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# 2-Cyanoanilinium dihydrogen phosphate

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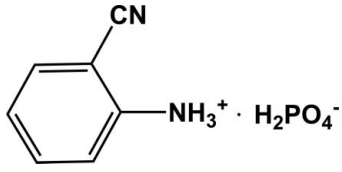
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.040; $wR$ factor = 0.102; data-to-parameter ratio = 16.4.

In the cation of the title compound, $C_7H_7N_2^+\cdot H_2PO_4^-$, the nitrile group and the benzene ring are almost coplanar (r.m.s. deviation = 0.0035 Å). The cations and anions are connected by intermolecular N—H···O, O—H···O and O—H···N hydrogen bonds, together with $\pi$–$\pi$ interactions [centroid–centroid distance = 3.8131 (9) Å], forming a three-dimensional network.

## Related literature

For applications of metal-organic coordination compounds, see: Fu *et al.* (2007); Chen *et al.* (2000); Fu & Xiong (2008); Xiong *et al.* (1999); Xie *et al.* (2003); Zhang *et al.* (2001). For nitrile derivatives, see: Fu *et al.* (2008); Wang *et al.* 2002.




## Experimental

### Crystal data

$C_7H_7N_2^+\cdot H_2PO_4^-$
$M_r$ = 216.13
Triclinic, $P\overline{1}$
$a$ = 6.1471 (12) Å
$b$ = 9.3192 (19) Å
$c$ = 9.3295 (19) Å
$\alpha$ = 117.20 (2)°
$\beta$ = 93.75 (2)°
$\gamma$ = 99.61 (2)°
$V$ = 462.51 (16) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.29 mm$^{-1}$
$T$ = 298 K
0.30 × 0.25 × 0.20 mm

### Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min}$ = 0.94, $T_{max}$ = 1.00
4831 measured reflections
2110 independent reflections
1852 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.102
$S$ = 1.08
2110 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.37 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1$B$···O4$^{i}$ | 0.89 | 1.93 | 2.819 (2) | 176 |
| N1—H1$C$···O1$^{ii}$ | 0.89 | 1.85 | 2.723 (2) | 166 |
| N1—H1$A$···O1$^{iii}$ | 0.89 | 1.87 | 2.730 (2) | 161 |
| O3—H3$A$···N2$^{iv}$ | 0.82 | 1.98 | 2.797 (2) | 176 |
| O2—H2$A$···O4$^{v}$ | 0.82 | 1.76 | 2.574 (2) | 172 |

Symmetry codes: (i) $x-1, y, z-1$; (ii) $-x+1, -y, -z+1$; (iii) $x, y, z-1$; (iv) $-x+2, -y, -z+1$; (v) $-x+2, -y+1, -z+2$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2201).

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# supplementary materials

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# 2-Cyanoanilinium dihydrogen phosphate

**L. Zhang**

## Comment

The construction of metal-organic coordination compounds has attracted much attention owing to potential functions, such as permittivity, fluorescence, magnetism and optical properties (Fu *et al.*, 2007; Chen *et al.*, 2000; Fu & Xiong (2008); Xie *et al.*, 2003; Zhang *et al.*,2001; Xiong *et al.*, 1999). Nitrile derivatives are a class of excellent ligands for the construction of novel metal-organic frameworks. (Wang *et al.* 2002; Fu *et al.*, 2008). We report here the crystal structure of the title compound, 2-cyanoanilinium dihydrogen phosphate .

In the 2-cyanoanilinium cation (Fig.1), the nitrile group and the benzene ring are almost coplanar. The nitrile group C7≡N2 bond length of 1.137 (3) Å is within the normal range.

In the crystal structure, all the amine group H atoms and $H_2PO_4^-$ H atoms are involved in N—H···O, O—H···O and O—H···N hydrogen bonds (Table 1) with N atoms of nitrile group and O atoms of $H_2PO_4^-$ anion. The benzene rings [Cg···Cg] of neighbouring cation systems are separated by 3.8131 (9) Å [Cg is the centroid of the benzene rings]. These hydrogen bonds and π–π interactions link the ionic units into a three-dimensional network (Fig. 2).

## Experimental

The commercial 2-aminobenzonitrile (3 mmol, 0.55 g) and $H_3PO_4$ (0.5 ml) were dissolved in ethanol (20 ml). Colourless block-shaped crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation at room temperature.

## Refinement

All H atoms attached to C atoms were positioned geometrically and treated as riding, with C-H = 0.93 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C). The H atoms of $H_2PO_4^-$ anion and amine group were located in difference Fourier maps and the last stage of refinement they were treated as riding on the O atoms and N atoms, with $U_{iso}$(H) = 1.5$U_{eq}$(O and N).

