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A Reinvestigation of the Structure of $Na_4P_2O_7.10H_2O$

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New data have been used in a refinement which leads to molecular dimensions P–O (bridge) 1·612 ± 0·005 Å, P–O (outer) 1·523 ± 0·004 Å and ∠P–O–P 130·2°.

Introduction

The crystal structure of sodium pyrophosphate decahydrate, $Na_4P_2O_7.10H_2O$, was determined by MacArthur & Beevers (1957) from photographic data for three projections. These data were later used by Cruickshank (1964) in a least-squares refinement, which yielded bond lengths in the pyrophosphate group with standard deviations of about 0·015 Å. In order to obtain more accurate dimensions, fresh three-dimensional data were collected and a full refinement carried out.

Crystal data

$Na_4P_2O_7.10H_2O$. $M = 446{\cdot}06$.
Monoclinic, $a = 17{\cdot}01 \pm 0{\cdot}02$, $b = 6{\cdot}96 \pm 0{\cdot}01$, $c = 14{\cdot}85 \pm 0{\cdot}02$ Å, $\beta = 112{\cdot}0 \pm 0{\cdot}2°$;
$V = 1630$ Å^3, $Z = 4$, $D_c = 1{\cdot}817$, D_m (MacArthur & Beevers, 1957) $= 1{\cdot}817$. $F(000) = 920$. Space group $C2/c$.

Experimental

The cell dimensions given above were measured from zero-layer precession and Weissenberg photographs. They are in agreement with the values given by Corbridge (1957) and by MacArthur & Beevers (1957) for the $I2/c$ cell.

Intensities were estimated visually from equi-inclination Weissenberg photographs of the layers $h0l$ to $h5l$, taken with Cu $K\alpha$ radiation. They were corrected for Lorentz and polarization factors with a DEUCE computer program written by J. G. Sime. This yielded a set of 1022 independent structure amplitudes, requiring six different scale factors. A structure factor calculation, using the coordinates and vibration parameters of Cruickshank (1964) transferred to the $C2/c$ cell, gave preliminary values for the layer scale factors and showed an initial residual R of 14·2%.

Least-squares refinement

The structure-factor least-squares program of J. G. F. Smith and D. W. J. Cruickshank for the KDF9 computer was used. The form-factors were taken from *International Tables for X-ray Crystallography* (1962) and the weighting scheme was

$$w = 1/(10 + |F_o| + 0{\cdot}005|F_o|^2).$$

Two cycles of full-matrix least-squares refinement of the coordinates and individual vibration parameters, together with an overall scale factor, reduced the residual to 9·2%. After two cycles of block-diagonal anisotropic refinement, a small number of indexing errors were corrected and the individual layers rescaled. Two more cycles then produced convergence to a residual of 7·8%.

An $(F_o - F_c)$ Fourier synthesis was then computed and of the twenty highest peaks, 0·5 to 0·7 e.Å^{-3}, nine were in positions expected for hydrogen atoms. No peak could be found at the position expected for the remaining hydrogen, H(42). However, since the posi-

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tion of this atom was indicated by a short O···O distance of 2·8 Å, a probable position for the atom could be assumed.

Using the contracted-atom *f* curve for hydrogen of Stewart, Davidson & Simpson (1965), two cycles of full-matrix refinement of the hydrogen coordinates and isotropic vibration parameters were carried out, followed by two cycles of block-diagonal refinement in which the parameters of all atoms were allowed to vary. The residual was reduced to 7·2%. No substantial shifts of the heavy atoms occurred, although all the O···O hydrogen-bond distances increased by amounts varying from 0·001 to 0·007 Å. In general the hydrogen atom coordinates changed to produce more reasonable O–H bond lengths and angles.

The final coordinates with their estimated standard deviations are given in Table 1, and the vibration parameters and their standard deviations in Table 2.

Table 1. *Final fractional coordinates and e.s.d.'s*

	x	y	z
P	0·0657 (1)	0·2710 (3)	0·3477 (1)
Na(1)	0·2413 (2)	0·3065 (5)	0·1069 (2)
Na(2)	0·3848 (2)	0·0845 (5)	0·3016 (2)
O(1)	0	0·1735 (11)	¼
O(2)	0·0254 (3)	0·4484 (8)	0·3702 (3)
O(3)	0·0778 (3)	0·1135 (9)	0·4209 (3)
O(4)	0·1447 (3)	0·3223 (8)	0·3272 (3)
W(1)	0·1014 (3)	0·3890 (9)	0·0540 (4)
W(2)	0·2405 (3)	0·0212 (8)	0·0214 (4)
W(3)	0·2302 (3)	0·0849 (10)	0·2516 (4)
W(4)	0·3926 (3)	0·2647 (8)	0·1710 (4)
W(5)	0·4160 (3)	0·3847 (9)	0·3891 (4)

Table 3. *Hydrogen parameters*

	x	y	z	U (Å^2)
H(11)	0·064 (7)	0·417 (16)	−0·012 (8)	0·075 (34)
H(12)	0·065 (10)	0·408 (24)	0·066 (11)	0·136 (66)
H(21)	0·192 (5)	−0·065 (13)	−0·005 (6)	0·045 (25)
H(22)	0·270 (8)	0·003 (20)	0·095 (8)	0·092 (40)
H(31)	0·193 (10)	0·175 (24)	0·257 (11)	0·147 (59)
H(32)	0·177 (6)	0·006 (16)	0·192 (7)	0·074 (31)
H(41)	0·432 (6)	0·171 (14)	0·152 (6)	0·059 (27)
H(42)	0·398 (14)	0·327 (32)	0·140 (14)	0·215 (88)
H(51)	0·467 (8)	0·411 (18)	0·410 (8)	0·082 (42)
H(52)	0·410 (10)	0·413 (26)	0·464 (11)	0·180 (68)

Table 2. *Vibration tensor components and e.s.d.'s* (Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
P	0·0142 (6)	0·0146 (13)	0·0145 (6)	0·0021 (13)	0·0068 (10)	0·0050 (13)
Na(1)	0·0282 (13)	0·0378 (25)	0·0359 (14)	0·0105 (28)	0·0235 (22)	0·0171 (27)
Na(2)	0·0275 (13)	0·0326 (24)	0·0311 (13)	0·0052 (26)	0·0243 (22)	0·0042 (26)
O(1)	0·0299 (32)	0·0145 (51)	0·0236 (30)	0	−0·0096 (50)	0
O(2)	0·0260 (21)	0·0119 (34)	0·0320 (22)	−0·0059 (42)	0·0213 (37)	0·0053 (30)
O(3)	0·0374 (25)	0·0357 (41)	0·0223 (22)	0·0189 (44)	0·0196 (39)	0·0021 (49)
O(4)	0·0221 (21)	0·0333 (40)	0·0363 (24)	−0·0178 (46)	0·0319 (38)	−0·0134 (43)
W(1)	0·0237 (21)	0·0535 (46)	0·0268 (23)	0·0065 (49)	0·0193 (37)	0·0116 (49)
W(2)	0·0273 (23)	0·0297 (40)	0·0336 (25)	0·0000 (48)	0·0080 (38)	−0·0053 (47)
W(3)	0·0266 (24)	0·0545 (50)	0·0465 (30)	−0·0309 (56)	0·0352 (47)	0·0051 (53)
W(4)	0·0315 (23)	0·0266 (40)	0·0375 (25)	0·0163 (49)	0·0317 (41)	0·0097 (47)
W(5)	0·0413 (28)	0·0402 (45)	0·0331 (25)	−0·0020 (50)	0·0295 (44)	−0·0024 (54)

