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The Crystal Structure of Monosodium Phosphoramidate,* $NaHPO_3NH_2$

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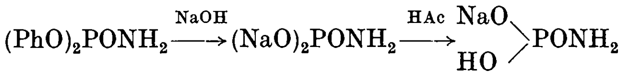
The crystal structure of monosodium phosphoramidate, $NaHPO_3NH_2$, has been determined by the use of three-dimensional Fourier methods. The unit-cell dimensions are: $a = 5{\cdot}773 \pm 0{\cdot}003$, $c = 6{\cdot}031 \pm 0{\cdot}003$ Å. There are two molecules per unit cell and the space group is $P6_3$. The structure shows that the phosphoramidate ion exists as a zwitter ion $[NH_3^+PO_3^-]^-$, the phosphorus atom being surrounded tetrahedrally by three oxygen and one nitrogen atoms. Each nitrogen atom is linked by three hydrogen bonds to oxygen atoms in neighbouring anions. Each sodium ion is surrounded by a distorted octahedral co-ordination group. The bond lengths are P–N = $1{\cdot}78 \pm 0{\cdot}03$ Å, P–O = $1{\cdot}51 \pm 0{\cdot}02$ Å, and N–H–O = $2{\cdot}84 \pm 0{\cdot}02$ Å. There are many similarities between the $[NH_3^+PO_3^-]^-$ ion and the zwitter ion molecule $NH_3^+SO_3^-$ present in sulphamic acid.

Introduction

Monosodium phosphoramidate presents several interesting features which can be investigated by an X-ray structure determination. One of these is the possibility of the phosphoramidate anion existing as a polar zwitter ion in the solid state. X-ray work has already shown that both glycine (Albrecht & Corey, 1940) and sulphamic acid (Kanda & King, 1951) (the latter being isoelectronic with the phosphoramidate ion) possess structures containing zwitter ions. Another feature of interest is the phosphorus–nitrogen bond; no accurate X-ray determination of the P–N single-bond distance has previously been made and sodium phosphoramidate offers itself as a suitable compound for this purpose.

Sodium phosphoramidate was prepared from diphenyl phosphoramidate. The latter was converted to the soluble disodium salt by hydrolysis with sodium hydroxide and the insoluble monosodium salt precipitated by addition of acetic acid according to the following scheme:



$$(PhO)_2PONH_2 \xrightarrow{NaOH} (NaO)_2PONH_2 \xrightarrow{HAc} \begin{matrix} NaO \\ HO \end{matrix} \rangle PONH_2$$

The insoluble nature of the compound prevented the preparation by growth from simple solution of specimens large enough for single-crystal work; recourse had therefore to be made to slow precipitation methods involving acidification of a solution of the disodium salt. Slow precipitation over periods of several hours failed to produce crystals larger than about 0·25 mm. in any dimension. Considerable difficulty was encountered in making material with an analysis identical with the theoretical for $NaHPO_3NH_2$. In all cases the proportions of nitrogen and phosphorus were a little lower and higher respectively than the theoretical. The powder diagrams of the specimens used for X-ray analysis showed no sign of impurities, however, and the cell dimensions found in single-crystal studies were always identical with those found from powder photographs. The traces of impurity which give rise to the difference between the observed and theoretical analyses are presumably the same as cause the difference between the observed density and that which we have calculated from unit-cell dimensions.

Crystallographic data

Sodium phosphoramidate crystallizes in the form of very small colourless six-sided prisms.

System: hexagonal.
Unit-cell dimensions: $a = 5{\cdot}773 \pm 0{\cdot}003$; $c = 6{\cdot}031 \pm 0{\cdot}003$ Å.
Space group: $P6_3$.
Number of molecules per cell: $n = 2$ units of $NaHPO_3NH_2$.
Density: $\varrho_o = 2{\cdot}17$ g.cm.$^{-3}$; $\varrho_c = 2{\cdot}27$ g.cm.$^{-3}$.
Optical properties (white light): uniaxial negative; $w = 1{\cdot}56$, $\varepsilon = 1{\cdot}52$.