## Figures

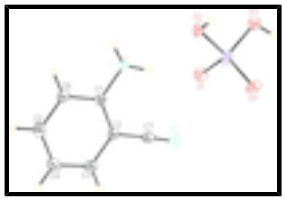

Fig. 1. A view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

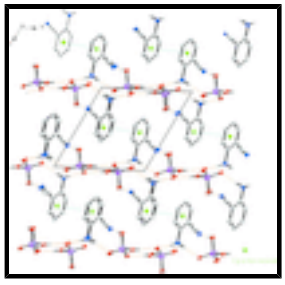

Fig. 2. The crystal packing of the title compound, viewed along the *a* axis showing the hydrogen bonds and the π–π interactions in the title compound. H atoms not involved in hydrogen bonding (dashed lines) have been omitted for clarity

**2-Cyanoanilinium dihydrogen phosphate**

*Crystal data*

| | |
|---|---|
| $C_7H_7N_2^+·H_2PO_4^-$ | $Z = 2$ |
| $M_r = 216.13$ | $F_{000} = 224$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.552$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $a = 6.1471$ (12) Å | Cell parameters from 1852 reflections |
| $b = 9.3192$ (19) Å | $\theta = 3.4$–$27.5°$ |
| $c = 9.3295$ (19) Å | $\mu = 0.29$ mm$^{-1}$ |
| $\alpha = 117.20$ (2)° | $T = 298$ K |
| $\beta = 93.75$ (2)° | Block, colourless |
| $\gamma = 99.61$ (2)° | 0.30 × 0.25 × 0.20 mm |
| $V = 462.51$ (16) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Rigaku Mercury2 diffractometer | 2110 independent reflections |
| Radiation source: fine-focus sealed tube | 1852 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.030$ |
| Detector resolution: 13.6612 pixels mm$^{-1}$ | $\theta_{max} = 27.5°$ |
| $T = 298$ K | $\theta_{min} = 3.4°$ |
| CCD profile fitting scans | $h = -7 \rightarrow 7$ |
| Absorption correction: multi-scan (CrystalClear; Rigaku, 2005) | $k = -12 \rightarrow 12$ |
| $T_{min} = 0.94$, $T_{max} = 1.00$ | $l = -12 \rightarrow 12$ |
| 4831 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.040$ | $w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.23P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.102$ | $(\Delta/\sigma)_{max} < 0.001$ |

| | |
|---|---|
| $S$ = 1.08 | $\Delta\rho_{max}$ = 0.33 e Å$^{-3}$ |
| 2110 reflections | $\Delta\rho_{min}$ = −0.37 e Å$^{-3}$ |
| 129 parameters | Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| Primary atom site location: structure-invariant direct methods | Extinction coefficient: 0.126 (9) |
| Secondary atom site location: difference Fourier map | |

