& Bauer, 1970). We are planning to investigate some additional vinyl sulfones as well as some disulfonylethylenes to provide more experimental test data for this hypothesis.

Fig. 3 shows a packing drawing viewed perpendicular to the *ab* plane. Since there are no close intermolecular distances to the viewing direction, only the molecules in one layer are shown. The shortest approaches are between hydrogen and the sulfone oxygen atoms and these distances are indicated with dotted lines in Fig. 3. The magnitudes of the distances indicate that H···O interactions are probably just those permitted by the van der Waals radii of H and O.

We are grateful to the National Science Foundation for support of this work through grant GP-15791 and for a Science Development Award to the Department of Chemistry which provided funds for the Picker diffractometer. Computer time was obtained, in part, through the facilities of the Computer Science Center, University of Maryland.

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The Crystal Structure of Compounds with (N-P)$_n$ Rings.
IX.* Octabromocyclotetraphosphazene, $N_4P_4Br_8$

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(*Received* 30 *March* 1971)

The crystal and molecular structure of octabromocyclotetraphosphazene, $N_4P_4Br_8$, has been determined from three-dimensional intensity data collected at 110°K with Zr-filtered Mo radiation on a Nonius automatic three-circle single-crystal diffractometer. The space group is $P4_2/n$ and the edges of the tetragonal unit cell, determined at 110°K, are $a = 11{\cdot}187$ (3) and $c = 6{\cdot}189$ (2) Å. The crystal structure is isomorphous with that of $N_4P_4Cl_8$ (*K* form). There are three intermolecular Br···Br distances (3·66, 3·74, and 3·79 Å) that are shorter than the corresponding van der Waals distance (3·90 Å). The molecules $N_4P_4Br_8$ possess crystallographic fourfold inversion symmetry. Mean values (and individual standard deviations) of chemically equivalent bond lengths are P–N, 1·575(6), and P–Br, 2·171 (2) Å. The more important valence angles are P–N–P, 131·0 (4), N–P–N, 120·1 (4), and Br–P–Br, 103·9 (1)°. The conformation of the eight-membered ring is intermediate between a boat and a saddle. The dihedral angles of the ring bonds are 17 and 59° and the distances from the ring atoms to the mean molecular plane are $\Delta P = 0{\cdot}36$ and $\Delta N = 0{\cdot}49$ Å ($\Delta P/\Delta N = 0{\cdot}74$). The molecular structure of $N_4P_4Br_8$ is compared with that of related compounds.

Introduction

The preparation of octabromocyclotetraphosphazene from phosphorus(V) bromide and ammonium bromide has been reported by Bode (1943) and by Bean & Shaw (1960). Improved preparative methods, with the use of phosphorus(III) bromide and bromine instead of the pentabromide, have been described by John & Moeller (1961, 1963) and by Coxon, Sowerby & Tranter (1965).

The infrared spectrum of $N_4P_4Br_8$ has been measured by several workers and shows the characteristic P–N stretching vibration at 1272 cm^{-1}. The ^{31}P nuclear magnetic resonance spectrum (Feistel, 1965) consists of a single peak with a very high chemical shift, *viz.* 69·9 ppm with respect to 85% orthophosphoric acid. The mass spectrum of $N_4P_4Br_8$ has been studied by Coxon, Palmer & Sowerby (1967).

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* Part VIII: Mani & Wagner (1971).

In a previous paper of this series (Zoer & Wagner, 1970) the crystal structure of trimeric bromocyclophosphazene, $N_3P_3Br_6$, has been described. The present paper reports the crystal structure determination of the tetrameric compound, $N_4P_4Br_8$, and gives a discussion of the geometrical aspects of the structure, in particular in relation to the structures of $N_4P_4Cl_8(K)$ and $N_3P_3Br_6$.

Experimental

Octabromocyclotetraphosphazene was prepared according to the method of John & Moeller (1963) and Coxon *et al.* (1965). The substance was separated from the reaction mixture by fractional crystallization from light petroleum. Recrystallization from the same solvent gave colourless and transparent crystals, elongated along the *c* axis and of suitable size for the X-ray diffraction work.

