

C4—C5	1.413 (2)	C11—C12	1.472 (6)
C5—C10	1.410 (2)	C12—O1	1.410 (3)
C5—C6	1.421 (2)	C13—O2	1.346 (15)
C6—C7	1.405 (2)	C13—C14	1.57 (2)
C7—C8	1.362 (2)	C14—O1	1.526 (13)
C8—O1	1.371 (2)		
C2—C1—C6	121.1 (2)	O1—C8—C9	121.1 (1)
C1—C2—C3	120.5 (2)	C10—C9—O2	118.7 (1)
C4—C3—C2	120.1 (2)	C10—C9—C8	120.0 (1)
C3—C4—C5	121.3 (1)	O2—C9—C8	121.3 (1)
C10—C5—C4	122.8 (1)	C9—C10—C5	121.4 (1)
C10—C5—C6	118.6 (1)	O2—C11—C12	112.7 (3)
C4—C5—C6	118.6 (1)	O1—C12—C11	112.4 (3)
C7—C6—C1	122.7 (1)	O2—C13—C14	104.8 (10)
C7—C6—C5	119.0 (1)	O1—C14—C13	107.6 (8)
C1—C6—C5	118.3 (1)	C8—O1—C12	115.9 (2)
C8—C7—C6	121.1 (1)	C8—O1—C14	110.3 (5)
C7—C8—O1	118.9 (1)	C13—O2—C9	117.4 (7)
C7—C8—C9	119.9 (1)	C9—O2—C11	114.2 (2)

La largeur de balayage est  $(0,75 + 0,5\text{tg}\theta)^\circ$ . Les intensités ont été corrigées des facteurs de Lorentz–polarisation. La structure a été résolue par les méthodes directes (*SHELXS86*; Sheldrick, 1990) puis affinée par la méthode des moindres carrés (*SHELXL93*; Sheldrick, 1993). Deux atomes de carbone du cycle *C* sont délocalisés sur deux positions C11, C12 et C13, C14 qu'ils occupent avec des taux respectifs 0,79 et 0,21.

Collection des données: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992; Enraf–Nonius, 1994). Affinement des paramètres de la maille: *CAD-4 EXPRESS*. Réduction des données: *MolEN* (Fair, 1990). Graphisme moléculaire: *ZORTEP* (Zsolnai, 1994). Logiciel utilisé pour préparer le matériel pour publication: *SHELXL93*.

Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: GS1007). Les processus d'accès à ces archives sont donnés au dos de la couverture.

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*Acta Cryst.* (1998). **C54**, 1867–1869

## Monoprotonated *o*-Phenylenediamine Dihydrogenphosphate

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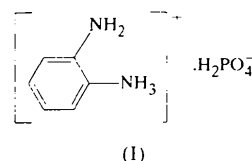
(Received 24 October 1997; accepted 6 July 1998)

## Abstract

The crystal structure of 2-aminophenylammonium dihydrogenphosphate,  $\text{C}_6\text{H}_9\text{N}_2^+\cdot\text{H}_2\text{PO}_4^-$ , consists of layers built up from  $\text{H}_2\text{PO}_4^-$  tetrahedra alternating with monoprotonated orthophenylenediamine molecules. Two types of hydrogen bond,  $\text{O}—\text{H}\cdots\text{O}$  and  $\text{N}—\text{H}\cdots\text{O}$ , ensure the cohesion and stability of the structure.

## Comment

The structure of the title compound, (I), consists of corrugated inorganic sheets alternating with organic layers consisting of monoprotonated orthophenylenediamine cations. The two types of layer are parallel to the *ab* plane (Fig. 1). In the inorganic layer, the phosphate entities are connected through a strong  $\text{O4}—\text{HO4}\cdots\text{O2}^{\text{ii}}$  hydrogen bond [Table 2; symmetry code: (ii)  $1+x, y, z$ ] with an  $\text{O}\cdots\text{O}$  distance of 2.513 (2) Å (Brown, 1976), and form infinite  $(\text{HPO}_4)_n$  chains parallel to *a*. All bond lengths and angles are typical of these species



(Soumhi & Jouini, 1995; Riou *et al.*, 1993). The phosphate groups also make strong  $\text{O3}—\text{HO3}\cdots\text{N2}^{\text{i}}$  hydrogen bonds to the organic cations, with an  $\text{O}\cdots\text{N}$  distance of 2.744 (3) Å [symmetry code: (i)  $-x, -y, 1-z$ ]. In addition, the cations participate in no fewer than five other hydrogen bonds of the  $\text{N}—\text{H}\cdots\text{O}$  type involving all amino-H atoms, although two of them,  $\text{N2}—\text{H1N2}\cdots\text{O1}^{\text{iii}}$  and  $\text{N2}—\text{H2N2}\cdots\text{O3}^{\text{v}}$  are comparatively weak [symmetry codes: (iii)  $x-1, y, z$ ; (v)  $1-x, -y, 1-z$ ]. The protonated and therefore positively charged N1 atom is involved in three comparatively strong  $\text{N}—\text{H}\cdots\text{O}$  bonds and is clearly donor in nature. Atom N2, by comparison, behaves as an acceptor, participating in an  $\text{O}—\text{H}\cdots\text{N}$  bond.