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on $F^2$, conventional R-factors R are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| N1 | 0.3606 (3) | 0.17867 (19) | 0.13975 (19) | 0.0252 (3) |
| H1A | 0.4996 | 0.1956 | 0.1197 | 0.038* |
| H1B | 0.2813 | 0.2336 | 0.1078 | 0.038* |
| H1C | 0.2980 | 0.0710 | 0.0852 | 0.038* |
| C2 | 0.5068 (3) | 0.1896 (2) | 0.3985 (2) | 0.0275 (4) |
| C1 | 0.3654 (3) | 0.2371 (2) | 0.3135 (2) | 0.0254 (4) |
| N2 | 0.7647 (4) | −0.0074 (3) | 0.2631 (3) | 0.0524 (6) |
| C7 | 0.6495 (4) | 0.0801 (3) | 0.3194 (3) | 0.0343 (5) |
| C3 | 0.5080 (4) | 0.2455 (3) | 0.5646 (3) | 0.0381 (5) |
| H3 | 0.6040 | 0.2152 | 0.6217 | 0.046* |
| C6 | 0.2255 (4) | 0.3362 (3) | 0.3937 (3) | 0.0406 (5) |
| H6 | 0.1296 | 0.3674 | 0.3374 | 0.049* |
| C5 | 0.2268 (5) | 0.3900 (3) | 0.5589 (3) | 0.0524 (7) |
| H5 | 0.1312 | 0.4571 | 0.6128 | 0.063* |
| C4 | 0.3683 (5) | 0.3452 (3) | 0.6444 (3) | 0.0479 (6) |
| H4 | 0.3687 | 0.3824 | 0.7554 | 0.057* |
| P1 | 0.87212 (8) | 0.26924 (6) | 0.96817 (6) | 0.02198 (17) |
| O4 | 1.1050 (2) | 0.36166 (16) | 1.05571 (18) | 0.0311 (3) |
| O3 | 0.8776 (2) | 0.16546 (19) | 0.77991 (17) | 0.0371 (4) |
| H3A | 0.9862 | 0.1229 | 0.7672 | 0.056* |
| O2 | 0.7151 (2) | 0.38600 (16) | 0.97509 (17) | 0.0294 (3) |
| H2A | 0.7833 | 0.4620 | 0.9628 | 0.044* |
| O1 | 0.7610 (2) | 0.15769 (17) | 1.02994 (18) | 0.0334 (4) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0267 (8) | 0.0251 (8) | 0.0264 (8) | 0.0079 (6) | 0.0025 (6) | 0.0141 (6) |
| C2 | 0.0282 (10) | 0.0272 (9) | 0.0308 (10) | 0.0111 (8) | 0.0046 (8) | 0.0151 (8) |
| C1 | 0.0274 (10) | 0.0233 (9) | 0.0269 (10) | 0.0076 (7) | 0.0031 (7) | 0.0128 (8) |
| N2 | 0.0607 (14) | 0.0626 (14) | 0.0557 (13) | 0.0420 (12) | 0.0216 (11) | 0.0354 (11) |
| C7 | 0.0382 (11) | 0.0409 (12) | 0.0354 (11) | 0.0170 (10) | 0.0054 (9) | 0.0252 (10) |
| C3 | 0.0446 (13) | 0.0445 (12) | 0.0315 (11) | 0.0167 (10) | 0.0029 (9) | 0.0216 (10) |
| C6 | 0.0442 (13) | 0.0484 (13) | 0.0360 (12) | 0.0294 (11) | 0.0081 (10) | 0.0192 (10) |
| C5 | 0.0595 (16) | 0.0646 (16) | 0.0396 (13) | 0.0418 (14) | 0.0199 (12) | 0.0194 (12) |
| C4 | 0.0612 (16) | 0.0555 (15) | 0.0277 (11) | 0.0264 (13) | 0.0098 (10) | 0.0156 (10) |
| P1 | 0.0221 (3) | 0.0226 (3) | 0.0254 (3) | 0.00653 (18) | 0.00367 (18) | 0.0144 (2) |
| O4 | 0.0277 (7) | 0.0282 (7) | 0.0405 (8) | 0.0032 (6) | −0.0050 (6) | 0.0213 (6) |
| O3 | 0.0372 (8) | 0.0480 (9) | 0.0272 (8) | 0.0222 (7) | 0.0062 (6) | 0.0144 (7) |
| O2 | 0.0253 (7) | 0.0276 (7) | 0.0427 (8) | 0.0101 (5) | 0.0087 (6) | 0.0211 (6) |
| O1 | 0.0370 (8) | 0.0290 (7) | 0.0422 (9) | 0.0056 (6) | 0.0087 (6) | 0.0238 (7) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| N1—C1 | 1.452 (2) | C6—C5 | 1.384 (3) |
| N1—H1A | 0.8900 | C6—H6 | 0.9300 |
| N1—H1B | 0.8900 | C5—C4 | 1.379 (4) |
| N1—H1C | 0.8900 | C5—H5 | 0.9300 |
| C2—C3 | 1.390 (3) | C4—H4 | 0.9300 |
| C2—C1 | 1.393 (3) | P1—O1 | 1.4972 (14) |
| C2—C7 | 1.431 (3) | P1—O4 | 1.5004 (15) |
| C1—C6 | 1.368 (3) | P1—O2 | 1.5537 (14) |
| N2—C7 | 1.137 (3) | P1—O3 | 1.5770 (15) |
| C3—C4 | 1.368 (3) | O3—H3A | 0.8200 |
| C3—H3 | 0.9300 | O2—H2A | 0.8200 |
| C1—N1—H1A | 109.5 | C1—C6—H6 | 120.1 |
| C1—N1—H1B | 109.5 | C5—C6—H6 | 120.1 |
| H1A—N1—H1B | 109.5 | C4—C5—C6 | 120.8 (2) |
| C1—N1—H1C | 109.5 | C4—C5—H5 | 119.6 |
| H1A—N1—H1C | 109.5 | C6—C5—H5 | 119.6 |
| H1B—N1—H1C | 109.5 | C3—C4—C5 | 119.5 (2) |
| C3—C2—C1 | 119.88 (18) | C3—C4—H4 | 120.2 |
| C3—C2—C7 | 118.03 (18) | C5—C4—H4 | 120.2 |
| C1—C2—C7 | 122.07 (18) | O1—P1—O4 | 113.96 (8) |
| C6—C1—C2 | 119.67 (19) | O1—P1—O2 | 107.38 (8) |
| C6—C1—N1 | 119.67 (17) | O4—P1—O2 | 112.70 (8) |
| C2—C1—N1 | 120.64 (16) | O1—P1—O3 | 109.65 (9) |
| N2—C7—C2 | 176.7 (2) | O4—P1—O3 | 109.18 (9) |
| C4—C3—C2 | 120.2 (2) | O2—P1—O3 | 103.43 (8) |
| C4—C3—H3 | 119.9 | P1—O3—H3A | 109.5 |
| C2—C3—H3 | 119.9 | P1—O2—H2A | 109.5 |