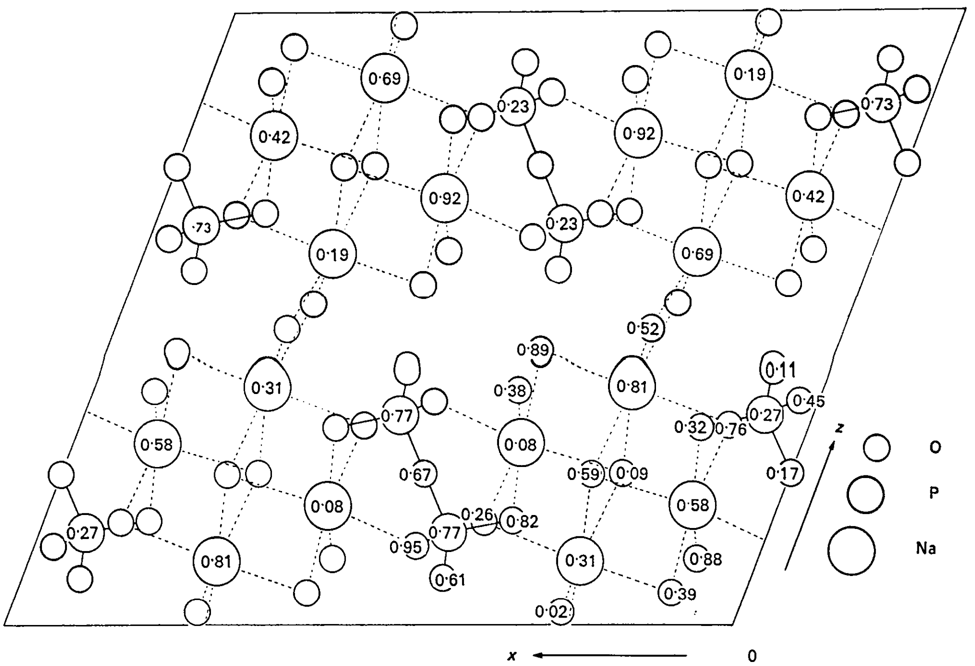

Fig. 1. Projection down [010].

The atom numbering is that used by MacArthur & Beevers. The hydrogen parameters are listed separately in Table 3, and Table 4 gives the observed and calculated structure factors.

The effect of including the $\Delta f'$ and $\Delta f''$ components of the anomalous scattering of Na, P and O was examined by carrying out a further two cycles of refinement. As anticipated for a centrosymmetric space group, this refinement produced negligible shifts to the coordinates (<0·002 Å) and insignificant changes to vibration parameters.

Discussion of the structure

General

The overall structure was described by MacArthur & Beevers (1957). This refinement has produced shifts of 0·02 – 0·04 Å from the coordinates obtained by Cruickshank (1964), with a larger shift of about 0·15 Å for the water molecule, *W*(1). A projection of the structure along the *b* axis is shown in Fig. 1, with the Na···O and P–O bonds indicated.

The sodium coordination

The bond lengths and angles at the sodium atoms are given in Table 5. The e.s.d.'s are 0·007 Å for the lengths and 0·2° for the angles. The mean Na···O length in the Na(1) octahedron is 2·48 Å, and in the Na(2) octahedron 2·45 Å. The two Na(1)···*W*(3) bonds are rather long, 2·70 and 2·77 Å. This is probably because the water molecule *W*(3) is bonded to five atoms (three sodium and two hydrogen) whilst all other water molecules coordinated to sodium form only four bonds. The water molecules *W*(1), *W*(2), and *W*(4) are each coordinated to two sodium atoms, whilst *W*(5) is coordinated to one sodium atom and is also the acceptor of a hydrogen bond from *W*(3).

The hydrogen bonding

Table 6 gives the hydrogen bond lengths and angles. The water molecules *W*(1) and *W*(2) each form two hydrogen bonds of lengths 2·7 – 2·8 Å. *W*(3), *W*(4) and *W*(5) each forms one hydrogen bond of about this length, and a second longer bond of 2·9 – 3·0 Å. Two of these longer bonds are to O(3), which is bonded to phosphorus and is also the acceptor of a third hydrogen bond. The other long hydrogen bond is the only one between two water molecules.

The standard deviations of the hydrogen atom coordinates are 0·1 to 0·2 Å. They are so high that the *W*–H and O–H distances are not very reliable. H(42),

