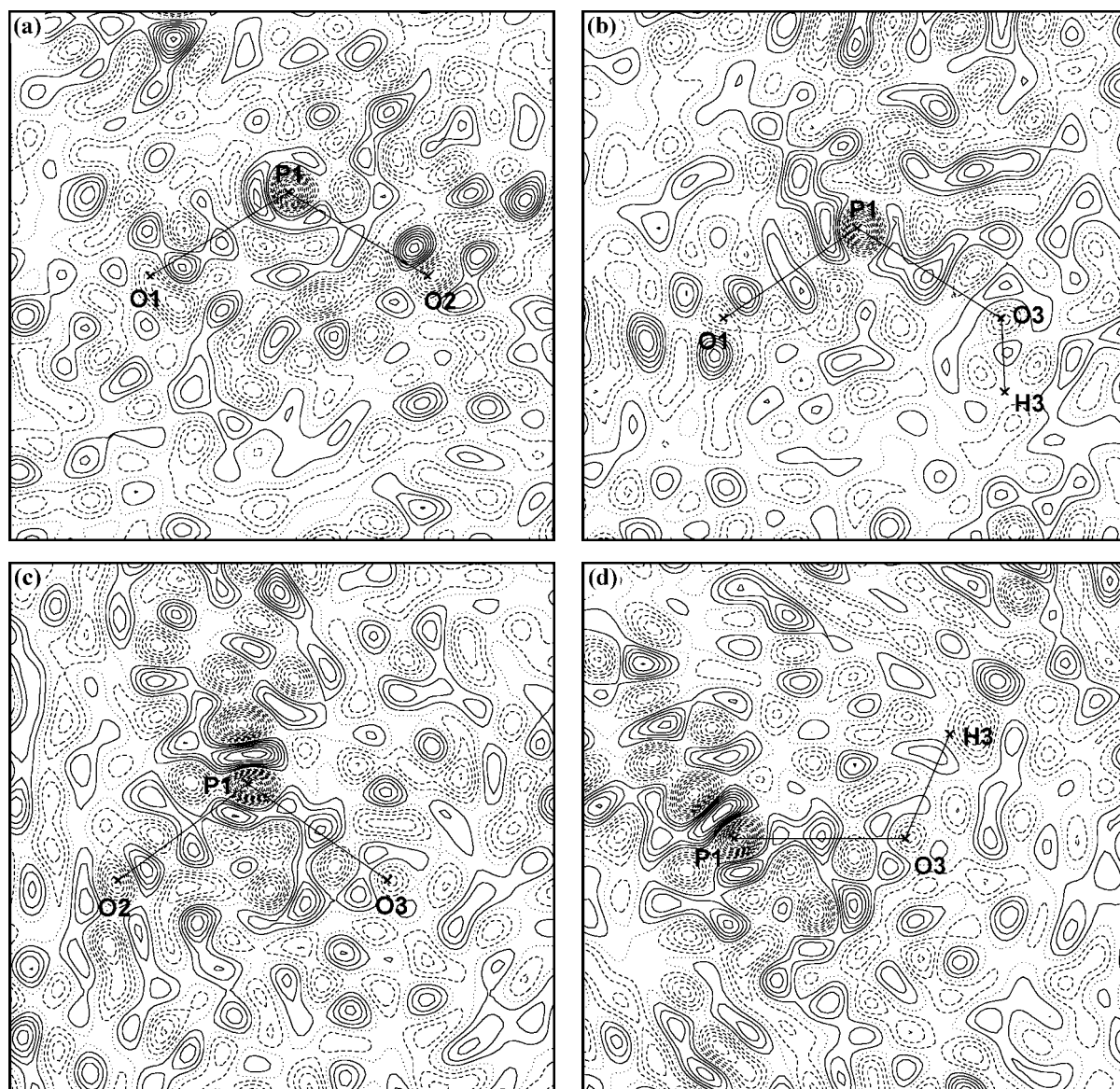
Parameters  $\kappa$  and  $\kappa'$  were not refined in the last refinement step; when they were refined, their maximum e.s.d.'s were  $\approx 0.01$ .