| | | | |
|---|---|---|---|
| C1—C6—C5 | 119.9 (2) | | |
| C3—C2—C1—C6 | −1.2 (3) | C2—C1—C6—C5 | 0.6 (4) |
| C7—C2—C1—C6 | 177.2 (2) | N1—C1—C6—C5 | 178.9 (2) |
| C3—C2—C1—N1 | −179.47 (18) | C1—C6—C5—C4 | 0.2 (4) |
| C7—C2—C1—N1 | −1.1 (3) | C2—C3—C4—C5 | −0.2 (4) |
| C1—C2—C3—C4 | 0.9 (3) | C6—C5—C4—C3 | −0.4 (4) |
| C7—C2—C3—C4 | −177.5 (2) | | |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1B···O4$^{i}$ | 0.89 | 1.93 | 2.819 (2) | 176 |
| N1—H1C···O1$^{ii}$ | 0.89 | 1.85 | 2.723 (2) | 166 |
| N1—H1A···O1$^{iii}$ | 0.89 | 1.87 | 2.730 (2) | 161 |
| O3—H3A···N2$^{iv}$ | 0.82 | 1.98 | 2.797 (2) | 176 |
| O2—H2A···O4$^{v}$ | 0.82 | 1.76 | 2.574 (2) | 172 |

Symmetry codes: (i) *x*−1, *y*, *z*−1; (ii) −*x*+1, −*y*, −*z*+1; (iii) *x*, *y*, *z*−1; (iv) −*x*+2, −*y*, −*z*+1; (v) −*x*+2, −*y*+1, −*z*+2.

**Fig. 1**

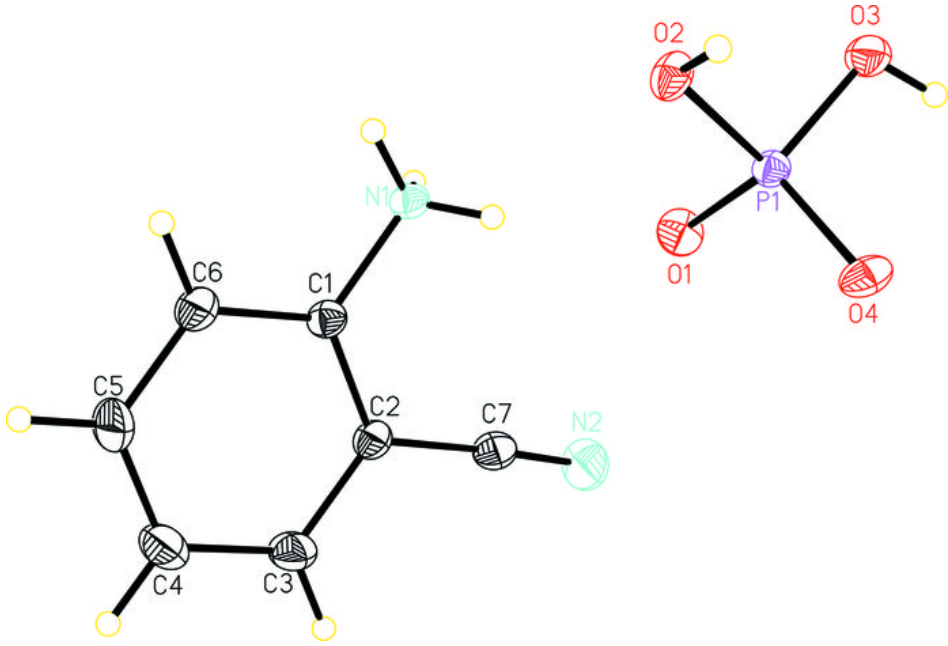

**Fig. 2**