Table 4. *Observed and calculated structure factors*

H	K	L	Fo	Fc
0	2	4	131.0	133.8
0	2	5	111.6	-115.3
0	2	6	64.0	-59.8
0	2	8	12.9	7.6
0	2	9	35.0	30.5
0	2	10	51.9	51.3
0	2	12	51.4	-52.0
0	2	15	21.4	-15.7
0	2	16	33.8	34.3
0	2	17	30.4	-31.6
2	2	0	48.2	-46.6
2	2	1	97.2	85.4
2	2	2	113.9	-102.7
2	2	3	90.6	93.2
2	2	4	21.1	23.7
2	2	5	114.3	-116.4
2	2	6	72.9	-77.4
2	2	7	15.6	-12.9
2	2	8	55.7	-60.5
2	2	9	50.7	51.9
2	2	10	77.9	85.1
2	2	11	19.6	-18.8
2	2	12	16.0	-15.6
2	2	14	31.3	-32.3
2	2	16	16.0	15.3
2	2	-1	42.7	39.2
2	2	-2	148.1	156.9
2	2	-3	133.0	135.1
2	2	-4	184.0	-214.5
2	2	-5	132.2	-129.3
2	2	-6	42.9	-40.4
2	2	-7	45.5	-36.4
2	2	-8	65.0	65.8
2	2	-9	43.2	-39.1
2	2	-10	28.1	26.4
2	2	-12	48.4	-51.0
2	2	-13	19.6	20.1
2	2	-16	25.5	24.0
2	2	-17	14.5	11.1
4	2	0	66.1	56.8
4	2	1	54.0	49.3
4	2	2	66.3	-63.3
4	2	3	71.6	61.7
4	2	4	59.8	56.2
4	2	5	86.8	-85.0
4	2	6	80.8	92.1
4	2	7	47.2	-46.7
4	2	8	34.8	-33.9
4	2	9	44.8	-45.9
4	2	10	22.7	-20.1
4	2	11	57.0	52.7
4	2	12	44.1	45.0
4	2	13	19.9	-18.2
4	2	14	19.3	-20.0
4	2	-1	96.7	80.5
4	2	-2	78.5	80.2
4	2	-4	45.1	-38.3
4	2	-5	16.3	12.1
4	2	-6	73.9	64.9
4	2	-7	36.2	-31.0
4	2	-8	49.6	52.9
4	2	-9	54.1	54.4
4	2	-10	64.7	-65.3
4	2	-11	39.4	-42.3
4	2	-12	11.2	-10.5
4	2	-13	19.7	21.1
4	2	-14	31.6	29.7
4	2	-15	21.1	-13.5
4	2	-18	30.1	-30.2
6	2	0	39.6	40.0
6	2	2	24.6	20.1
6	2	3	89.9	-91.5
6	2	4	119.2	-129.1
6	2	5	51.4	50.9
6	2	6	46.0	42.4
6	2	8	19.3	-19.1
6	2	10	29.7	-23.9
6	2	11	24.0	20.0
6	2	12	27.8	28.4
6	2	-2	84.6	-77.4
6	2	-3	9.5	5.0
6	2	-4	102.7	-106.5
6	2	-5	41.1	39.9
6	2	-6	24.7	22.7
6	2	-7	76.6	-76.6
6	2	-8	51.0	52.4
6	2	-9	35.2	36.2
6	2	-10	14.4	-14.6
6	2	-11	56.9	64.7
6	2	-12	27.3	-27.9
6	2	-13	19.7	-20.4
6	2	-14	45.6	43.6
6	2	-15	15.1	-16.2
6	2	-16	9.7	-10.6
6	2	-17	33.7	-30.4
6	2	-18	6.5	-8.2
8	2	0	47.6	49.8
8	2	1	94.1	-96.4
8	2	2	25.0	19.9
8	2	3	64.1	72.9
8	2	4	17.5	-14.9
8	2	5	43.1	44.4
8	2	6	56.2	58.3
8	2	8	30.0	24.7
8	2	9	15.7	-13.5
8	2	10	31.4	-29.5
8	2	-1	46.2	-44.0
8	2	-2	38.2	-39.5
8	2	-3	72.9	-71.4
8	2	-4	36.5	33.6
8	2	-5	83.9	77.6
8	2	-6	66.7	63.1
8	2	-7	15.6	15.5
8	2	-8	31.4	-29.4
8	2	-9	24.5	22.0
8	2	-10	60.2	-62.3
8	2	-14	50.0	52.5
8	2	-15	10.6	10.1
8	2	-16	37.7	-36.0
8	2	-17	8.5	-9.7
8	2	-18	17.6	-17.4
10	2	0	41.8	37.1
10	2	1	67.0	-72.6
10	2	2	38.2	36.4
10	2	3	35.6	34.6
10	2	4	56.4	-60.4
10	2	5	19.5	19.3
10	2	6	41.7	-41.8
10	2	7	27.4	24.5
10	2	8	21.4	19.5
10	2	-2	65.9	-70.7
10	2	-3	9.2	9.2
10	2	-4	59.3	-58.0
10	2	-5	45.0	-48.1
10	2	-6	78.1	82.6
10	2	-7	26.1	25.6
10	2	-8	30.6	-26.7
10	2	-9	37.3	-40.0
10	2	-10	18.9	-17.1
10	2	-12	35.9	36.2
10	2	-13	33.9	33.5
10	2	-16	16.4	-16.9
10	2	-18	25.8	25.2
12	2	0	28.8	-29.2
12	2	1	24.6	25.8
12	2	2	53.4	52.7
12	2	3	19.7	20.6
12	2	6	15.1	-17.6
12	2	8	37.2	40.1
12	2	9	28.9	-28.5
12	2	-1	18.5	-18.6
12	2	-4	55.2	52.4
12	2	-5	37.0	36.6
12	2	-6	45.4	43.7
12	2	-7	18.6	19.7
12	2	-8	72.8	-79.0
12	2	-9	27.2	-31.2
12	2	-10	15.9	-14.6
12	2	-11	48.9	-54.8
12	2	-12	46.6	49.5
12	2	-13	27.1	24.3
12	2	-14	25.1	-26.5
12	2	-16	21.7	-21.3
12	2	-17	21.3	20.3
12	2	-18	16.2	16.7
14	2	0	46.2	-48.2
14	2	1	27.7	29.5
14	2	2	50.6	49.2
14	2	3	32.6	-34.1
14	2	5	30.8	-30.9
14	2	6	46.8	-49.5
14	2	-1	16.0	15.9
14	2	-2	27.7	-28.7
14	2	-3	11.3	14.0
14	2	-4	29.7	30.6
14	2	-5	25.1	27.8
14	2	-6	19.5	-18.7
14	2	-7	57.1	-62.2
14	2	-9	16.1	16.6
14	2	-10	32.0	35.3
14	2	-14	29.6	-28.7
16	2	0	39.7	-39.7
16	2	4	33.2	33.9
16	2	-2	22.1	20.8
16	2	-4	44.8	46.1
16	2	-5	19.4	20.4
16	2	-6	38.0	-35.0
16	2	-8	33.3	-34.4
16	2	-10	36.5	36.8
16	2	-11	23.4	23.9
16	2	-12	17.3	-18.0
16	2	-13	9.4	-14.0
18	2	0	17.0	-14.3
18	2	1	25.8	-29.2
18	2	2	15.3	-13.9
18	2	3	9.3	9.1
18	2	-1	20.2	21.0
18	2	-2	9.4	12.1
18	2	-5	22.4	-22.5
18	2	-6	20.1	-21.0
18	2	-7	10.0	-14.2
18	2	-8	22.1	23.1
18	2	-9	9.6	9.7
18	2	-10	26.4	24.9
18	2	-11	36.8	38.3
18	2	-12	30.7	-31.3
20	2	-1	21.5	-19.3
20	2	-2	40.3	43.9
20	2	-3	12.5	13.3
20	2	-4	21.2	-21.4
20	2	-8	13.0	11.3
20	2	-10	16.8	-16.0
20	2	-12	14.2	-16.4
1	3	0	19.2	-15.5
1	3	1	59.7	67.3
1	3	2	35.8	-33.2
1	3	3	90.9	-97.6
1	3	4	68.6	-70.3
1	3	5	77.3	-70.5
1	3	6	52.2	52.8
1	3	7	26.4	-22.2
1	3	8	10.8	-9.9
1	3	9	45.3	48.1
1	3	10	34.0	-38.3
1	3	11	27.4	30.9
1	3	12	17.1	-19.5
1	3	13	28.2	-26.0