Preliminary X-ray experimental work

A 19 cm. powder photograph taken with Cu $K\alpha$ radiation gave a series of lines which could be fitted with an expression of the form $\sin^2\theta = A(h^2+hk+k^2)+Cl^2$. From single-crystal c- and a-axis oscillation photographs, the only systematic absences found to occur were those of type $(00l)$ when l was odd; moreover the c-axis photographs were observed to be identical at intervals of 60°. These data were consistent with hexagonal space groups $P6_3$, $P6_3/m$ or $P6_322$. The unit-cell dimensions were obtained from measurement of the high-angle α_1 and α_2 lines on the powder photo-

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* Nomenclature agreed by the Chemical Society and the American Chemical Society, September 1952.

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graph. The crystal density, determined by flotation in a mixture of carbon tetrachloride and methylene iodide, showed that the cell contained 2 units of $NaHPO_3NH_2$.

Deduction of space group and atomic arrangement

Since a difference exists between the point groups 6 and $6/m$ on the one hand, and 62 on the other, a study of the $(hki0)$ reflexions from the c-axis photographs enabled a choice to be made. Reflexions of the type $(hki0)$ were found to have different intensities from those of the type $(khi0)$ with the same θ values, and on this basis space group $P6_32$ could be rejected.

At this stage it was provisionally assumed that the anion would consist of one nitrogen and three oxygen atoms arranged approximately tetrahedrally around the phosphorus atom. Since each cell contains only two of these anions, if the space group is centrosymmetrical, they must lie either (a) on centres of symmetry at $(0, 0, 0)$ and $(0, 0, \frac{1}{2})$, (b) on a mirror plane perpendicular to 6_3 axis at $(0, 0, \frac{1}{4})$ and $(0, 0, \frac{3}{4})$, or (c) on a mirror plane perpendicular to the threefold axes at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$ or $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ and $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$.

A tetrahedral ion has no centre of symmetry, and cannot lie with the phosphorus atom as in (a). In addition, such an ion cannot lie with the phosphorus atom in the mirror plane and with the P–N link along the 6_3 or the threefold axis. If, then, this assumption is right, space group $P6_3/m$ cannot be the correct one.

Further support for this contention resulted from the observation of a feeble but distinct pyroelectric effect, which indicated the absence of a centre of symmetry in the crystal structure.

The special and general positions for space group $P6_3$ are:

$$
\begin{aligned}
n = 2\colon\ & (a)\ (0, 0, z),\ (0, 0, \tfrac{1}{2}+z)\ \text{or} \\
& (b)\ (\tfrac{1}{3}, \tfrac{2}{3}, z),\ (\tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{2}+z); \\
n = 6\colon\ & (c)\ (x, y, z),\ (\bar{y}, x-y, z),\ (y-x, \bar{x}, z), \\
& (\bar{x}, \bar{y}, \tfrac{1}{2}+z),\ (y, y-x, \tfrac{1}{2}+z),\ (x-y, x, \tfrac{1}{2}+z).
\end{aligned}
$$

Assuming an approximately tetrahedral ion with dimensions P–O $\sim 1{\cdot}55$ Å and P–N $\sim 1{\cdot}80$ Å, positions (a) for the phosphorus atoms can be excluded. Two such ions cannot both lie on the 6_3 axis without considerable mutual interference. If, however, the ions are placed with the phosphorus and nitrogen atoms on the threefold axes, i.e. at positions (b), a quite feasible arrangement results. The sodium ions can then be assigned positions (a), the oxygen atoms will occupy positions (c), being grouped with threefold symmetry round the phosphorus atoms.

Intensity data

Experimental intensity data were obtained by visual estimation from oscillation photographs taken with Cu $K\alpha$ radiation. Series of 15° oscillations, each with 5° overlap, were made about the a and c axes using different crystals, each between 0·1 and 0·2 mm. in all dimensions. A multiple-film technique was employed, using four films interleaved with aluminium foil. A standard set of intensities was obtained with the use of a specially adapted film cylinder. Using these, the intensities of the zero layer line reflexions were first estimated and were then used as standards for estimation of the general layer line intensities, making appropriate corrections for oblique incidence effects.