The crystal data are given in Table 1. The unit-cell edges were determined both at room temperature and at 110°K. Experimental details are given in Table 2. The values at the latter temperature were used in the subsequent structure analysis. Coxon *et al.* (1965), using room temperature powder diffraction data, obtained for the *c* axis a value (6·29 Å) comparable to ours, but for the *a* axis a smaller value (11·14 Å).

Table 1. *Crystal data*

Compound	$N_4P_4Br_8$, M.W.: 819·2	
Crystal system	Tetragonal	
Unit cell	298°K	110°K
	$a = 11{\cdot}272$ (5) Å	11·187 (3) Å
	$c = 6{\cdot}284$ (2)	6·189 (2)
Space group	$P4_2/n$ (No. 86)	
Systematic absences	$hk0$ for $h+k$ odd	
	$00l$ for l odd	
Density	D_m not measured	
	D_c (at 298°K) = 3·41 g.cm^{-3} for $Z = 2$	
$F(000)$	736	
μ(Mo)	223 cm^{-1}	

The intensities were measured at 110°K on a Nonius diffractometer. Details are included in Table 2. Attenuation filters were used when measuring the strong reflexions and one of the standard reflexions was monitored every 50 reflexions. The long-range variation in the intensities measured for the standard reflexions was less than 5%.

Net intensities were calculated from the peak and background counts and put on the same relative scale by means of the standard reflexions. Reflexions having a negative net intensity were not considered further. Lorentz and polarization corrections were applied to the remaining 1817 reflexions and the weights, based on the uncertainties in the counting rates and in the attenuation filter factors, were calculated. Also, an absorption correction following the method of Busing & Levy (1957) was applied, in which the transmission factor varied from 0·12 to 0·17.

Structure determination

The space group of $N_4P_4Br_8$ is the same as that of $N_4P_4Cl_8$ (*K* form) (Hazekamp, Migchelsen & Vos, 1962) and the crystals of the two compounds have unit-cells of very similar dimensions. Thus it appeared probable that the two crystal structures are isomorphous. This conclusion could easily be verified by inspection of a three-dimensional Patterson synthesis, which showed maxima consistent with the positions of the atoms in $N_4P_4Cl_8(K)$.

Refinement of the crystal structure was carried out by minimizing the function $\sum w[|F_o| - K|F_c|]^2$, summed over the 1817 observed independent reflexions, by block-diagonal least-squares analysis. An extinction parameter (Zachariasen, 1967, 1968) was refined in addition to the positional and anisotropic thermal parameters of the atoms. The atomic scattering factors were taken from Doyle & Turner (1968) and dispersion corrections (*International Tables for X-ray Crystallography,* 1962) were applied to the scattering factors of phosphorus and bromine. The weighting scheme used was $w = \{w_c^{-1} + p|F_o|^2\}^{-1}$, where w_c is the weight from counting statistics and p is a constant. For p the

Table 2. *Experimental details of unit-cell determination and intensity measurements*

Unit-cell determination:	
Method	Weissenberg photographs
Layer lines (and number of independent reflexions)	298°K: $hk0$ (80), $0kl$ (77) 110°K: $0kl$ (84)
Radiation	Cu K radiation, $\lambda(\alpha_1) = 1{\cdot}54051$, $\lambda(\alpha_2) = 1{\cdot}54433$ Å
Calibration	NaCl reflexions, a(NaCl) = 5·640 Å
Intensity measurements:	
Method	Nonius automatic three-circle single-crystal diffractometer
Radiation	Mo radiation, Zr filtered, take-off angle 6°
Crystal	size 0·3 × 0·1 × 0·1 mm, mounted with [001] parallel to φ
Range	$(\sin\theta)/\lambda \le 0{\cdot}9$ Å^{-1}, 2447 independent reflexions
Scan method	θ–2θ, stationary background
Scan angle	1·2–2·1° (in 2θ)
Scan speed	2·4° min^{-1} (in 2θ)
Standard reflexions	812, 313, 151
Temperature	110°K

value 4×10^{-4} was chosen, resulting in a fairly constant value of $\langle w|\Delta F|^2\rangle$.

