Acta Cryst. (1964). **17**, 671

Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N. I. $NaPO_3NH_3$

By D. W. J. Cruickshank*

School of Chemistry, The University, Leeds 2, England

(*Received* 4 *June* 1963)

The crystallographic data given by Hobbs, Corbridge & Raistrick (1953) have been used in a structure refinement. The revised bond lengths are P–O = $1{\cdot}522 \pm 0{\cdot}011$ Å and P–N = $1{\cdot}769 \pm 0{\cdot}019$ Å.

This paper is the first of a set describing the refinement of a series of silicate, phosphate and sulphate structures. The work was undertaken to provide experimental results relevant to a theory of the role of 3*d* orbitals in π bonds between (*a*) Si, P, S or Cl and (*b*) O or N (Cruickshank, 1960, 1961*a*). With the exception of the refinement of $(NO_2^+)_2S_3O_{10}^{2-}$ (original data of Eriks & MacGillavry, 1954) where one atom was shifted 0·6 Å, the refinements have confirmed the general results reported by the original authors. For three of the structures the coordinate changes did not exceed 0·02 Å, so that the present work has confirmed even the detailed dimensions reported originally. For six other structures maximum changes of 0·04 Å to 0·19 Å have occurred, and these alterations have often led to significantly better agreement between observed and theoretical bond lengths. The refinements have generally increased the precision of the results, and in one case, $(RbPO_3)_\infty$ (Corbridge, 1956), the e.s.d.'s are one-third of those previously estimated. The structure of H_3PO_4 (Furberg, 1955) was also refined in the same way, but the results were so close to those given by Furberg as not to be worth recording separately. The important point about the present work is that it has provided a series of results all obtained by the same refinement technique. For the interpretations of the results in terms of the π-bonding theory reference should be made to Cruickshank (1961*a*).

Each refinement used the data given by the original authors and started from the parameters given by those authors. All the calculations were carried out on the Leeds University Pegasus computer with the programs written by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). The scattering factors for N, O, Na, K^+, Ca and Rb^+ were those given by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1958), that for Si was given by Tomiie & Stam (1958), and those for P and S were based on the Tomiie & Stam results but were adjusted slightly by comparison with the results of Berghuis *et al.* for adjacent atoms in the periodic table.

For many of the structures allowance was made for the anisotropic vibrations of the atoms; the vibrations were expressed in terms of the mean-squares amplitude tensor U_{ij} such that

$$\overline{u^2} = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} l_i l_j$$

is the mean-square vibration in the direction of a unit vector **l**, whose components are (l_1, l_2, l_3) with respect to the reciprocal axes (Cruickshank, 1956*a*).

For some structures it was evident that the ions were undergoing angular oscillations, and corrections to the dimensions were made by the method described by Cruickshank (1956*b*,*c*, 1961*b*).

The crystal structure of monosodium phosphoramidate, $NaPO_3NH_3$, was determined by Hobbs, Corbridge & Raistrick (1953) by three-dimensional Fourier methods. As the backshift corrections used were rather large, and as small ions have often been found to require appreciable corrections for molecular angular oscillations, it seemed desirable to refine the structure further by least squares.

The space group is $P6_3$, with cell dimensions $a = 5{\cdot}773$, $c = 6{\cdot}031$ Å. The structure consists of Na^+ cations and $(PO_3^{2-}\text{-}NH^+)$ anions. Each ion lies on a threefold axis; for the anion this coincides with the P–N bond. There is thus only one independent atom of each kind.

The data used in the refinement were the 119 non-zero $|F_o|$ given by Hobbs *et al.* Seven cycles of least-squares refinement were carried out. The maximum coordinate shift was 0·026 Å for the *z* coordinate of the oxygen. The residual R dropped from the 10·4% given by Hobbs *et al.* to a final 6·4% (hydrogen atoms were included at assumed positions). The revised atomic coordinates are given in Table 1 and the vibration parameters in Table 2. Anisotropic vibration amplitudes were determined for all atoms, except hydrogen for which an isotropic U of 0·020 Å^2 was assumed. The $|F_o|$ scale factor determined by the least-squares process was $1{\cdot}042 \pm 0{\cdot}07$. The weighting scheme used was

$$w = 1/(9{\cdot}6 + |F_o| + |F_o|^2/22{\cdot}8)\;,$$

without the factor 1·042 applied to the $|F_o|$.

---

* Present address: Chemistry Department, The University, Glasgow W.2, Scotland.