Lorentz, polarisation and angular-velocity corrections were applied by the use of Kaan & Cole charts. The crystals used were considerably smaller than the optimum dimensions and no corrections for absorption were made. A total of 1074 spots was estimated, giving a final list of 119 non-equivalent (hkl)-type reflexions of measurable intensity plus 12 of zero intensity.

The c-axis projection

A study of the structure in c projection was made first since it is centrosymmetrical and because only the x and y parameters of the oxygen atoms had to be found. It was apparent that the signs of many of the $(hki0)$ terms could be determined with reasonable certainty by calculation of the structure factors including the sodium nitrogen and phosphorus contributions only.

A Fourier synthesis was carried out with these terms, but the positions of the oxygen atoms were not determined without ambiguity and some trial-and-error work had to be done. From the previous assumption of a tetrahedral anion with P–O $\sim 1{\cdot}55$ Å, it follows that, with both the phosphorus and nitrogen atoms lying on the threefold axis, the projections of the P–O links will lie at mutual angles of 120° on a circle of radius $\sim 1{\cdot}44$ Å in projection.

The effect of rotation of the oxygen atoms about the threefold axes on those structure factors of uncertain sign was studied. Structure factors were calculated for 10° intervals of rotation, and a position of optimum agreement between observed and calculated values was found. These approximate oxygen coordinates enabled further refining syntheses to be made, and the final c-axis projection is shown in Fig. 1.

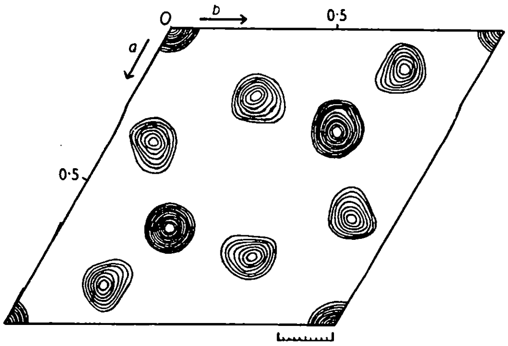


Fig. 1. Electron density: c-axis projection. Contours at arbitrary intervals.

Three-figure Beevers & Lipson strips were used for all syntheses, the electron density being evaluated over a mesh of $\frac{1}{60}$th intervals of the unit-cell edge. The final oxygen parameters obtained from this map were $x = 0{\cdot}132$, $y = 0{\cdot}768$.

The a-axis projection

By means of a study with models, it was apparent from packing considerations that the possible positions of the phosphorus atom would be limited to between about $z = 0{\cdot}30$ and $z = 0{\cdot}34$ if the sodium ions were put at $z = 0$ and $z = \frac{1}{2}$. Taking a minimum Na–O distance of $\sim 2{\cdot}5$ Å, it was found that with the phosphorus atom outside the above limits a serious overlap would occur between the sodium ions and some part of the tetrahedral anion.

These considerations enabled sufficient structure factor agreement to be obtained for Fourier syntheses to be done, and the final one is shown in Fig. 2. The z-coordinates obtained from this map were $z_P = 0{\cdot}321$, $z_N = 0{\cdot}618$, $z_O = 0{\cdot}257$.

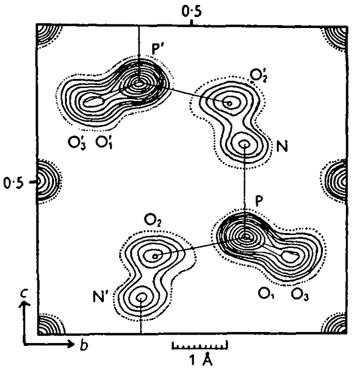


Fig. 2. Electron density: a-axis projection. Contours at arbitrary intervals.

Three-dimensional section and line syntheses

Successive three-dimensional section and line syntheses were done, starting with the coordinates obtained from the projection syntheses. The line syntheses were carried out along the threefold axes to include the phosphorus and nitrogen atoms, and through each of the three oxygen atoms. The sections were taken through the mean plane of the oxygen atoms, calculated in each case from the results of the previous line syntheses.

The electron-density functions were evaluated at points over a mesh of intervals $\frac{1}{60}$th of the cell edges in the case of the sections, and the line syntheses were evaluated at intervals of $\frac{1}{120}$th of c.