At the end of the refinement the reliability indices were $R\equiv\{\sum|\Delta F|^2/\sum|F_o|^2\}^{1/2}=10\%$ and $R_w\equiv\{\sum w|\Delta F|^2/\sum w|F_o|^2\}^{1/2}=7{\cdot}3\%$ and the extinction parameter p_{ex} (Zoer & Wagner, 1970) had the value 0·032. In the last cycle the changes in the positional or thermal parameters were smaller than 0·1 of the standard deviations.

The final atomic coordinates are given in Table 3 and the parameters of the anisotropic temperature factors in Table 4. The standard deviations in these Tables are the quantities calculated from the residuals in the least-squares analysis. No thermal motion corrections were applied to the coordinates. Observed and calculated structure factors are compared in Table 5. In this Table the extinction corrections are applied to the observed amplitudes $|F_o|$.

Table 3. *Final atomic coordinates* ($\times10^4$) *with standard deviations in parentheses*

	x	y	z
N(1)	1170 (5)	1597 (5)	1701 (11)
P(1)	2049 (2)	807 (2)	3086 (3)
Br(1)	1413 (1)	551 (1)	6359 (1)
Br(2)	1930 (1)	− 966 (1)	1657 (1)

Description and discussion of the structure

The molecules $N_4P_4Br_8$ occupy the special twofold position (*a*) of the space group $P4_2/n$ and thus have crystallographic fourfold inversion symmetry. A projection of the crystal structure on the (001) plane is shown in Fig. 1 and a view of one of the molecules along the [100] direction is given in Fig. 2. The numbering of the atoms in the Figures corresponds to that used in the Tables.

As shown in Fig. 1 there are some relatively short intermolecular Br···Br distances. Close intermolecular contacts have also been observed in the crystal structure of $N_3P_3Br_6$ (Zoer & Wagner, 1970), and, in some cases, were part of approximately linear three-atom arrays. It is found that in the crystal structure of $N_4P_4Br_8$ such linear arrays do not occur. Thus the explanation of the short Br···Br distances by assuming some degree of three-centre four-electron bonding (as discussed in relation to the $N_3P_3Br_6$ structure) does not apply to the $N_4P_4Br_8$ structure.

The shortest Br···Br distances (3·66, 3·74, and 3·79 Å) are only a little longer than the corresponding Cl···Cl distances (3·62, 3·69, and 3·68 Å*) in the crystal structure of $N_4P_4Cl_8(K)$. In the latter case all distances are longer than the Cl···Cl van der Waals distance of 3·60 Å. In the former case the three Br···Br distances are shorter than the corresponding van der Waals distance by 0·1 or 0·2 Å, if the value of 1·95 Å given by Pauling (1960) is adopted as the van der Waals radius of bromine. Indeed, the present work suggests that the van der Waals radius of bromine is better represented by a value of 1·80 or 1·85 Å, and the results from the crystal structure analysis of $N_5P_5Br_{10}$ (Hartsuiker & Wagner, to be published) give rise to the same conclusion.

The molecules $N_4P_4Br_8$ and $N_4P_4Cl_8(K)$, as occurring in the respective crystal structures, are built in a very similar way. The only significant difference is, of course, the length of the exocyclic bonds (P–Br, 2·17; P–Cl, 1·99 Å). There is no difference in P–N bond length, angle P–N–P, or angle N–P–N. Even the successive angles N–P–Hal are the same in the two molecules and the angle Hal–P–Hal is larger in the case

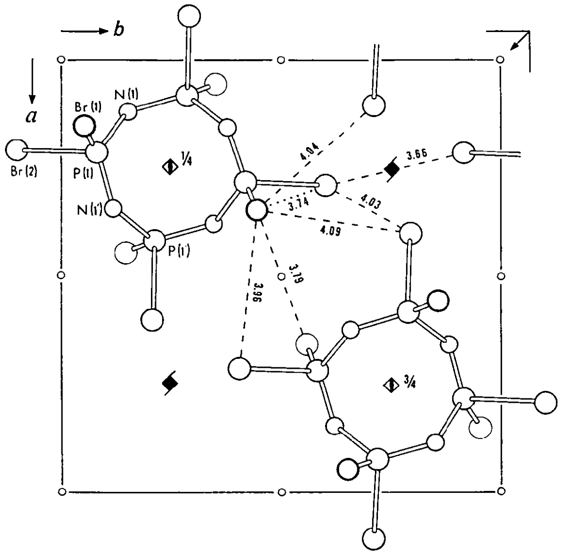

Fig. 1. Projection of the crystal structure of $N_4P_4Br_8$ onto the (001) plane. Short intermolecular Br···Br distances are indicated by dashed lines. The distance 3.74 Å is from Br(1) of the molecule at z to Br(2) of the molecule at $z+1$.