1	3	15	25.2	25.9
1	3	16	16.1	-16.4
1	3	-1	23.0	-18.2
1	3	-2	42.3	40.7
1	3	-3	16.0	-15.8
1	3	-4	54.4	70.4
1	3	-5	57.1	50.3
1	3	-6	57.7	56.6
1	3	-7	56.8	-57.8
1	3	-8	52.3	-48.6
1	3	-9	29.2	29.7
1	3	-11	24.3	28.4
1	3	-12	30.1	29.3
1	3	-13	26.8	-25.0
1	3	-15	20.0	-20.3
1	3	-16	14.2	-14.7
1	3	-17	17.9	21.5
3	3	0	79.4	-75.4
3	3	2	83.3	82.9
3	3	3	23.8	-19.5
3	3	4	8.3	-5.1
3	3	5	43.0	39.3
3	3	6	39.3	-39.9
3	3	7	42.4	-40.1
3	3	9	56.3	57.4
3	3	10	24.5	27.5
3	3	12	11.6	15.8
3	3	13	26.1	-25.1
3	3	14	27.6	27.4
3	3	15	20.1	20.5
3	3	-1	25.7	24.9
3	3	-2	51.0	-48.4
3	3	-3	14.8	-13.3
3	3	-4	9.5	9.8
3	3	-5	13.1	13.8
3	3	-6	50.5	44.7
3	3	-7	69.1	-64.7
3	3	-8	20.0	-18.8
3	3	-9	15.2	13.1
3	3	-10	25.7	-25.1
3	3	-11	72.6	84.4
3	3	-12	37.8	-34.1
3	3	-13	50.2	-54.5
3	3	-17	21.0	22.6
5	3	0	10.2	-10.1
5	3	1	57.8	-54.6
5	3	2	29.2	-26.9
5	3	3	70.1	67.9
5	3	4	39.6	-36.6
5	3	5	30.9	-28.6
5	3	7	26.0	-23.9
5	3	9	21.3	18.4
5	3	10	24.3	22.7
5	3	12	28.1	-29.2
5	3	13	18.4	-14.9
5	3	-1	77.6	64.5
5	3	-2	79.2	92.8
5	3	-3	17.5	-15.1
5	3	-4	15.1	12.8
5	3	-5	132.9	-132.4
5	3	-6	8.7	-9.6
5	3	-7	61.3	-55.0
5	3	-8	20.2	-16.8
5	3	-9	73.3	73.6
5	3	-10	47.2	48.8
5	3	-11	44.0	46.3
5	3	-12	38.7	38.9
5	3	-13	40.5	-41.4
5	3	-17	33.1	32.2
7	3	0	22.6	-19.0
7	3	1	38.2	-36.3
7	3	2	40.2	39.3
7	3	3	37.8	35.9
7	3	4	21.7	17.2
7	3	5	56.0	54.0
7	3	8	21.3	-22.8
7	3	9	39.8	-35.5
7	3	10	19.7	20.8
7	3	12	15.3	12.1
7	3	-2	41.9	-41.4
7	3	-3	144.6	140.9
7	3	-4	43.4	-40.1
7	3	-5	136.6	-134.7
7	3	-6	21.1	-16.3
7	3	-7	19.9	18.1
7	3	-8	47.7	-46.0
7	3	-9	39.2	41.3
7	3	-10	28.5	26.8
7	3	-11	47.4	-49.3
7	3	-12	12.3	-14.1
7	3	-14	16.7	-18.3
7	3	-15	31.1	31.3
7	3	-16	13.8	16.3
7	3	-17	16.2	-15.0
9	3	0	10.4	-9.1
9	3	1	21.5	-19.3
9	3	3	49.6	-50.9
9	3	5	27.2	27.9
9	3	6	21.3	17.4
9	3	9	53.8	-53.1
9	3	11	23.0	24.0
9	3	-1	58.2	50.8
9	3	-2	79.1	83.9
9	3	-3	31.3	-28.2
9	3	-4	33.1	29.3
9	3	-5	28.7	-27.1
9	3	-6	74.8	-76.9
9	3	-7	51.7	49.4
9	3	-9	66.5	67.0
9	3	-10	77.9	79.0
9	3	-11	91.7	-107.3
9	3	-13	17.1	15.9
9	3	-15	21.5	22.1
9	3	-17	25.1	-27.7
11	3	0	46.1	-49.8
11	3	1	23.8	23.2
11	3	3	87.5	-98.9
0	0	2	83.5	-81.2
0	0	4	131.1	-139.5
0	0	6	27.8	28.2
0	0	8	23.6	19.4
0	0	10	25.7	-22.9
0	0	12	25.8	28.2
2	0	0	61.6	58.6
2	0	2	54.0	48.2
2	0	4	190.1	-206.0
2	0	6	39.9	-36.7
2	0	8	68.6	63.4
2	0	10	105.8	-108.7
2	0	12	38.7	-37.1
2	0	14	100.0	96.4
2	0	-2	135.6	-122.6
2	0	-4	36.3	-30.8
2	0	-6	131.8	130.2
2	0	-8	132.3	-136.2
2	0	-12	54.5	53.9
2	0	-14	23.0	-21.8
2	0	-16	14.0	-13.3
4	0	0	28.0	-25.6
4	0	2	142.9	144.9
4	0	6	138.3	-139.0
4	0	8	174.4	192.5
4	0	10	19.9	-19.5
4	0	12	41.2	-39.1
4	0	14	21.4	22.5
4	0	16	23.0	23.8
4	0	-2	53.1	-52.3
4	0	-4	100.4	94.9
4	0	-6	57.6	-51.6
4	0	-8	136.1	135.3
4	0	-12	56.1	53.9
4	0	-14	67.3	-69.2
4	0	-16	34.3	-33.0
4	0	-18	12.3	12.4
6	0	0	234.9	-289.7
6	0	4	42.5	45.4
6	0	6	21.2	17.9
6	0	12	43.7	-41.5
6	0	14	19.9	-17.7
6	0	-2	136.3	-138.5
6	0	-4	95.0	95.3
6	0	-6	23.9	21.1
6	0	-10	34.7	-31.2
6	0	-12	35.5	28.9
6	0	-14	29.7	28.1
6	0	-18	13.3	16.4
8	0	0	109.1	102.2
8	0	2	46.2	43.4
8	0	4	74.7	73.1
8	0	6	29.1	-28.3
8	0	10	73.4	72.0
8	0	-2	129.6	-135.0
8	0	-4	66.6	63.1
8	0	-6	16.7	-19.3
8	0	-10	25.4	22.6
8	0	-12	62.1	-65.4
8	0	-14	23.2	-23.8
8	0	-16	64.1	58.4
10	0	0	24.3	-22.9
10	0	2	63.2	-64.6
10	0	4	55.4	51.4
10	0	6	44.3	-46.2
10	0	8	49.3	-44.8
10	0	10	13.7	18.4
10	0	-2	36.4	39.8
10	0	-4	41.9	40.0
10	0	-8	54.9	-56.2
10	0	-10	17.2	-17.9
10	0	-12	40.8	-40.6
10	0	-14	32.6	29.2
10	0	-16	71.2	69.7
10	0	-18	37.8	-34.3
12	0	0	62.7	62.0
12	0	2	8.0	-5.6
12	0	4	14.3	16.9
12	0	6	43.1	-40.7
12	0	10	14.2	15.8
12	0	-2	88.5	91.0
12	0	-4	83.3	-82.4
12	0	-8	86.2	88.5
12	0	-10	53.9	-52.8
12	0	-12	29.7	-28.5
12	0	-18	21.7	-21.7
14	0	2	44.2	-47.5
14	0	4	35.1	-34.8
14	0	6	30.0	30.4
14	0	-6	13.9	-12.5
14	0	-8	40.7	39.5
14	0	-10	43.6	-42.5
14	0	-12	56.3	57.4
14	0	-14	49.4	46.5
14	0	-16	51.3	-48.1
14	0	-18	23.1	-23.2
16	0	0	39.8	39.8
16	0	2	29.7	30.1
16	0	4	14.4	-16.1
16	0	6	28.3	28.9
16	0	-2	66.9	-71.6
16	0	-4	16.4	-16.5
16	0	-6	16.5	17.5
16	0	-12	7.6	9.0
16	0	-14	25.2	23.2
16	0	-16	49.1	-49.2
18	0	2	12.6	-9.6
18	0	-2	48.1	-47.0
18	0	-4	30.2	27.8
18	0	-6	33.2	31.1
18	0	-8	56.8	-54.7
18	0	-10	20.4	-17.3
18	0	-12	64.4	64.4
20	0	0	5.7	-6.4