The final three-dimensional syntheses, using 390 terms, are shown in Figs. 3 and 4. In these final syntheses the electron-density function was evaluated at points at intervals of $\frac{1}{200}$th of the cell edges in the regions of the peak maxima. The coordinates of the peak maxima were obtained by an interpolation method (Booth, 1948) and are given in the complete list of atomic coordinates in Table 1.

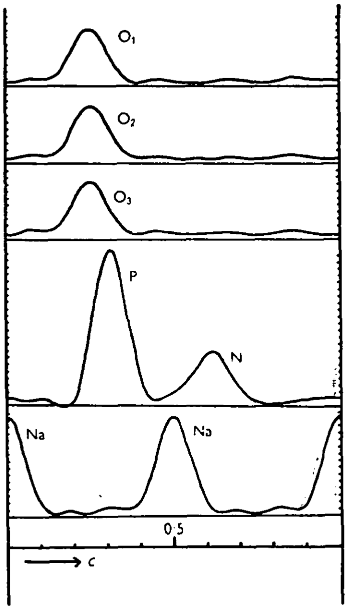


Fig. 3. Three-dimensional line syntheses. Electron-density distribution along lines parallel to c.

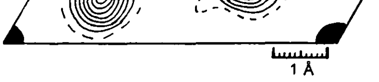


Fig. 4. Composite electron-density map from three-dimensional Fourier syntheses parallel to (0001). Contours at intervals of 1 e.Å^{-3}; lowest contour broken. Section through phosphorus atom is 0·34 Å out of plane of maximum density.

Table 1. *Final atomic coordinates*

	x		y		z	
	Obs.	Corr.	Obs.	Corr.	Obs.	Corr.
Na	0	—	0	—	0	0·000
P	$\frac{1}{3}$	—	$\frac{2}{3}$	—	0·311	0·311
N	$\frac{1}{3}$	—	$\frac{2}{3}$	—	0·618	0·607
O	0·153	0·153	0·778	0·779	0·255	0·255
O	0·222	0·221	0·375	0·374	0·255	0·255
O	0·625	0·626	0·847	0·847	0·255	0·255

In order to correct for termination-of-series errors, section and line syntheses were carried out using the F_c values obtained from the final syntheses with the