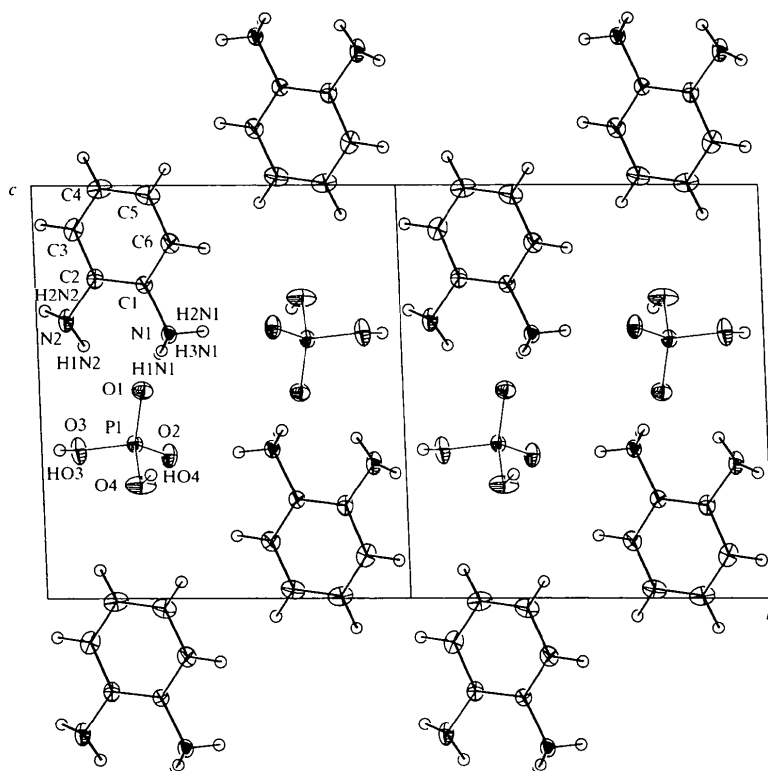


Fig. 1. Projection of the title compound in the [100] direction. Displacement ellipsoids are plotted at the 50% probability level.

## Experimental

In an attempt to synthesize a novel material containing boron in combination with phosphorus as the tetrahedral atoms,  $(NH_2C_6H_4NH_3)H_2PO_4$  was prepared hydrothermally from a 1:3:3:72 mixture of  $H_3BO_3$  (0.05 g),  $H_3PO_4$  (0.23 g),  $C_6H_8N_2$  (0.25 g) and  $H_2O$  (1.0 g). A thick gel formed and was heated at 373 K for 10 d: a crystalline product was obtained.

$\omega/2\theta$  scans

Absorption correction:

$\psi$  scan (North *et al.*, 1968)

$T_{min} = 0.935$ ,  $T_{max} = 1.000$

1865 measured reflections

1639 independent reflections

$R_{int} = 0.020$

$\theta_{max} = 24.96^\circ$

$h = -5 \rightarrow 0$

$k = -11 \rightarrow 11$

$l = -12 \rightarrow 12$

1 standard reflection

frequency: 120 min

intensity decay: 0.5%

## Crystal data

$C_6H_9N_2^+ \cdot H_2PO_4^-$

$M_r = 206.14$

Triclinic

$P\bar{1}$

$a = 4.556(2) \text{ \AA}$

$b = 9.689(2) \text{ \AA}$

$c = 10.752(2) \text{ \AA}$

$\alpha = 91.30(2)^\circ$

$\beta = 95.16(2)^\circ$

$\gamma = 100.71(2)^\circ$

$V = 464.1(2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.475 \text{ Mg m}^{-3}$

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 6-17^\circ$

$\mu = 0.282 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Needle

$0.36 \times 0.11 \times 0.07 \text{ mm}$

Brown

## Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.091$

$S = 1.092$

1639 reflections

163 parameters

All H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.1667P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max} = 0.266 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -0.289 \text{ e \AA}^{-3}$

Extinction correction:

*SHELXL93* (Sheldrick, 1993)