20	0	-2	23.5	-20.5
20	0	-4	11.7	9.5
20	0	-6	40.9	39.7
20	0	-8	47.5	-47.8
20	0	-10	5.6	-4.8
20	0	-12	9.6	11.8
1	1	0	65.2	-63.2
1	1	1	92.1	-101.4
1	1	2	53.1	46.7
1	1	3	101.3	-96.3
1	1	4	7.3	9.2
1	1	5	56.9	59.2
1	1	6	50.2	-45.9
1	1	7	10.2	7.1
1	1	8	27.3	-25.7
1	1	9	83.4	-89.0
1	1	10	12.9	-12.9
1	1	11	64.2	64.9
1	1	12	27.8	25.3
1	1	13	34.6	30.7
1	1	14	34.5	-29.1
1	1	15	22.5	-19.8
1	1	17	10.7	-8.4
1	1	-1	78.4	65.5
1	1	-2	20.8	20.7
1	1	-3	7.3	-5.8
1	1	-4	25.6	21.1
1	1	-5	57.7	54.7
1	1	-6	97.0	-98.2
1	1	-7	16.5	14.7
1	1	-8	80.1	82.5
1	1	-9	26.5	23.2
1	1	-10	35.0	33.5
1	1	-11	73.9	-80.0
1	1	-12	42.0	43.0
1	1	-13	19.7	19.0
1	1	-15	43.8	43.5
1	1	-16	9.1	-7.2
1	1	-17	23.4	-23.5
3	1	1	92.4	92.4
3	1	2	24.7	-22.5
3	1	3	94.8	-103.0
3	1	4	54.4	50.4
3	1	5	52.1	-49.2
3	1	6	107.2	115.7
3	1	7	40.6	37.1
3	1	8	42.3	-40.8
3	1	9	10.5	10.9
3	1	11	16.0	13.9
3	1	12	8.0	8.6
3	1	13	25.3	25.6
3	1	15	20.5	-17.4
3	1	16	19.9	19.4
3	1	-1	139.6	174.0
3	1	-2	28.0	-27.2
3	1	-3	134.1	-151.4
3	1	-4	17.5	-13.7
3	1	-5	106.5	-107.2
3	1	-6	140.4	-152.2
3	1	-7	33.2	28.8
3	1	-8	73.6	-72.9
3	1	-9	62.8	61.0
3	1	-10	51.7	50.0
3	1	-16	28.4	-24.0
3	1	-17	25.6	-25.5
5	1	0	54.9	53.2
5	1	1	71.8	-73.4
5	1	2	73.3	-75.6
5	1	3	37.5	34.6
5	1	4	105.0	107.9
5	1	7	65.2	70.6
5	1	8	55.2	-56.7
5	1	9	31.4	-31.0
5	1	10	36.8	-38.9
5	1	11	62.2	-62.0
5	1	13	29.3	25.5
5	1	15	27.4	27.5
5	1	-1	91.7	88.5
5	1	-2	22.1	-21.8
5	1	-3	88.4	-88.0
5	1	-4	126.3	123.9
5	1	-5	32.3	-30.3
5	1	-6	33.4	32.3
5	1	-7	11.0	9.3
5	1	-8	13.4	-13.5
5	1	-9	65.9	-61.1
5	1	-10	35.4	32.0
5	1	-13	81.7	88.0
5	1	-14	16.0	-13.1
5	1	-15	27.9	-25.7
5	1	-16	25.7	22.5
5	1	-17	21.6	-19.5
7	1	0	98.7	-98.1
7	1	1	111.0	114.5
7	1	2	64.7	-65.2
7	1	4	33.8	30.5
7	1	5	54.5	-55.2
7	1	7	40.0	38.2
7	1	8	21.0	19.7
7	1	11	37.3	-32.7
7	1	14	21.3	22.5
7	1	-1	41.1	36.2
7	1	-2	96.6	104.2
7	1	-3	86.7	-88.0
7	1	-4	34.8	-34.5
7	1	-5	27.4	-23.9
7	1	-6	31.9	30.0
7	1	-7	37.7	37.1
7	1	-8	39.6	-37.6
7	1	-9	41.1	-40.4
7	1	-10	36.8	-34.5
7	1	-11	36.7	35.4
7	1	-12	13.5	-15.0
7	1	-13	22.7	21.8
7	1	-14	28.9	-30.0
7	1	-15	73.1	-71.8
7	1	-17	24.7	21.0
9	1	0	19.5	-17.4
9	1	1	6.4	5.7
9	1	2	25.0	-23.4
9	1	3	18.5	14.4
9	1	5	31.6	-31.7
9	1	6	13.7	-15.4
9	1	7	39.4	38.1
9	1	8	13.8	14.5
9	1	9	10.9	-12.3
9	1	10	25.9	-19.3
9	1	11	24.7	-21.0
9	1	12	24.9	20.9
9	1	13	18.3	-17.4
9	1	-1	98.2	-104.7
9	1	-2	19.5	18.8
9	1	-3	20.2	19.6
9	1	-4	58.5	60.3
9	1	-5	172.7	195.0
9	1	-6	25.5	24.3
9	1	-7	102.3	-105.7
9	1	-8	94.1	105.4
9	1	-9	33.8	-31.0
9	1	-10	46.6	-48.9
9	1	-11	34.3	31.4
9	1	-12	25.1	23.8
9	1	-15	30.7	-28.5
9	1	-17	31.5	29.8
9	1	-18	16.4	14.3
11	1	3	54.9	52.9
11	1	4	61.6	-59.5
11	1	5	49.6	-46.3
11	1	6	45.2	39.0
11	1	7	45.3	-38.6
11	1	9	53.9	51.4
11	1	11	17.5	16.7
11	1	-1	77.7	-75.6
11	1	-2	19.3	-17.1
11	1	-3	40.0	38.8
11	1	-4	28.6	-22.1
11	1	-5	33.3	33.2
11	1	-6	69.2	-67.7
11	1	-7	45.3	-39.7
11	1	-8	26.2	-26.6
11	1	-9	80.4	86.4
11	1	-10	40.9	39.8
11	1	-12	17.9	-18.8
11	1	-13	92.5	-94.9
11	1	-15	29.8	26.0
11	1	-17	29.4	28.0
11	1	-18	13.7	13.5
13	1	0	67.1	66.1
13	1	1	107.1	-122.4
13	1	3	48.2	45.7
13	1	4	17.7	18.2
13	1	5	21.8	21.5
13	1	7	33.5	-31.5
13	1	9	15.3	15.7
13	1	-1	34.6	32.8
13	1	-2	21.6	-17.9
13	1	-3	54.7	52.1
13	1	-4	26.2	27.0
13	1	-5	38.6	-36.0
13	1	-6	43.1	-41.2
13	1	-7	15.4	-12.1
13	1	-9	41.1	39.1
13	1	-10	40.8	39.3
13	1	-11	36.0	-32.6
13	1	-15	36.5	34.7
13	1	-16	31.1	28.0
15	1	2	15.4	-16.3
15	1	5	25.7	25.0
15	1	7	19.2	-18.8
15	1	-1	62.8	63.1
15	1	-2	48.2	44.9
15	1	-3	30.0	-27.6
15	1	-4	52.6	-55.3
15	1	-5	81.8	-89.0
15	1	-6	19.7	-21.1
15	1	-7	53.9	55.1
15	1	-8	25.4	-26.8
15	1	-9	21.2	17.6
15	1	-10	11.3	14.6
15	1	-11	36.9	-32.6
15	1	-14	20.7	-17.2
15	1	-15	19.0	16.9
17	1	3	35.9	-34.1
17	1	4	16.8	13.3
17	1	5	14.8	15.7
17	1	-1	45.7	40.7
17	1	-2	15.1	17.3
17	1	-6	11.0	12.3
17	1	-7	13.4	-14.6
17	1	-8	47.5	41.0
17	1	-10	27.8	-23.3
17	1	-11	27.0	-21.5
17	1	-13	38.8	34.2
17	1	-14	19.6	-15.9
17	1	-15	7.4	9.8
19	1	0	15.0	-13.5
19	1	1	33.1	32.4
19	1	-3	37.7	-33.3
19	1	-7	26.7	24.5
19	1	-8	23.8	19.3
19	1	-11	27.2	-22.8
19	1	-12	24.1	-20.8
21	1	-3	17.3	-20.3
21	1	-5	30.6	31.1
21	1	-7	12.3	11.6
21	1	-8	15.9	16.9
21	1	-9	29.9	-29.9
0	2	1	13.7	14.0
0	2	2	89.8	87.2
0	2	3	149.1	175.5