Table 3. *Observed and calculated structure amplitudes*

hkil	F_o	F_c	α_o
0002	32·1	31·7	194·4
0004	29·5	29·8	39·0
0006	11·7	12·1	273·9
$10\bar{1}0$	0	1·8	0
$10\bar{1}1$	25·9	30·7	209·1
$10\bar{1}2$	20·7	21·7	7·1
$10\bar{1}3$	24·3	26·7	37·2
$10\bar{1}4$	14·7	14·7	30·3
$10\bar{1}5$	8·8	7·9	255·3
$10\bar{1}6$	5·6	6·2	51·9
$10\bar{1}7$	8·3	7·0	145·4
$20\bar{2}0$	13·7	11·1	180·0
$20\bar{2}1$	17·5	17·2	147·9
$20\bar{2}2$	28·2	29·9	6·4
$20\bar{2}3$	15·2	13·4	293·7
$20\bar{2}4$	10·0	9·3	116·5
$20\bar{2}5$	13·2	13·2	158·4
$20\bar{2}6$	8·6	9·3	34·9
$20\bar{2}7$	11·5	13·4	352·1
$30\bar{3}0$	29·1	27·8	0
$30\bar{3}1$	11·7	8·9	1·8
$30\bar{3}2$	9·4	7·9	321·4
$30\bar{3}3$	7·1	6·8	185·4
$30\bar{3}4$	13·9	12·7	81·5
$30\bar{3}5$	3·2	4·5	8·8
$30\bar{3}6$	14·1	13·6	325·4
$40\bar{4}0$	6·2	5·5	180·0
$40\bar{4}1$	8·6	6·5	254·0
$40\bar{4}2$	16·5	16·6	9·3
$40\bar{4}3$	11·3	9·4	82·9
$40\bar{4}4$	7·7	7·1	302·5
$40\bar{4}5$	7·9	7·2	322·8
$50\bar{5}0$	3·8	5·1	0
$50\bar{5}1$	9·0	7·6	44·2
$50\bar{5}2$	5·3	4·4	22·5
$50\bar{5}3$	9·0	8·9	242·2
$50\bar{5}4$	10·7	10·6	157·2
$60\bar{6}0$	16·2	13·9	0
$60\bar{6}1$	0	1·5	1·5
$60\bar{6}2$	4·9	3·3	246·6
$11\bar{2}0$	30·1	35·9	0
$11\bar{2}1$	10·7	8·7	1·8
$11\bar{2}2$	13·0	12·2	337·1
$11\bar{2}3$	7·7	5·2	185·5
$11\bar{2}4$	15·4	14·7	84·6
$11\bar{2}5$	0	3·1	9·1
$11\bar{2}6$	14·3	15·7	33·1
$11\bar{2}7$	0	2·0	192·9
$12\bar{3}0$	4·7	4·4	0
$12\bar{3}1$	15·4	14·7	38·6
$12\bar{3}2$	15·2	14·7	9·7
$12\bar{3}3$	16·5	15·9	232·3
$12\bar{3}4$	13·3	13·0	328·7
$12\bar{3}5$	7·0	6·3	105·9
$12\bar{3}6$	4·1	4·6	63·0
$13\bar{4}0$	7·5	5·0	180·0
$13\bar{4}1$	20·1	20·2	202·6
$13\bar{4}2$	18·8	18·9	8·9
$13\bar{4}3$	17·1	18·4	37·4
$13\bar{4}4$	7·0	7·6	302·1
$13\bar{4}5$	7·0	6·9	244·9
$13\bar{4}6$	6·2	6·5	39·5
$14\bar{5}0$	24·1	25·2	0
$14\bar{5}1$	0	0·4	180·0
$14\bar{5}2$	6·0	5·4	238·8
$14\bar{5}3$	0	0·3	7·1
$14\bar{5}4$	10·9	11·4	61·6
$15\bar{6}0$	5·6	7·0	0
$15\bar{6}1$	8·3	7·3	39·8
$15\bar{6}2$	0	1·7	56·7
$15\bar{6}3$	9·0	8·1	237·9
$21\bar{3}0$	18·4	18·9	0
$21\bar{3}1$	15·4	14·3	219·9
$21\bar{3}2$	3·2	3·1	36·2
$21\bar{3}3$	16·0	15·6	53·3
$21\bar{3}4$	19·4	20·1	343·4
$21\bar{3}5$	7·0	6·3	288·0
$21\bar{3}6$	4·7	4·5	136·1
$22\bar{4}0$	34·2	41·6	0
$22\bar{4}1$	0	1·0	2·1
$22\bar{4}2$	12·4	11·2	211·0
$22\bar{4}3$	0	0·6	187·1
$22\bar{4}4$	17·5	17·6	47·4
$22\bar{4}5$	0	0·5	8·1
$22\bar{4}6$	8·5	9·2	291·8
$23\bar{5}0$	6·0	5·5	180·0
$23\bar{5}1$	17·9	17·7	20·8
$23\bar{5}2$	16·0	15·9	9·3
$23\bar{5}3$	15·6	16·2	217·3
$23\bar{5}4$	5·6	6·3	294·7
$23\bar{5}5$	4·9	6·6	56·4
$24\bar{6}0$	0	2·1	180·0
$24\bar{6}1$	8·5	6·4	229·9
$24\bar{6}2$	9·6	10·3	10·9
$24\bar{6}3$	8·5	7·9	66·5
$25\bar{7}0$	11·5	11·4	0
$31\bar{4}0$	6·8	6·2	0
$31\bar{4}1$	11·5	10·1	47·0
$31\bar{4}2$	10·3	8·6	14·7
$31\bar{4}3$	12·4	11·8	241·2
$31\bar{4}4$	11·7	12·3	333·1
$31\bar{4}5$	6·2	6·2	120·6
$31\bar{4}6$	3·2	3·3	81·7
$32\bar{5}0$	5·3	3·5	180·0
$32\bar{5}1$	11·7	10·1	216·3
$32\bar{5}2$	15·4	13·9	10·2
$32\bar{5}3$	12·4	11·3	54·5
$32\bar{5}4$	6·0	6·9	306·8
$32\bar{5}5$	4·9	4·9	287·6
$33\bar{6}0$	17·3	17·6	0
$33\bar{6}1$	4·5	4·6	1·9
$33\bar{6}2$	3·8	3·9	277·9
$34\bar{7}0$	3·2	1·5	180·0
$34\bar{7}1$	4·9	4·1	67·5
$41\bar{5}0$	16·5	16·2	0
$41\bar{5}1$	10·0	9·9	181·7
$41\bar{5}2$	6·8	6·5	319·9
$41\bar{5}3$	7·7	7·9	5·3
$41\bar{5}4$	10·5	9·3	93·6
$41\bar{5}5$	6·0	7·7	189·0
$42\bar{6}0$	0	0·4	0
$42\bar{6}1$	7·3	5·6	60·6
$42\bar{6}2$	7·5	8·0	13·6
$42\bar{6}3$	9·0	7·5	74·1
$43\bar{7}0$	6·8	5·1	0
$43\bar{7}1$	8·8	6·4	218·4
$51\bar{6}0$	4·1	3·3	180·0
$51\bar{6}1$	8·3	6·6	224·3
$51\bar{6}2$	10·3	10·7	10·6
$51\bar{6}3$	9·4	7·7	62·0
$52\bar{7}0$	15·0	15·6	0