Extinction coefficient:

0.019 (6)

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

P1—O1	1.499 (2)	P1—O3	1.571 (2)
P1—O2	1.502 (2)	N1—C1	1.458 (2)
P1—O4	1.546 (2)	N2—C2	1.414 (3)
O1—P1—O2	113.4 (1)	O1—P1—O3	110.4 (1)
O1—P1—O4	111.6 (1)	O2—P1—O3	105.2 (1)
O2—P1—O4	110.6 (1)	O4—P1—O3	105.1 (1)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O3—HO3...N2 <sup>i</sup>	0.76 (3)	1.99 (3)	2.744 (3)	169 (3)
O4—HO4...O2 <sup>ii</sup>	0.81 (3)	1.70 (3)	2.513 (2)	175 (3)
N1—H1N1...O1 <sup>iii</sup>	0.91 (3)	1.88 (3)	2.784 (2)	176 (2)
N1—H2N1...O2 <sup>iv</sup>	0.89 (3)	1.85 (3)	2.731 (2)	178 (2)
N1—H3N1...O1	0.84 (3)	1.97 (3)	2.809 (3)	176 (2)
N2—H1N2...O1 <sup>iii</sup>	0.85 (3)	2.16 (3)	2.972 (3)	161 (2)
N2—H2N2...O3 <sup>v</sup>	0.87 (3)	2.29 (3)	3.051 (3)	147 (2)

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

Data collection: CAD-4 EXPRESS (Duisenberg, 1992; Macíček & Jordanov, 1992). Cell refinement: CAD-4 EXPRESS. Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1225). Services for accessing these data are described at the back of the journal.

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*Acta Cryst.* (1998). C54, 1869–1871

*trans*-2,2'-Dichloro-4,4'-dimethylazobenzene

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(Received 29 April 1998; accepted 26 June 1998)

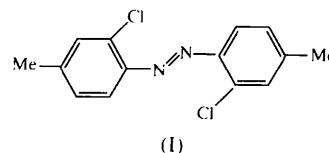
Abstract

The X-ray crystal structure of the title compound, C<sub>14</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>2</sub>, reveals a *trans* geometry of the two Cl atoms in the *ortho* position with respect to the azo

group. In the crystal packing the aromatic rings are stacked in a herring-bone mode along the *y* direction.

Comment

Azobenzenes have been extensively used as ligands suitable for investigation on cyclometallated systems (Ryabov, 1990). In the course of our ongoing work on the synthesis and structural characterization studies of cyclopalladated mesogens containing azobenzene ligands (Crispini *et al.*, 1996), the title compound, (I), was synthesized and we report here its crystal structure. The compound was synthesized using 2-chloro-*p*-toluidine and following the synthetic routine recently reported in the literature (Bermúdez *et al.*, 1994).



The molecule occupies a special position at an inversion centre and is essentially planar. The torsion angle about the central bond of 180° confirms a *trans* conformation with both aromatic rings in a parallel orientation, typical for stilbenes and diphenylazobenzenes (Bouwstra *et al.*, 1985; Klebe, 1994). Moreover, both these molecules display preferences for planarity of the entire Ph—X—X—Ph (X = C, N) fragment, with exceptions, due to the steric repulsion, in examples with non-H atoms at the *ortho* positions. The torsion angles about the N—C bond [N1'—N1—C1—C2 = -166.4 (2) and N1'—N1—C1—C6 = 14.4 (3)°] are comparable with the corresponding values of the related compound *trans*-2,2'-dichloroazobenzene [168.5 and -14.3°] (Komeyama *et al.*, 1973) and greater than values found for 4,4'-disubstituted azobenzenes like 4,4'-azodiphenetole (175.0, -171.7 and 7.7, -6.4°) (Galigne, 1970) and 4,4'-dibromoazobenzene (178.3 and -1.3°) (Howard *et al.*, 1994).

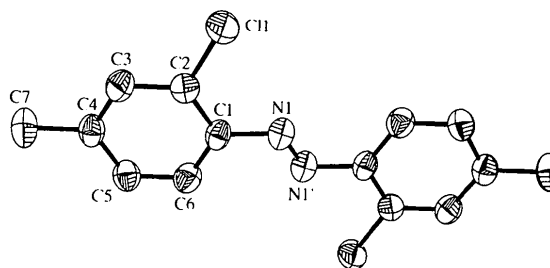


Fig. 1. Structure of the molecule showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

The packing type can be easily identified as the simplest pattern observed for aromatic hydrocarbons: the herring-bone motif HB (Gavezzotti & Desiraju, 1988; Desiraju & Gavezzotti, 1989). As shown in Fig. 2,