Table 4 (*cont.*)

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
11	3	4	41.6	38.6	0	4	12	19.8	20.4	8	4	11	20.6	-19.0	3	5	5	59.5	61.3
11	3	5	47.7	51.8	0	4	13	22.7	-24.8	8	4	-1	32.0	22.5	3	5	8	21.0	19.9
11	3	7	22.1	23.9	0	4	14	16.4	17.0	8	4	-2	86.4	79.7	3	5	9	20.7	-15.8
11	3	8	30.2	-29.7	0	4	15	9.5	-14.7	8	4	-4	12.0	-12.2	3	5	10	14.0	13.8
11	3	-1	38.0	35.8	2	4	0	11.5	-11.1	8	4	-5	39.9	36.5	3	5	11	18.4	-19.4
11	3	-2	27.7	24.6	2	4	1	85.9	89.9	8	4	-6	25.4	-22.2	3	5	12	30.1	26.6
11	3	-3	58.3	-62.6	2	4	2	22.3	22.4	8	4	-7	18.6	-16.6	3	5	-1	66.2	62.6
11	3	-4	30.7	-31.6	2	4	4	77.7	-77.4	8	4	-9	37.3	-40.3	3	5	-2	69.0	69.3
11	3	-5	49.2	49.3	2	4	5	15.9	9.0	8	4	-10	35.3	33.9	3	5	-5	30.1	-31.7
11	3	-7	78.8	86.5	2	4	6	32.4	30.2	8	4	-11	70.4	73.6	3	5	-6	21.5	-19.3
11	3	-8	29.0	27.2	2	4	7	26.3	-24.9	8	4	-14	25.9	-27.7	3	5	-7	54.2	55.8
11	3	-9	59.1	-58.1	2	4	8	44.0	45.9	8	4	-15	30.8	-30.3	3	5	-10	25.7	-26.0
11	3	-10	27.3	-26.5	2	4	9	14.4	-14.2	10	4	0	55.5	-50.9	3	5	-11	25.4	-25.7
11	3	-11	21.3	-22.9	2	4	10	38.4	-37.1	10	4	1	14.1	-11.0	5	5	2	30.0	26.0
11	3	-12	42.1	-45.8	2	4	11	24.6	21.5	10	4	2	35.2	-35.4	5	5	3	63.8	-66.2
11	3	-14	19.4	17.2	2	4	13	38.0	37.9	10	4	3	55.2	59.2	5	5	4	23.8	-24.3
11	3	-15	17.8	18.6	2	4	15	34.5	-37.8	10	4	4	20.5	16.2	5	5	7	21.0	23.3
11	3	-17	31.0	-34.9	2	4	-1	40.9	-38.2	10	4	6	19.5	17.5	5	5	10	27.9	-11.1
13	3	0	27.4	27.3	2	4	-2	139.4	-146.2	10	4	7	22.5	-26.3	5	5	11	28.7	-25.2
13	3	1	32.4	34.5	2	4	-3	46.9	-40.4	10	4	8	35.3	-31.1	5	5	12	43.5	37.5
13	3	2	38.4	-41.1	2	4	-4	30.7	24.0	10	4	-1	83.0	-79.4	5	5	-1	52.1	44.6
13	3	3	20.6	-18.9	2	4	-5	43.3	-36.9	10	4	-3	18.9	17.6	5	5	-3	74.4	-63.8
13	3	4	11.5	-13.4	2	4	-6	45.6	44.9	10	4	-5	13.5	15.6	5	5	-4	22.7	-21.2
13	3	5	45.3	-46.4	2	4	-7	91.3	92.9	10	4	-6	43.4	-36.9	5	5	-7	57.5	63.3
13	3	6	28.1	29.5	2	4	-8	32.9	-30.1	10	4	-8	28.4	30.8	5	5	-8	63.4	73.9
13	3	7	30.9	33.0	2	4	-9	60.5	-63.5	10	4	-9	40.8	-42.4	5	5	-9	41.4	-39.6
13	3	8	12.2	-11.1	2	4	-10	40.4	-42.5	10	4	-10	29.1	28.9	5	5	-14	29.5	30.1
13	3	-1	21.2	20.1	2	4	-11	25.2	-24.0	10	4	-11	14.4	18.7	5	5	-15	16.6	-17.3
13	3	-2	50.2	51.3	2	4	-12	20.3	24.8	12	4	4	30.3	28.9	7	5	0	68.1	64.1
13	3	-3	91.2	-109.3	2	4	-14	12.5	14.0	12	4	6	46.3	46.6	7	5	1	70.3	72.7
13	3	-4	29.7	-28.3	4	4	0	57.3	56.6	12	4	8	17.9	-20.5	7	5	2	36.7	-31.3
13	3	-5	44.5	47.6	4	4	1	73.0	66.2	12	4	-3	95.5	89.6	7	5	3	24.8	-25.0
13	3	-6	27.2	29.3	4	4	2	109.1	120.9	12	4	-5	35.2	-35.3	7	5	4	29.3	-26.9
13	3	-7	43.2	43.2	4	4	3	58.1	-50.5	12	4	-6	14.4	-4.8	7	5	5	33.2	-31.3
13	3	-8	24.5	25.6	4	4	4	44.2	-42.3	12	4	-7	41.0	-38.0	7	5	6	29.5	29.5
13	3	-9	38.8	-39.4	4	4	5	52.2	-48.3	12	4	-8	20.5	18.3	7	5	7	43.0	41.0
13	3	-11	17.0	15.9	4	4	6	26.6	-29.0	12	4	-9	29.0	32.0	7	5	-1	33.6	-25.7
13	3	-13	15.9	18.2	4	4	7	53.2	51.6	12	4	-12	35.7	-38.3	7	5	-4	33.8	-29.3
13	3	-15	13.3	-15.5	4	4	8	35.3	34.4	12	4	-14	28.4	27.9	7	5	-5	26.3	26.0
13	3	-16	18.0	-16.1	4	4	9	25.2	-23.3	14	4	1	23.3	-19.7	7	5	-6	71.3	-77.4
13	3	-17	17.7	18.2	4	4	10	20.1	26.2	14	4	2	28.9	-25.0	7	5	-7	19.9	21.8
15	3	1	50.8	47.4	4	4	12	34.2	-33.4	14	4	5	31.0	34.6	7	5	-8	14.5	15.6
15	3	3	14.5	15.8	4	4	14	12.7	12.7	14	4	6	15.6	16.3	7	5	-9	33.0	-35.4
15	3	4	22.9	-21.3	4	4	-1	27.4	-22.9	14	4	-3	14.3	12.9	7	5	-11	26.2	19.7
15	3	5	41.8	-42.9	4	4	-2	37.8	-31.0	14	4	-4	24.9	-26.0	9	5	0	49.8	53.9
15	3	6	18.5	20.3	4	4	-3	56.1	47.2	14	4	-6	20.3	21.1	9	5	1	41.3	41.2
15	3	-1	37.7	-37.5	4	4	-4	58.1	44.1	14	4	-10	33.2	-33.8	9	5	5	53.9	-50.9
15	3	-2	40.0	-40.5	4	4	-5	32.8	26.3	14	4	-11	26.1	-26.9	9	5	-1	40.1	-41.8
15	3	-3	17.2	17.0	4	4	-6	27.0	21.5	14	4	-14	31.9	35.6	9	5	-2	38.5	-37.7
15	3	-4	17.2	-15.9	4	4	-7	45.5	-40.2	14	4	-15	16.5	18.1	9	5	-4	24.4	-25.3
15	3	-5	12.2	-8.9	4	4	-8	65.3	-69.8	16	4	0	32.8	30.7	9	5	-6	51.9	62.3
15	3	-6	38.5	36.5	4	4	-10	20.0	20.2	16	4	3	37.3	-33.2	9	5	-7	35.5	-38.1
15	3	-9	49.1	-44.2	4	4	-13	31.2	33.4	16	4	-1	44.7	37.5	9	5	-8	25.6	-22.7
15	3	-10	20.2	-20.6	4	4	-17	13.3	-25.8	16	4	-4	26.1	-23.9	9	5	-9	21.0	21.6
15	3	-11	33.9	30.5	6	4	1	55.7	55.0	16	4	-5	13.1	-17.5	11	5	0	21.0	22.3
15	3	-13	20.2	16.3	6	4	2	11.7	15.7	16	4	-6	41.3	42.2	11	5	3	24.6	26.0
15	3	-15	16.0	-14.0	6	4	3	12.4	9.8	16	4	-10	51.9	-53.1	11	5	-1	14.8	-14.7
17	3	0	21.7	17.8	6	4	4	13.0	-6.7	16	4	-11	29.7	29.5	11	5	-2	25.7	-26.9
17	3	1	25.5	25.6	6	4	5	19.4	19.7	16	4	-13	18.2	-18.4	11	5	-3	25.6	26.7
17	3	2	18.2	16.2	6	4	6	86.4	-94.8	18	4	-6	25.5	26.1	11	5	-7	25.7	-26.7
17	3	3	29.2	33.1	6	4	7	41.0	-39.9	18	4	-7	10.3	13.4	11	5	-8	44.3	-43.9
17	3	4	19.9	-25.5	6	4	9	14.0	18.0	18	4	-8	20.1	-18.2	11	5	-12	38.9	37.3
17	3	-1	28.8	-25.7	6	4	10	26.4	28.8	1	5	2	23.1	-22.7	11	5	-13	36.6	-31.2
17	3	-2	10.6	10.7	6	4	12	31.6	-35.2	1	5	3	56.8	-55.1	11	5	-14	48.8	-46.1
17	3	-3	15.3	14.6	6	4	13	15.4	15.4	1	5	4	75.5	78.7	13	5	0	56.7	-58.7
17	3	-7	45.5	-38.6	6	4	-1	106.5	-94.5	1	5	5	44.0	45.9	13	5	1	23.4	-24.9
17	3	-9	26.0	21.5	6	4	-2	27.6	20.5	1	5	6	53.7	-54.2	13	5	2	40.9	43.2
17	3	-10	20.5	18.8	6	4	-3	27.0	-22.9	1	5	7	19.9	15.8	13	5	-1	14.2	13.6
19	3	-1	13.5	-14.1	6	4	-4	18.3	15.6	1	5	8	46.2	-52.8	13	5	-3	14.5	10.6
19	3	-3	25.6	27.2	6	4	-5	46.3	42.1	1	5	9	29.7	-34.9	13	5	-4	46.0	48.9
19	3	-4	11.9	-9.9	6	4	-6	39.7	-35.8	1	5	10	29.3	26.9	13	5	-5	29.1	-25.2
19	3	-5	15.0	10.4	6	4	-7	21.5	16.8	1	5	13	22.2	13.5	13	5	-6	28.9	26.3
19	3	-7	28.9	-29.0	6	4	-8	41.4	-36.5	1	5	-3	17.4	17.3	13	5	-9	27.5	24.7
19	3	-8	8.5	-11.1	6	4	-9	23.3	-25.5	1	5	-4	36.6	32.3	13	5	-13	16.4	-18.7
19	3	-10	19.2	-16.1	6	4	-10	20.1	21.6	1	5	-5	60.5	-63.2	15	5	0	19.9	-21.9
19	3	-11	16.0	14.2	6	4	-14	22.7	-24.2	1	5	-6	43.6	39.0	15	5	1	10.6	-13.6
0	4	1	75.9	-101.4	6	4	-16	22.0	21.6	1	5	-9	46.6	48.6	15	5	-3	12.6	15.5
0	4	4	41.9	-39.0	8	4	0	32.8	-27.7	1	5	-11	25.1	-25.1	15	5	-4	15.4	20.4
0	4	5	39.0	31.4	8	4	1	28.6	-25.2	1	5	-12	36.0	-35.6	15	5	-5	26.1	-29.7
0	4	6	106.0	103.6	8	4	2	26.5	22.7	3	5	1	22.7	-17.1	15	5	-6	45.0	-46.7
0	4	7	35.1	-33.2	8	4	4	34.7	35.7	3	5	2	75.9	-75.6	15	5	-7	28.7	30.2
0	4	8	29.8	28.9	8	4	6	32.5	-35.5	3	5	3	37.6	-34.0	15	5	-8	21.6	21.8
0	4	9	26.0	24.5	8	4	9	25.4	28.5	3	5	4	21.4	16.3	15	5	-11	30.2	-31.2
0	4	10	35.4	-42.3	8	4	10	33.7	36.4										