Table 4. *Parameters* (*in* $\text{Å}^2\times10^{-4}$) *of the anisotropic temperature factors* $\exp\left[-2\pi^2(h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12}+\ldots)\right]$ *with standard deviations in parentheses*

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
N(1)	144 (26)	74 (22)	134 (29)	41 (37)	19 (44)	−22 (46)
P(1)	70 (7)	63 (6)	88 (7)	− 8 (10)	10 (12)	15 (12)
Br(1)	110 (3)	196 (3)	98 (3)	−44 (5)	1 (5)	38 (5)
Br(2)	177 (3)	67 (3)	161 (3)	11 (5)	−41 (5)	9 (6)

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* The shortest Cl···Cl distance in the crystal structure of $N_4P_4Cl_8(K)$ has erroneously been given by Hazekamp, Migchelsen & Vos (1962) as 3·68 Å.

Table 5. *Observed and calculated structure factors*

The structure factor amplitudes are on ten times the absolute scale.

H	K	L	|Fo|	|Fc|
3	1	0	3078	3021
5	1	0	823	793
7	1	0	159	49
9	1	0	503	487
11	1	0	569	532
13	1	0	693	699
15	1	0	629	638
17	1	0	568	597
19	1	0	410	474
2	2	0	1434	1489
6	2	0	3479	3596
8	2	0	618	642
10	2	0	1399	1422
12	2	0	739	756
16	2	0	202	108
18	2	0	172	142
1	3	0	1783	1670
3	3	0	1288	1346
5	3	0	988	1051
7	3	0	73	44
9	3	0	1186	1212
11	3	0	212	196
13	3	0	749	776
15	3	0	482	508
19	3	0	314	387
0	4	0	2132	1831
4	4	0	436	461
6	4	0	180	285
8	4	0	29	68
10	4	0	332	328
12	4	0	1772	1822
14	4	0	393	408
16	4	0	918	908
18	4	0	161	274
1	5	0	1897	1811
3	5	0	1606	1673
5	5	0	1275	1368
7	5	0	1533	1637
9	5	0	942	1018
11	5	0	1167	1208
13	5	0	298	303
15	5	0	608	620
17	5	0	287	322
19	5	0	363	393
0	6	0	475	458
2	6	0	416	401
4	6	0	289	244
6	6	0	1147	1208
8	6	0	107	48
10	6	0	397	383
12	6	0	507	512
14	6	0	199	136
16	6	0	175	224
18	6	0	728	743
1	7	0	1430	1366
3	7	0	1044	1074
5	7	0	402	430
7	7	0	711	743
9	7	0	493	515
11	7	0	965	944
13	7	0	735	748
15	7	0	498	568
17	7	0	514	554
0	8	0	1112	1031
2	8	0	230	289
4	8	0	2119	2204
6	8	0	470	473
8	8	0	654	667
10	8	0	339	361
12	8	0	401	434
14	8	0	194	186
16	8	0	230	124
18	8	0	158	206
1	9	0	1194	1142
3	9	0	636	629
5	9	0	317	309
7	9	0	846	989
9	9	0	349	343
11	9	0	446	434
13	9	0	672	669
15	9	0	283	238
17	9	0	439	434
0	10	0	459	423
2	10	0	198	222
4	10	0	384	393
6	10	0	261	268
8	10	0	685	710
10	10	0	1378	1432
12	10	0	283	287
14	10	0	376	409
16	10	0	144	135
1	11	0	1094	1018
3	11	0	315	309
5	11	0	817	833
7	11	0	873	984
9	11	0	472	505
11	11	0	359	374
13	11	0	534	601
15	11	0	333	279
0	12	0	276	266
2	12	0	558	543
4	12	0	780	803
6	12	0	309	306
8	12	0	127	74
10	12	0	523	562
12	12	0	411	403
14	12	0	320	345
16	12	0	578	601
1	13	0	1218	1184
3	13	0	140	84
5	13	0	261	289
7	13	0	140	211
9	13	0	319	319
11	13	0	311	305
13	13	0	286	312
15	13	0	229	212
0	14	0	304	302
2	14	0	1068	1068
4	14	0	268	226
6	14	0	562	556
8	14	0	246	177
10	14	0	276	323
12	14	0	212	63
14	14	0	211	209
1	15	0	753	722
3	15	0	144	189
5	15	0	566	544
7	15	0	713	741
9	15	0	395	446
11	15	0	430	497
13	15	0	166	114
2	16	0	506	525
4	16	0	234	172
6	16	0	135	239
8	16	0	725	729
10	16	0	288	275
12	16	0	224	230
1	17	0	186	162
3	17	0	570	567
5	17	0	688	761
7	17	0	408	434
0	18	0	431	416
2	18	0	553	562
6	18	0	189	31
8	18	0	496	552
1	19	0	23	37
5	19	0	276	266
0	20	0	542	548