F_o values. The parameter changes were in most cases very small and the corrected values are listed in Table 1. The largest shift was found to be in the case of the nitrogen atom, which amounted to 0·06 Å. This shift was not considered unduly large in view of the proximity of the relatively heavy phosphorus atom and the fact that both the phosphorus and nitrogen atoms lie on the three-fold axis. Since the structure is non-centrosymmetric, and the z parameters are affected solely by non-centrosymmetric planes, the shift of the nitrogen atom was taken to be twice that indicated by the correction synthesis (Cruickshank, 1950).

In the case of the oxygen atoms, the n-shift rule (Shoemaker *et al.*, 1950) should be applied; this requires the shifts to be multiplied by a factor between 1 and 2 depending on the relative importance of the real and complex structure factors. Since, however, the oxygen shifts were small compared with that of nitrogen, and were only in the x and y parameters, a factor of unity was taken, which, together with the double shift for nitrogen, was found to give the best overall structure-factor agreement.

The final bond lengths are probably correct to within about ±0·02 Å, except the P–N distance, which may be less accurate in view of the large termination-of-series error on the nitrogen parameter. The final bond lengths, interatomic distances and angles calculated from the corrected coordinates are given in

Table 2. Other distances and angles are shown in the diagrams.

A temperature factor of $B = 1{\cdot}0$ Å^2 was used, this being the value which gave the best overall structure-factor agreement. The final list of observed and calculated structure factors is given in Table 3.

The value of the function

$$R = \Sigma||F_o|-|F_c||\div\Sigma|F_o| \text{ was } 10{\cdot}4\% .$$

(With parameters uncorrected for termination of series errors, $R = 11{\cdot}1\%$.)

Table 2. *Interatomic distances and angles in sodium phosphoramidate*

P–N = 1·785 Å
P–O$_1$ = 1·511   O$_1$–O$_2$ = 2·557 Å
P–O$_2$ = 1·517   O$_2$–O$_3$ = 2·557
P–O$_3$ = 1·517   O$_3$–O$_1$ = 2·557

N–O$_1'$ = 3·215   N–H–O$_1'$ = 2·842
N–O$_2'$ = 3·213   N–H–O$_2'$ = 2·844
N–O$_3'$ = 3·219   N–H–O$_3'$ = 2·839

O$_1$PO$_2$ = 115° 11′   NPO$_1$ = 102° 55′
O$_2$PO$_3$ = 115 2   NPO$_2$ = 102 56
O$_3$PO$_1$ = 115 17   NPO$_3$ = 102 56

PNO$_1'$ = 108 20   O$_1$NO$_2'$ = 110 32
PNO$_2'$ = 108 18   O$_2$NO$_3'$ = 110 37
PNO$_3'$ = 108 20   O$_3$NO$_1'$ = 110 42

The observed intensities were put on an absolute scale by calculating the average ratio F_o/F_c from all planes, and slightly adjusting this factor until the value of R was a minimum.

