Crystal Structure of Compounds with (N–P)$_n$ Rings. Part X.[1] Decabromocyclopentaphosphazene, $N_5P_5Br_{10}$

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The title compound, crystallizes in space-group $P\bar{1}$ with unit-cell dimensions a = 13·760(2), b = 9·352(1), c = 10·329(1) Å, α = 93·78(1), β = 122·57(1), γ = 107·27(1)°, Z = 2. The structure was solved from diffractometer data (110 K) by the symbolic addition method and refined by block-diagonal least-squares analysis to R 0·12 for 3260 observed reflexions. The molecule has a pseudo-mirror plane passing through a PBr_2 group and the opposite nitrogen atom. The ten-membered ring is puckered with a phosphorus atom deviating 0·54 Å from the average ring plane and with one re-entrant angle at a nitrogen atom. The mean P–N and P–Br bond lengths are 1·571(17) and 2·175(6) Å. The N–P–N angles fall into two different groups [mean values 120·5(9) and 114·3(9)°] and there are three kinds of P–N–P angles [mean values 143·8(10), 136·6(11), and 131·2(11)°]. There are some short intermolecular Br · · · Br distances (3·45, 3·45, and 3·48 Å).

We now report the crystal-structure analysis of decabromocyclopentaphosphazene $N_5P_5Br_{10}$, in order to compare the molecular dimensions and the conformation of the ring with those of other medium-sized cyclophosphazenes,[2-4] in particular, the corresponding chloro-compound. The crystal and molecular structures of the lower bromocyclophosphazenes, $N_3P_3Br_6$[5] and $N_4P_4Br_8$,[1] have been described and the present work provides an extension of the structural knowledge in this series.

EXPERIMENTAL

The crystals used in the X-ray work were obtained by evaporating a solution of the compound in light petroleum (b.p. 60—80 °C). Only few crystals were obtained, of varying shape and usually exposing a great many crystal planes.

Crystal Data.—$N_5P_5Br_{10}$, M = 1024·2, Triclinic, a = 13·760(2), b = 9·352(1), c = 10·329(1) Å, α = 93·78(1), β = 122·57(1), γ = 107·27(1)°. U = 1027 Å^3, D_m = 3·06 (from ref. 6), Z = 2, D_c = 3·31 g. cm^{-3}, $F(000)$ = 920. Space-group $P\bar{1}$. λ(Mo-K_α) = 0·7107 Å, μ(Mo-K_α) = 210·8 cm^{-1}.

Measurements.—The unit-cell constants were determined from zero-level Weissenberg photographs around the a, b, and c axes, taken with Cu-K_α radiation at 110 K. The unit-cell constants were calculated by a least-squares procedure and are approximately the same as those given in ref. 6. D_m was not measured, but D_c for Z = 2 agrees approximately with D_m from ref. 6. No systematically absent reflexions were observed; on the basis of the distribution of the normalized structure-factors (see later) the space-group was taken to be $P\bar{1}$, rather than $P1$.

The intensities were measured on a Nonius automatic three-circle single-crystal diffractometer with zirconium filtered molybdenum radiation at 110 K. The crystal with dimensions *ca.* 0·20 × 0·17 × 0·12 mm was mounted with c^* parallel to the ϕ-axis of the goniometer. The θ—2θ scanning method was used, with a scanning angle varying from 1·7—2·3° in 2θ, a constant scanning speed of 2·4° min^{-1} in 2θ, and stationary background measurements before and after the scan. 6077 independent reflexions in the range $0 < (\sin\theta)/\lambda < 0{\cdot}70$ Å^{-1} were measured. One of three standard reflexions was monitored every 50 reflexions. The net intensities were calculated from the measured peak and background counts and scaled to the same relative scale by means of the standard reflexions. Reflexions for which the net intensity was negative, or for which it was $<30\%$ of the difference in background counts, were considered unobserved. For the remaining 3335 reflexions, the Lorentz and polarization factors were applied and the weights based on the counting-rate uncertainties were calculated. A correction for absorption was computed.[7] For this correction the crystal boundaries were described by 13 planes.

Structure Determination.—The structure was solved by the symbolic addition method.[8] An average isotropic temperature factor was calculated by the method of Wilson[9] and used in the calculation of the normalized structure-factors $|E|$. Quantities characterizing the distribution of the $|E|$ values are given in Table 1. Comparison with the theoretical values of these quantities shows $P\bar{1}$ to be the more probable space-group.