0	1	1	460	379
1	1	1	596	622
2	1	1	832	825
3	1	1	1396	1393
4	1	1	942	888
5	1	1	546	540
6	1	1	498	476
8	1	1	368	374
9	1	1	605	608
10	1	1	549	563
11	1	1	915	901
12	1	1	1347	1335
13	1	1	472	470
14	1	1	598	600
15	1	1	263	229
16	1	1	747	751
17	1	1	302	352
18	1	1	168	153
19	1	1	168	2
20	1	1	229	152
0	2	1	468	483
1	2	1	200	197
2	2	1	1559	1654
3	2	1	1456	1494
4	2	1	498	466
5	2	1	667	684
6	2	1	199	206
7	2	1	336	351
8	2	1	355	289
9	2	1	1188	1226
10	2	1	464	448
11	2	1	202	196
12	2	1	134	118
13	2	1	297	293
14	2	1	699	681
16	2	1	100	54
17	2	1	171	87
20	2	1	232	85
0	3	1	2669	2273
1	3	1	1314	1248
2	3	1	1746	1762
3	3	1	919	952
4	3	1	246	253
5	3	1	525	553
6	3	1	142	144
7	3	1	481	489
8	3	1	453	475
9	3	1	717	729
10	3	1	135	120
11	3	1	67	54
12	3	1	162	173
14	3	1	133	101
15	3	1	433	387
16	3	1	69	62
17	3	1	437	432
18	3	1	598	586
19	3	1	317	275
0	4	1	1237	1103
1	4	1	922	843
3	4	1	1448	1511
4	4	1	1168	1266
5	4	1	139	95
6	4	1	136	66
7	4	1	990	1028
8	4	1	981	1013
9	4	1	1010	1053
10	4	1	498	506
11	4	1	315	370
12	4	1	176	46
13	4	1	127	37
14	4	1	290	322
15	4	1	599	615
17	4	1	324	338
18	4	1	76	79
19	4	1	341	342
0	5	1	248	284
1	5	1	1280	1221
2	5	1	452	442
3	5	1	1030	1072
4	5	1	1802	1910
5	5	1	678	711
6	5	1	1644	1909
7	5	1	196	201
8	5	1	879	891
9	5	1	513	524
10	5	1	275	299
11	5	1	216	237
12	5	1	133	96
13	5	1	346	367
14	5	1	554	564
15	5	1	136	198
16	5	1	261	218
17	5	1	58	24
18	5	1	229	14
19	5	1	142	14
0	6	1	247	178
1	6	1	2691	2506
2	6	1	905	871
3	6	1	54	18
4	6	1	199	205
5	6	1	795	835
6	6	1	984	947
7	6	1	352	350
8	6	1	1011	1035
10	6	1	399	426
11	6	1	331	297
12	6	1	144	217
13	6	1	418	411
14	6	1	683	657
15	6	1	213	242
16	6	1	277	273
17	6	1	322	296
18	6	1	110	109
19	6	1	221	163
0	7	1	927	854
1	7	1	811	764
2	7	1	354	394
3	7	1	483	476
4	7	1	828	848
5	7	1	211	182
6	7	1	667	755
7	7	1	639	644
8	7	1	168	175
9	7	1	953	969
10	7	1	867	898
11	7	1	473	474
12	7	1	618	639
14	7	1	518	530
15	7	1	238	227
16	7	1	118	47
17	7	1	217	116
18	7	1	141	165
0	8	1	1222	1134
1	8	1	1434	1346
2	8	1	120	87
3	8	1	226	210
4	8	1	99	65
5	8	1	822	880
6	8	1	258	278
7	8	1	1206	1248
8	8	1	452	476
9	8	1	98	58
10	8	1	97	9
11	8	1	486	515
12	8	1	603	598
13	8	1	297	111
14	8	1	193	96
15	8	1	182	226
16	8	1	205	163
17	8	1	80	14
18	8	1	73	82
0	9	1	1126	1049
1	9	1	80	56
2	9	1	420	431
3	9	1	368	362
4	9	1	399	397
6	9	1	896	930
7	9	1	410	418
8	9	1	470	478
9	9	1	184	135
10	9	1	128	65
11	9	1	249	224
12	9	1	224	186
13	9	1	377	421
14	9	1	361	296
15	9	1	447	451
16	9	1	485	515
17	9	1	221	232
0	10	1	77	76
1	10	1	1318	1268
2	10	1	783	774
4	10	1	215	201
5	10	1	322	336
6	10	1	727	741
7	10	1	883	911
8	10	1	226	229
9	10	1	88	170
10	10	1	41	89
11	10	1	243	237
12	10	1	237	189
13	10	1	634	626
14	10	1	118	162
16	10	1	243	15
17	10	1	448	441
0	11	1	577	546
1	11	1	619	584
2	11	1	1349	1298
3	11	1	534	526
4	11	1	1433	1444
5	11	1	59	59
6	11	1	571	573
7	11	1	113	145
8	11	1	235	234
9	11	1	285	198
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6	2	10	445	485
7	2	10	255	289
0	3	10	291	272
2	3	10	397	407
3	3	10	319	349
4	3	10	422	483
5	3	10	271	67
1	4	10	397	363
0	5	10	439	398
1	5	10	202	39
1	7	10	332	351
4	8	10	542	509