Discussion of structure

The phosphoramidate ion has complete threefold symmetry about the phosphorus–nitrogen bond direction which is coincident with a threefold axis of the unit cell. The nitrogen atom is linked by hydrogen bonds to three oxygen atoms, each belonging to a different ion. In this way the threefold symmetry is preserved, all the hydrogen atoms being structurally equivalent. The anion exists as a zwitter ion and can be written $[\mathrm{NH}_3^+.\mathrm{PO}_3^-]^-$. The experimental value for the N–H–O distance, 2·84 Å, agrees with that often found for such a linkage, e.g. sulphamic acid, 2·82 Å; diketopiperazine, 2·85 Å; $NH_4H_2PO_2$, 2·81 Å; acetamide, 2·83 Å; cyanuric acid, 2·83 and 2·88 Å. The distribution of the bonds around the nitrogen atom is approximately tetrahedral, which is to be expected as a result of the positive charge conferred by the zwitter-ion effect. In addition to the three oxygen atoms linked by hydrogen bonds, each nitrogen is surrounded by three other oxygen atoms at a greater distance of 3·21 Å. The hydrogen bond system links all the anions in a continuous network in three-dimensions. Moreover, the binding of the structure should be increased by the electrostatic attraction between the charged extremes of the polar anions.

Each sodium ion is six-coordinated by oxygen in an approximately octahedral arrangement, with three Na–O distances of 2·39 Å on one side, and three of length 2·43 Å on the other. Every oxygen atom is shared between two cations in the coordination scheme, which results in a continuous chain in the *c*-axis direction (Fig. 6). The Na–O distances of 2·39 and 2·43 Å can be compared with the values found in other structures, e.g. sodium bromate, 2·38 Å; sodium nitrate, 2·40 Å; sodium nitrite, 2·48 Å; sodium sulphate, 2·41 Å; sodium formate, 2·44 Å; sodium bicarbonate, 2·47 Å; and sodium sesquicarbonate, 2·45 Å.

The disposition of the bonds round the phosphorus

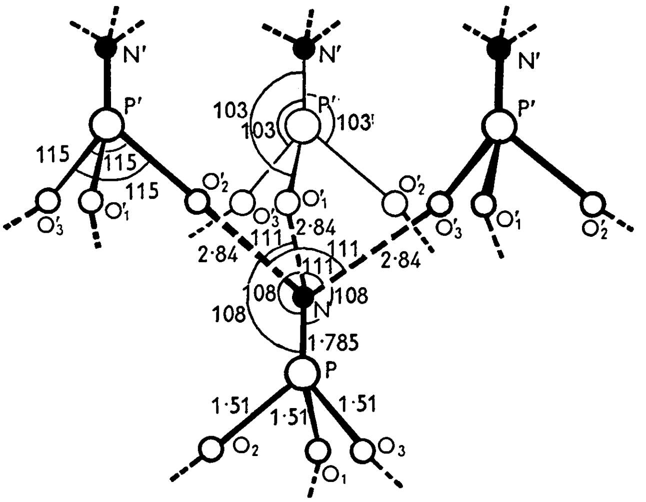


Fig. 5.

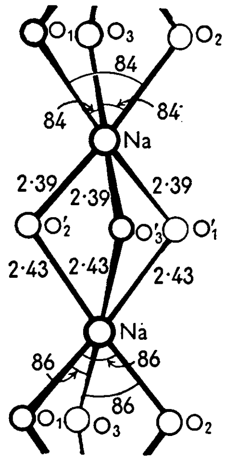
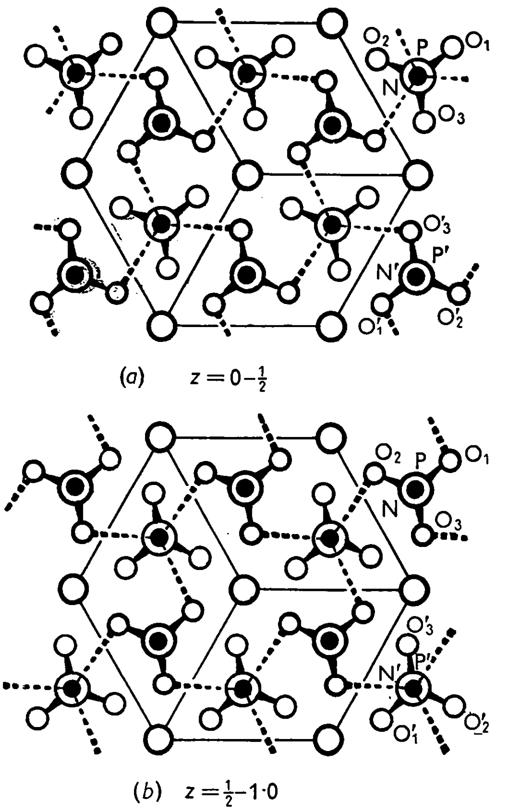