with a W–H distance of 0·66 Å, is obviously very poorly located. This is the hydrogen which was not found in the difference map.

The pyrophosphate group

The dimensions of the pyrophosphate group are given in Table 7. The estimated standard deviations are 0·005 Å for the P–O bond lengths, 0·6° for the P–O–P angle, and 0·3° for the O–P–O angles. As noted by Cruickshank (1964), the vibration parameters for the oxygen atoms are higher than those for phosphorus, so that some correction of the bonds to allow for rotational motions is necessary. The U_{ij} for the atoms of the group, referred to inertial axes, are given in Table 8. Axis 1 is the axis of minimum inertia (and is very close to the P···P line), while axis 2 is that of maximum inertia. Axis 3 coincides with the crystallographic twofold axis. The values of the U_{ij} are not consistent with appreciable rigid body vibrations of the whole P_2O_7 group, but suggest that the two PO_4 tetrahedra vibrate individually as rigid bodies, for the phosphorus atoms show small and approximately isotropic vibrations, while the oxygen atoms are markedly anisotropic. The bridge oxygen, O(1), has the largest individual U_{ii}. This is normal to the P–O–P plane, suggesting a vibration in which the group 'folds' along the symmetry axis while the phosphorus atoms remain stationary. The U_{ij} of the terminal oxygen atoms are consistent with a vibration of this kind. In addition, the three terminal oxygen atoms show appreciable vibrations consistent with a rotational oscillation of the PO_3 group about the axis of the bridge bond. Separate vibration corrections need to be applied for each of these types of motion. Since the bridge oxygen is constrained by symmetry to move in a straight line normal to the P–O–P plane no correction is necessary to the P–O(1) length. The rotational oscillation about the P–O(1) axis requires a correction of about 0·005 Å to the three terminal bonds. The folding vibration requires a further correction of about 0·007 Å to the P–O(4) bond, and about 0·004 Å to

Table 5. *Bond lengths and angles at the sodium atoms*

Bond		Bond	
Na(1)–W(1)	2·292 Å	Na(2)–W(4)	2·360 Å
Na(1)–W(2)	2·353	Na(2)–W(5)	2·415
Na(1)–W(2′)	2·377	Na(2)–O(2)	2·416
Na(1)–W(4)	2·405	Na(2)–W(3)	2·457
Na(1)–W(3)	2·705	Na(2)–W(1)	2·479
Na(1)–W(3′)	2·772	Na(2)–O(4)	2·554

Angle		Angle	
W(1) –Na(1)–W(2)	103·4°	W(4)–Na(2)–W(5)	85·2°
W(1) –Na(1)–W(2′)	91·7	W(4)–Na(2)–O(2)	101·7
W(1) –Na(1)–W(4)	172·0	W(4)–Na(2)–W(3)	97·8
W(1) –Na(1)–W(3)	92·3	W(4)–Na(2)–W(1)	171·6
W(1) –Na(1)–W(3′)	87·2	W(4)–Na(2)–O(4)	79·5
W(2) –Na(1)–W(2′)	88·6	W(5)–Na(2)–O(2)	97·2
W(2) –Na(1)–W(4)	84·3	W(5)–Na(2)–W(3)	99·3
W(2) –Na(1)–W(3)	87·5	W(5)–Na(2)–W(1)	94·4
W(2) –Na(1)–W(3′)	164·6	W(5)–Na(2)–O(4)	164·7
W(2′)–Na(1)–W(4)	86·2	O(2) –Na(2)–W(3)	155·4
W(2′)–Na(1)–W(3)	175·0	O(2) –Na(2)–W(1)	70·0
W(2′)–Na(1)–W(3′)	102·4	O(2) –Na(2)–O(4)	85·4
W(4) –Na(1)–W(3)	90·3	W(3)–Na(2)–W(1)	90·6
W(4) –Na(1)–W(3′)	85·7	W(3)–Na(2)–O(4)	83·5
W(3) –Na(1)–W(3′)	80·8	W(1)–Na(2)–O(4)	100·6

P–O(2) and P–O(3). The corrected bond lengths are then 1·519 for P–O(2), 1·512 for P–O(3), and 1·537 Å for P–O(4).

The mean terminal P–O bond length is therefore 1·523 ± 0·004 Å, and the bridge bond length is 1·612 ± 0·005 Å, where the e.s.d.'s include an allowance for the uncertainties in the rotational corrections. The difference of about 0·1 Å therefore falls midway between the 0·2 Å difference found in $S_2O_7^{2-}$ (Lynton & Truter, 1960) and the zero difference found typically in $Si_2O_7^{6-}$ groups.

However several other pyrophosphate structures have been determined recently, notably by Calvo, and these show a considerable range in the pyrophosphate dimensions. In β-$Zn_2P_2O_7$ (Calvo, 1965*a*) and in β-$Mg_2P_2O_7$ (Calvo, 1965*b*) the terminal bonds are of mean length 1·539 and 1·555 Å respectively, and the bridge bonds are 1·557 and 1·569 Å. The differences in the two types of bond are only 0·02 Å as compared with 0·09 Å in the sodium salt. In both of these structures, however, the P–O–P angle is 180° as compared with 130° in sodium pyrophosphate, and the greater angle would be expected to make the π-bond orders, and therefore the bond lengths, more nearly equal. There is also considerable uncertainty as to what rotational corrections are necessary for the zinc and magnesium salts. Intermediate dimensions are found for α-$Cu_2P_2O_7$ (Robertson & Calvo, 1966) which has 1·53, 1·58 Å and 157°, and for α-$Mg_2P_2O_7$ (Calvo, 1966) which has 1·51 ± 0·02, 1·59 ± 0·02 Å, and 144°. In β-$Ca_2P_2O_7$ Webb (1966) has found two non-equivalent anions with P–O–P angles of 131 and 138°; the terminal P–O bonds average 1·518 ± 0·021 Å and the bridge bonds 1·615 ± 0·017 Å. These dimensions are close to those in sodium pyrophosphate. The results for all these salts show a clear correlation between the P–O–P angle and the difference between the two types of P–O bond.