of $N_4P_4Br_8$ by only 1°. Furthermore, the two molecules exhibit the same ring conformation, which is intermediate between a boat and a saddle. The dihedral angles* assignable to the ring bonds are [$N_4P_4Cl_8(K)$ in parentheses]: -59 (-57)° for P(1)–N(1) and -17 (-16)° for P(1)–N(1′). The distances from the ring atoms to the mean molecular plane are $\Delta P=0{\cdot}36$ (0·35) and $\Delta N=0{\cdot}49$ (0·47) Å. The ratio $\Delta P/\Delta N$ is 0·74 (0·75).

The *K* form of $N_4P_4Cl_8$ is at room temperature a metastable modification, which transforms into the stable modification (or *T* form) upon heating. The difference between the two crystal modifications is essentially a difference between the ring conformations of the molecules (Wagner & Vos, 1968*a*). We have investigated whether this type of conformational isomerism in the solid state is also shown by $N_4P_4Br_8$, but X-ray photographs exposed at 120°C during 16 hours gave no indication of a phase transition.

There are two independent P–Br bonds in the crystal structure of $N_4P_4Br_8$ which differ 0·010 Å in length. The average value, 2·171 (2) Å, is 0·009 Å greater than the average P–Br bond length, 2·162 (2) Å, in $N_3P_3Br_6$. Chemically, these differences can be said to be insignificant, although they are significant on the basis of the standard deviations from the least-squares analysis.