	H21	H22	H41	H42	H5	H6	H71	H72	H3	H401	H402
$P_e$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$P_v$	0.60(2)	=H21	=H21	=H21	0.79(2)	=H5	=H5	=H5	0.63(2)	=H3	=H3
$\kappa$	1.14	=H21	=H21	=H21	1.16	=H5	=H5	=H5	1.15	=H3	=H3
$\kappa'$	1.60	=H21	=H21	=H21	1.73	=H5	=H5	=H5	2.01	=H3	=H3
$P_{10}$	0.061(9)	0.099(10)	0.090(9)	0.088(9)	0.089(9)	0.086(9)	0.085(8)	0.093(9)	0.113(11)	0.027(7)	0.056(8)

Supplementary table 5. Full list of distances among atoms, residual maxima (max1 to max5) and residual minima (min1 to min5) on residual map at the end of multipole refinement (Å). Peak heights (eÅ<sup>-3</sup>) are: max1 = 0.93, max2 = 0.88, max3 = 0.85, max4 = 0.83, max5 = 0.83, min1 = -1.25, min2 = -1.01, min3 = -0.94, min4 = -0.88 and min5 = -0.84.

max1-P1	1.74153(10)	max5-min2	0.452414
max1-N1	1.2893(5)	max5-min4	0.889681
max1-C7	0.3491(5)	min1-P1	0.04469(10)
max1-H71	1.410634	min1-O1	1.5194(4)
max1-H72	1.162874	min1-O2	1.5167(4)
max1-max5	1.448831	min1-O3	1.5337(5)
max1-min1	1.763578	min1-C7	1.8630(5)
max1-min2	1.57131	min1-max1	1.763578
max1-min3(-x,1-y,1-z)	1.772783	min1-max2	1.406665
max1-min4	1.277408	min1-max3(1/2-x,-1/2+y,3/2-z)	1.786445
max2-P1	1.39483(10)	min1-max4	1.275452
max2-O1	0.3755(5)	min1-max5	0.328485
max2-H22(-1/2+x,1/2-y,-1/2+z)	1.912664	min1-min2	0.600442
max2-H42(1/2-x,-1/2+y,3/2-z)	1.855243	min1-min4	1.15371
max2-max5	1.555359	min2-P1	0.56360(11)
max2-min1	1.406665	min2-O1	1.2316(4)
max2-min2	1.260438	min2-O2	1.8449(5)
max2-min4	1.683809	min2-C7	1.6213(5)
max3-P1(1/2-x,1/2+y,3/2-z)	1.79967(10)	min2-H72	1.970772
max3-O2(-x,1-y,1-z)	1.9637(4)	min2-max1	1.57131
max3-O3(1/2-x,1/2+y,3/2-z)	1.7129(5)	min2-max2	1.260438
max3-C7(1/2-x,1/2+y,3/2-z)	1.9421(4)	min2-max3(1/2-x,-1/2+y,3/2-z)	1.740532
max3-H71(1/2-x,1/2+y,3/2-z)	1.565543	min2-max4	1.617925
max3-H3(1/2-x,1/2+y,3/2-z)	1.289585	min2-max5	0.452414
max3-max5(1/2-x,1/2+y,3/2-z)	1.750271	min2-min1	0.600442
max3-min1(1/2-x,1/2+y,3/2-z)	1.786445	min2-min4	0.660511
max3-min2(1/2-x,1/2+y,3/2-z)	1.740532	min3-N1(-x,1-y,1-z)	1.0553(4)
max4-P1	1.26930(10)	min3-C5(-x,1-y,1-z)	1.7165(5)
max4-O2	0.2974(4)	min3-C6(-x,1-y,1-z)	0.6648(5)
max4-H3(-1/2+x,1/2-y,-1/2+z)	1.762186	min3-H6(-x,1-y,1-z)	1.403507
max4-H401(1/2+x,1/2-y,-1/2+z)	1.837002	min3-max1(-x,1-y,1-z)	1.772782
max4-max5	1.317888	min4-P1	1.11111(10)
max4-min1	1.275452	min4-O1	1.5841(4)
max4-min2	1.617925	min4-O2	1.9581(5)
max4-min4	1.748363	min4-C7	1.3653(5)
max5-P1	0.29887(10)	min4-H72	1.425259
max5-O1	1.6032(4)	min4-max1	1.277408
max5-O2	1.5796(5)	min4-max2	1.683809
max5-O3	1.7393(5)	min4-max4	1.748363
max5-C7	1.5530(5)	min4-max5	0.889681
max5-max1	1.448831	min4-min1	1.15371
max5-max2	1.555359	min4-min2	0.660511
max5-max3(1/2-x,-1/2+y,3/2-z)	1.750272	min5-C2	1.5276(5)
max5-max4	1.317888	min5-N3	1.1222(6)
max5-min1	0.328485	min5-C4	1.5260(4)

Supplementary figure 1. Residual maps of showing regions of P-O bonds. Atom labelling and symmetry codes are the same as in Figure 3 of the main article. Contours at  $0.1 \text{ e}\text{\AA}^{-3}$ . Positive, zero and negative contours are full, dotted and dashed lines, respectively.



Supplementary figure 2. Residual maps showing regions of hydrogen bonding interactions. Atom labelling and symmetry codes are the same as in Figure 4 in the main article. Contours at  $0.1 \text{ e}\text{\AA}^{-3}$ . Positive, zero and negative contours are full, dotted and dashed lines, respectively.