In the present structure there are some interesting distortions within the P_2O_7 group, which are similar to those found by Beagley (1965) in an electron-diffraction study of gaseous Cl_2O_7. First, the $-PO_3$ group is twisted by 23° about the O(1)–P axis to take O(3) out of the P–O–P plane. Second, the $-PO_3$ group is tilted so that its axis of approximate trigonal symmetry deviates by about 1·5° from the P–O(1) line, in such a way that O(1)–P–O(3) is the smallest of the angles at P. From the intramolecular contacts listed in Table 7 the most likely cause of this tilt is the pressure of P′ on O(2) indicated by the distance P′–O(2) = 3·26 Å which is close to the sum of van der Waals radii (1·9 + 1·4 = 3·3 Å). Apart from P′–P = 2·92 Å,

Table 6. *Hydrogen bond lengths and angles*

Bond		Bond		Bond		Angle	
W(1)–O(2′)	2·786 Å	*W*(1)–H(11)	0·97 Å	H(11)–O(2′)	1·87 Å	*W*(1)–H(11)–O(2′)	156°
W(1)–O(2)	2·812	*W*(1)–H(12)	0·72	H(12)–O(2)	2·10	*W*(1)–H(12)–O(2)	168
						H(11)–*W*(1)–H(12)	85
W(2)–O(3)	2·770	*W*(2)–H(21)	0·98	H(21)–O(3)	1·87	*W*(2)–H(21)–O(3)	152
W(2)–O(4)	2·737	*W*(2)–H(22)	1·03	H(22)–O(4)	1·94	*W*(2)–H(22)–O(4)	133
						H(21)–*W*(2)–H(22)	112
W(3)–O(4)	2·708	*W*(3)–H(31)	0·92	H(31)–O(4)	1·85	*W*(3)–H(31)–O(4)	153
W(3)–*W*(5)	2·934	*W*(3)–H(32)	1·14	H(32)–*W*(5)	1·80	*W*(3)–H(32)–*W*(5)	171
						H(31)–*W*(3)–H(32)	92
W(4)–O(2)	2·793	*W*(4)–H(41)	1·05	H(41)–O(2)	1·79	*W*(4)–H(41)–O(2)	159
W(4)–O(3)	2·919	*W*(4)–H(42)	0·66	H(42)–O(3)	2·29	*W*(4)–H(42)–O(3)	159
						H(41)–*W*(4)–H(42)	87
W(5)–O(3)	3·059	*W*(5)–H(51)	0·83	H(51)–O(3)	2·31	*W*(5)–H(51)–O(3)	151
W(5)–O(3′)	2·783	*W*(5)–H(52)	1·18	H(52)–O(3′)	1·65	*W*(5)–H(52)–O(3′)	160
						H(51)–*W*(5)–H(52)	93

Table 7. *Dimensions of the pyrophosphate group*

Bond		Angle		Distance	
P–O(1)	1·612 Å	P–O(1)–P′	130·2°	P —P′	2·925 Å
P–O(2)	1·510	O(1)–P–O(2)	108·9	O(1)–O(2)	2·541
P–O(3)	1·503	O(1)–P–O(3)	101·8	O(1)–O(3)	2·419
P–O(4)	1·526	O(1)–P–O(4)	106·6	O(1)–O(4)	2·516
		O(2)–P–O(3)	112·8	O(2)–O(3)	2·509
		O(2)–P–O(4)	111·1	O(2)–O(4)	2·503
		O(3)–P–O(4)	115·0	O(3)–O(4)	2·555

Table 8. *Vibration tensor components of the atoms of the pyrophosphate group, referred to inertial axes* (Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
P	0·0134	0·0175	0·0145	0·0034	−0·0036	0·0016
O(1)	0·0173	0·0496	0·0129	0·0000	0·0000	0·0034
O(2)	0·0288	0·0282	0·0142	0·0088	0·0032	0·0088
O(3)	0·0256	0·0359	0·0346	−0·0132	−0·0156	−0·0132
O(4)	0·0357	0·0193	0·0321	−0·0006	0·0184	0·0080

there are no other contacts between the two $-PO_3$ groups corresponding to standard van der Waals distances, though the 23° twist of each $-PO_3$ group may be caused by repulsions O(2')–O(2), O(2')–O(4), O(4')–O(2) and O(4)–O(4'), which are considerably relieved in the twisted configuration to give a nearly staggered structure with O(2')–O(2) = 3·34 and O(2')–O(4) = O(4')–O(2) = 3·37 Å.

Similar tilts of the $-SO_3$ groups relative to the S–O (bridge) directions occur in crystalline $K_2S_2O_7$ (Lynton & Truter, 1960), $K_2NH(SO_3)_2$ (Cruickshank & Jones, 1963) and $K_2CH_2(SO_3)_2$ (Truter, 1962). Lacking the results for gaseous Cl_2O_7, these authors did not appreciate that the distortions were of intramolecular origin. Hirshfeld (1964) would consider that such tilts indicate bent X–O(bridge) bonds, and on his recipe the 'valency angles' in the bisulphates are 118° when O is the bridge atom, 119° for NH and 114° for CH_2, as compared with geometrical S–A–S angles of 124°, 126° and 120°. In Cl_2O_7 the reduction is to 109° from 119°. These 'valency angles' are more acceptable than the geometrical angles. The corresponding 'valency angle' for sodium pyrophosphate is 127°.

Of the three bond lengths in the $-PO_3$ group, P–O(3) = 1·512 Å is slightly the shortest. This seems to correlate with the involvement of O(3) in the smallest O–P–O(1) angle, since a similar effect occurs in the above three sulphates.

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A Refinement of the Structure of S_3O_9

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After refinement with the data of Pascard & Pascard-Billy (1965) the molecular dimensions are S–O (ring) 1·626 ± 0·007 Å, S–O(axial) 1·371 ± 0·013 Å, and S–O(equatorial) 1·430 ± 0·013 Å. Owing to the polar space group, it was found necessary to correct for the imaginary component of the anomalous scattering of S and O.

Introduction

The γ form of sulphur trioxide was examined by Westrik & MacGillavry (1941), who showed that it contained cyclic S_3O_9 molecules. Pascard & Pascard-Billy (1965) obtained fresh three-dimensional data and carried out a refinement of the structure. Their published molecular dimensions, however, showed anomalies as there were some large differences between the lengths of chemically equivalent bonds. Thus the six S–O bonds of the ring ranged from 1·53 to 1·65 Å, and the three equatorial S–O bonds were 1·40, 1·33 and 1·40 Å, all with quoted standard deviations of 0·016 Å. Because of these rather implausible dimensions, the published data of Pascard & Pascard-Billy were used for a new least-squares refinement.

Cell dimensions

The space group is $P2_1nb$ with 4 molecules in the cell. The cell dimensions given by Pascard & Pascard-Billy are $a = 5·13 \pm 0·05$, $b = 10·82 \pm 0·02$, $c = 12·40 \pm 0·02$ Å, corresponding to 5·3, 10·7 and 12·3 Å given by Westrik & MacGillavry. At a late stage of our refinement we wondered whether the unusually short bond-lengths of the axial S–O bonds were really due to an error in the a-axis dimension. Mr Kreuger and Dr C. Stam of the University of Amsterdam were then kind enough to make measurements of a new $h0l$ Weissenberg photo-

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