An interesting point is the lengths of the P–N bonds in $N_3P_3Br_6$ and $N_4P_4Br_8$ in relation to the conformations of the rings and the values of the angles P–N–P. A comparison of the two molecular structures shows the following. In $N_3P_3Br_6$ the three independent P–N bond lengths are equal within experimental error with an average value of 1·576 (5) Å. The $(N\text{–}P)_3$ ring is approximately planar and the average angle P–N–P is 121·4 (4)°. In $N_4P_4Br_8$ the two independent P–N bond lengths are again equal and the average value, 1·575 (4) Å, is the same as for the trimer. However, the $(N\text{–}P)_4$ ring is considerably puckered and the angle P–N–P, 131·0 (4)°, is about 10° larger than in the trimeric molecule.

From other structural studies it is known that the length of a P–N bond in a $(N\text{–}P)_n$ ring does not depend on the molecular conformation, *i.e.* on the value of the dihedral angle of that bond. For instance, in $N_4P_4Cl_8$ the P–N bonds have the same lengths in the boat conformation of the molecule (*K* form) and in the chair conformation (*T* form), and in the medium-sized ring compounds $N_6P_6(NMe_2)_{12}$ (Wagner & Vos, 1968*b*) and $N_8P_8(OMe)_{16}$ (Paddock, Trotter & Whitlow, 1968) all P–N bonds in a ring are equally long, despite the fact that in the former molecule the dihedral angles of the ring bonds are alternately 17° and 97° (*i.e.* near to 0° and near to 90°) and in the latter molecule cover a range of values from 28 to 170°.

Thus, considering the two uniformly and similarly substituted molecules $N_3P_3Br_6$ and $N_4P_4Br_8$ we can say that the difference in ring conformation has no effect on the lengths of the P–N bonds. Since the P–N bonds in the two molecules are equal, we may say, by consequence, that in this case there is no dependence of the P–N bond length on the angle P–N–P.

This conclusion is supported by a similar result from the structures of $N_3P_3Cl_5F$ (Olthof, 1969) and $N_4P_4Cl_8$ (*K* or *T* form). [One would prefer to compare the structure of $N_3P_3Cl_6$ with that of $N_4P_4Cl_8$. However, the crystal structure of $N_3P_3Cl_6$ (Wilson & Carroll, 1960) is not known very accurately and $N_3P_3Cl_5F$ may be taken instead, because in the crystal structure of the latter compound the fluorine atom is distributed statistically over the six halogen positions and the averaged effect of the one fluorine atom on the P–N bond lengths will be small.] In this case the angle P–N–P is around 122° in the trimer and around 134° in the tetramers, whereas the P–N bond lengths are 1·563 (4) Å in $N_3P_3Cl_5F$, 1·570 (6) Å in $N_4P_4Cl_8$ (*K*), and 1·559 (6) Å in $N_4P_4Cl_8(T)$. The values show that, here again, there is no significant change in bond length in going from the trimer to the tetramers.

In contrast with the above results a few cyclophosphazene structures have been described, where a shortening of the P–N bond length is observed accompanying a widening of the angle P–N–P. The dominant case are the structures of $N_3P_3F_6$ [P–N 1·560 (6) Å, P–N–P 120·6 (5)°, Dougill, 1963] and $N_4P_4F_8$ [P–N 1·507 (8) Å, P–N–P 147(1)°, McGeachin & Tromans, 1961]. Smaller differences are involved in the structures of $N_4P_4(NMe_2)_8$ [P–N 1·578 (7) Å, P–N–P 133·0 (6)°, Bullen, 1962] and $N_6P_6(NMe_2)_{12}$ [P–N 1·563 (7) Å, P–N–P 147·5 (7)°, Wagner & Vos, 1968*b*]. Finally, there is a variation in the P–N bond lengths and in the angles P–N–P of different sections of the molecule $N_5P_5Cl_{10}$. Although not all differences are significant, the diagram given by Schlueter & Jacobson (1968) and showing a decrease in P–N bond length with increasing angle P–N–P is very suggestive.