Fig. 6.

Fig. 5. Environment of the phosphoramidate ion. N–H–O bonds shown broken. All distances in Ångström units and all angles in degrees.

Fig. 6. Coordination of Na$^+$ ions. All distances in Ångström units and all angles in degrees.

atom is like that of a somewhat flattened tetrahedron, with angles as shown in Fig. 5. The mutual repulsion of the oxygen atoms probably contributes to this flattening effect. The experimental P–O distance of 1·51 Å can be compared with the P–O distances of 1·51 Å in $Al(PO_3)_3$, 1·51 Å in $NH_4H_2PO_2$, 1·51 Å in SiP_2O_7, 1·56 Å in KH_2PO_4, 1·44–1·59 Å in $(NH_4PO_3)_4$ and 1·54 Å in BPO_4.



(a) $z = 0–\frac{1}{2}$

(b) $z = \frac{1}{2}–1·0$

Fig. 7. Sodium phosphoramidate structure in *c* projection. Nitrogen atoms are full circles and N–H–O links are shown broken. (*a*) Linkages to anion below the lettered one; (*b*) linkages to anion above.

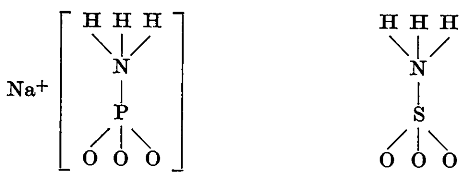
It is worth noting that, owing to the nature of the structure, it is possible for the substance to exist in enantiomorphous forms which cannot normally be distinguished from each other by the usual X-ray methods. One is the image of the other projected across the mirror plane carrying two adjacent threefold axes. We have made no effort to look for laevo- and dextrorotatory crystals.

An interesting comparison (Table 4) can be made between the structure of the phosphoramidate ion and that of the isoelectronic sulphamic acid molecule which has already been shown to exist as a zwitter ion in the crystalline state (Kanda & King, 1951).

In the case of sulphamic acid, the tetrahedral distribution of bonds around sulphur is rather more distorted than that in the phosphoramidate ion. The experimental values for both P–N and S–N indicate single bonds, and agree closely with the values predicted by the sum of their respective covalent radii (Gordy, 1947; Pauling, 1944) after the appropriate corrections for electronegativity difference have been made. Sodium phosphoramidate may also be compared with glycine (Albrecht & Corey, 1940) which appears to exist in the zwitter ion form $NH_3^+CH_2COO^-$ in the crystalline state. In this latter structure the C–N distance is rather shorter than expected, namely 1·39±0·02 Å (r_C+r_N = 1·51 Å). Moreover, the layer-type structure results in a less symmetrical hydrogen bond system round the nitrogen than is the case with sodium phosphoramidate where threefold symmetry is imposed crystallographically.

Table 4. *Comparison between sodium phosphoramidate and sulphamic acid*

Sodium phosphoramidate Sulphamic acid



NPO	103°	NSO	98° (average)
OPO	115°	OSO	117°
N–H–O	2·84 Å	N–H–O	2·82, 2·83 Å
P–N	1·785±0·03 Å	S–N	1·73±0·05 Å

Sum of covalent radii:

r_P+r_N = 1·84 Å (r_S+r_N) = 1·78 Å

Sum of covalent radii with Schomaker–Stevenson electronegativity correction:

P–N = 1·76 Å S–N = 1·74 Å

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