Table 1. *Atomic coordinates* (Å)

	x	y	z
Na	0·000	0·000	0·000
P	1·924 = $\frac{1}{3}a$	3·849 = $\frac{2}{3}a$	1·882
N	1·924 = $\frac{1}{3}a$	3·849 = $\frac{2}{3}a$	3·645
O	0·873	4·479	1·516
H (assumed)	2·81	3·74	3·97

Table 2. *Mean square vibration amplitudes* (Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Na	0·018	0·018	0·012	0·009	0·000	0·000
P	0·006	0·006	0·011	0·003	0·000	0·000
N	0·016	0·016	0·014	0·008	0·000	0·000
O	0·017	0·011	0·024	0·011	−0·001	−0·007

The coordinate e.s.d.'s given by the least-squares process are 0·008 Å for Na, 0·007 Å for P, 0·018 Å for N and 0·008 Å for O. The e.s.d.'s of the U_{ij} range from 0·001 Å^2 for U_{11} of P to 0·007 Å^2 for U_{33} of N. The vibrations of the oxygen and nitrogen atoms in the PO_3NH_3 ion are rather greater than those of the phosphorus and imply molecular angular oscillations about any axis of about 4° r.m.s. amplitude. Correspondingly, the P–O and P–N bond lengths should be increased by about 0·006 Å as compared with those calculated from the coordinates of Table 1.

With these corrections the molecular dimensions are P–O = 1·522 ± 0·011 Å, P–N = 1·769 ± 0·019 Å, ∠N–P–O = 103° 58′ and ∠O–P–O′ = 114° 22′. The lengths are within 0·016 Å and the angles within 1° 2′ of those given by Hobbs *et al.*

Since the nitrogen is bonded to three hydrogen atoms, there can be no π character in the P–N bond. Consequently we may take 1·77 ± 0·02 Å as the value of the P–N single-bond length. This is close to the 1·76 Å estimated by the Schomaker–Stevenson method. The P–O length is about 0·02 Å shorter than in the phosphate ion. The increased π-bond order in the phosphoramidate ($2\times\frac{1}{3}$ as against $2\times\frac{1}{4}$) is evidently partially offset by a reduced effective nuclear charge for the 3d-orbitals.

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A.L. (1955). *Acta Cryst.* **8**, 478.

Corbridge, D. E. C. (1956). *Acta Cryst.* **9**, 308.

Cruickshank, D. W. J. (1956*a*). *Acta Cryst.* **9**, 747.

Cruickshank, D. W. J. (1956*b*). *Acta Cryst.* **9**, 754.

Cruickshank, D. W. J. (1956*c*). *Acta Cryst.* **9**, 757.

Cruickshank, D. W. J. (1960). *Acta Cryst.* **13**, 1033.

Cruickshank, D. W. J. (1961*a*). *J. Chem. Soc.* 5486.

Cruickshank, D. W. J. (1961*b*). *Acta Cryst.* **14**, 896.

Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. & Truter, M. R. (1961). *Computing Methods and the Phase Problem*, p. 32. Oxford: Pergamon Press.

Eriks, K. & MacGillavry, C. H. (1954). *Acta Cryst.* **7**, 430.

Furberg, S. (1955). *Acta Chem. Scand.* **9**, 1557.

Hobbs, E., Corbridge, D. E. C. & Raistrick, B. (1953). *Acta Cryst.* **6**, 621.

Tomiie, Y. & Stam, C. H. (1958). *Acta Cryst.* **11**, 126.

Acta Cryst. (1964). **17**, 672

Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N.

II. $Na_4P_2O_7.10H_2O$

By D. W. J. Cruickshank*

School of Chemistry, The University, Leeds 2, England

(*Received* 4 *June* 1963)

The crystallographic data given by MacArthur & Beevers (1957) have been used in a structure refinement. The revised molecular dimensions are P–O(bridge) = 1·61 ± 0·015, P–O(outer) = 1·51 ± 0·015 Å, <P–O–P = 133 °38′.

The crystal structure of sodium pyrophosphate decahydrate, $Na_4P_2O_7.10H_2O$, was determined by MacArthur & Beevers (1957) by difference syntheses for the three principal zones, which were refined to residuals R of about 22%. The interesting results obtained for the dimensions of other isoelectronic X_2O_7 ions, notably $S_2O_7^{2-}$ (Lynton & Truter, 1960) and $Si_2O_7^{6-}$ (Cruickshank, Lynton & Barclay, 1962) suggested that improved dimensions of the pyrophosphate $P_2O_7^{4-}$ ion would be worth seeking.

The space group is $I2/c$, with cell dimensions $a = 17·93$, $b = 6·96$, $c = 14·85$ Å and $\beta = 118° 31′$. Each P_2O_7 ion lies on a twofold axis which passes through

---

* Present address: Chemistry Department, The University, Glasgow W. 2, Scotland.