The conclusion from the above discussion seems to be that it is not possible in general to postulate a

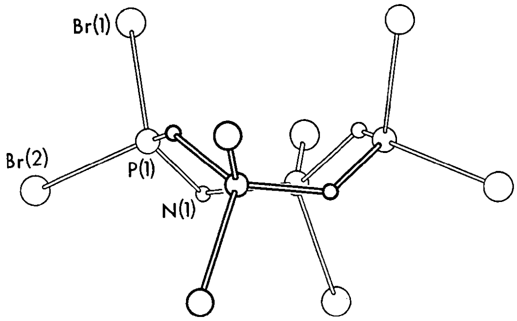

Fig. 2. Molecule $N_4P_4Br_8$ viewed along the [100] direction.

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* The dihedral angle assignable to the bond *B–C* of a cyclic compound ...*A–B–C–D*... is taken to be positive, if, when viewed in the direction $B \rightarrow C$, the bond *A–B* must be rotated clockwise over the smallest angle to bring it in the eclipsed position with the bond *C–D*.

dependence of the P–N bond length on the angle P–N–P in cyclophosphazenes. This may be a bit disappointing, because it would be possible to explain qualitatively such a relationship by considering the hybridization of the atomic orbitals at nitrogen and the π bonding capability of the s–p lone pair hybrid as a function of the size of the angle P–N–P. Apparently, such an argument would be too simple to explain adequately the relevant structural features of the cyclophosphazenes.

The authors are indebted to Professor Aafje Vos for her interest in this work.

Table 6. *Intramolecular distances and angles in the* $N_4P_4Br_8$ *molecule*

Standard deviations in parentheses

P(1)——N(1)	1·576 (6) Å	P(1)—N(1′)–P(1′)	131·0 (4)°
P(1)——N(1′)	1·574 (6)	N(1) –P(1)—N(1′)	120·1 (4)
P(1)——Br(1)	2·166 (2)	Br(1)–P(1)—Br(2)	103·9 (1)
P(1)——Br(2)	2·176 (2)	N(1) –P(1)—Br(1)	112·2 (3)
Br(1)···Br(2)	3·418 (1)	N(1) –P(1)—Br(2)	104·6 (2)
P(1) ···P(1′)	2·865 (3)	N(1′)–P(1)—Br(1)	105·8 (3)
N(1) ···N(1′)	2·729 (9)	N(1′)–P(1)—Br(2)	109·2 (2)
N(1) ···Br(1)	3·123 (6)		
N(1) ···Br(2)	2·991 (6)		
N(1′)···Br(1)	3·004 (6)		
N(1′)···Br(2)	3·075 (6)		

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The Crystal and Molecular Structure of 1-Kestose

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(*Received* 4 *March* 1971)

The crystal structure of 1-kestose, O-α-D-glucopyranosyl-(1 → 2)-O-β-D-fructofuranosyl-(1 → 2)-β-D-fructofuranoside, $C_{18}H_{32}O_{16}$, has been determined by direct methods using the tangent formula for phase determination. The space group is $P2_12_12_1$, 4 molecules in a unit cell with $a=7{\cdot}935$ (5), $b=9{\cdot}994$ (8), $c=26{\cdot}699$ (9) Å. The structure was refined to $R=0{\cdot}039$ for 2089 reflections measured with Cu $K\alpha$ radiation. The α-D-glucopyranoside unit of the molecule has the normal $C1$ chair conformation, with a primary alcohol group that is disordered over two orientations. Fructofuranoside units have puckered rings with different conformations: C′(4) is the principal out-of-plane atom in one, while C″(3) is the principal out-of-plane atom in the other. The conformation of the 1 → 2 linkage in the sucrose moiety is different from that in the trisaccharides planteose and raffinose, and is closer to that observed in sucrose. The 1 → 2 linkage of the inulobiose moiety is *anti*, with the four atoms C′(2), C′(1), O′(1) and C″(2) forming a planar chain. All hydrogen bonding is intermolecular, with the majority of the hydroxyls functioning as both donor and acceptor groups. The exception is O′(4), which is a donor only. Of the five ether oxygen atoms, only the ring oxygen atom O″(2) accepts a hydrogen bond.

Introduction

Three non-reducing trisaccharides are synthesized through the enzymatic action of invertase on sucrose by transfructosylation, *i.e.*, the transfer of a β-D-fructofuranosyl radical from one molecule of sucrose to one of the three primary alcoholic groups of another sucrose molecule (Bacon & Bell, 1953; Gross, 1962;