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[1] Part IX, H. Zoer and A. J. Wagner, *Acta Cryst.*, 1972, **B28**, 252.

[2] A. J. Wagner and A. Vos, *Acta Cryst.*, 1968, **B24**, 1423.

[3] N. L. Paddock, J. Trotter, and S. H. Whitlow, *J. Chem. Soc.* (*A*), 1968, 2227.

[4] A. W. Schlueter and R. A. Jacobson, *J. Chem. Soc.* (*A*), 1968, 2317.

[5] H. Zoer and A. J. Wagner, *Acta Cryst.*, 1970, **B26**, 1812.

[6] G. E. Coxon, D. B. Sowerby, and G. C. Tranter, *J. Chem. Soc.*, 1965, 5697.

[7] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[8] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[9] A. J. C. Wilson, *Nature*, 1942, **150**, 151.

For the 249 reflexions having $|E| > 2$, all triplets of reflexions to be used in the Σ_2 relation, $s(E_{\mathrm{H+H'}}) \simeq s(E_{\mathrm{H}}) \cdot s(E_{\mathrm{H'}})$, were sought and their triple products calculated. Table 2 lists the reflexions which were chosen to determine the origin, together with the reflexions to which a symbolic sign was given. Starting with this set, it was possible to give a real or symbolic sign to all 249 reflexions, under the condition that a sign was accepted only, when the probability of the corresponding relation was at least 98%. Using the sign indications for *a*, *b*, *c*, and *d* having the highest probability ($b = +$, $d = +$, $a = c$) an *E* map was calculated on the assumption $b = d = +$, $a = c = -$. This map proved to be correct and revealed the position of the bromine and the phosphorus atoms. After a structure-factor calculation based on the positions of the heavy atoms, the positions of the nitrogen atoms were found from an observed Fourier synthesis.

TABLE 1

Distribution of the normalized structure-factors

	Observed	Calculated	
		Centrosymm.	Non-centrosymm.
$\langle\|E\|^2\rangle$	0·994	1·000	1·000
$\langle\|E\|^2 - 1\rangle$	0·940	0·968	0·736
$\langle\|E\|\rangle$	0·806	0·798	0·886
$\|E\| > 1$ (%)	32·8	32·0	36·8
$\|E\| > 2$ (%)	4·2	5·0	1·8
$\|E\| > 3$ (%)	0·2	0·3	0·01

TABLE 2

Starting set for phase determination

Reflexion	$\|E\|$	Sign
$\bar{8}, \bar{1}, 11$	3·915	+
$\bar{4}, \bar{2}, 5$	3·828	+
$\bar{7}, \bar{4}, 3$	3·676	+
$\overline{14}, 4, 6$	3·335	a
$\bar{1}, 9, 6$	3·307	b
$5, \bar{1}, 9$	3·194	c
$6, \bar{9}, 1$	2·823	d

Refinement.—The crystal structure was refined by block-diagonal least-squares analysis,[10] in which the function $\Sigma w[|F_o| - k|F_c|]^2$, summed over 3335 independent reflexions, was minimized. Besides refinement of the positions of the atoms, the thermal motions were refined anisotropically for the bromine and phosphorus atoms, and isotropically for the nitrogen atoms.

After the first stages of the refinement *R* was 0·17 and the weighted factor, *R'*, was 0·09 $[R' = \{\Sigma w|\Delta F|^2/\Sigma w|F_o|^2\}^{\frac{1}{2}}]$. At this point, 75 reflexions having $|F_c|$ values <5 and $|F_o|$ values of *ca.* 35 were removed from the refinement, because of apparent inaccuracies in the measured structure-factors. The refinement was continued with 3260 reflexions and the final values of *R* and *R'* were 0·12 and 0·08. In the last cycle the changes in the positional and thermal parameters were $<0{\cdot}1\sigma$. The atomic scattering factors were taken from ref. 11. 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; $p = 0{\cdot}0005$ in order to make $\langle w|\Delta F|^2\rangle$, averaged over groups of reflexions, approximately independent of $|F|$.

The final atomic co-ordinates with the standard deviations as determined from the least-squares residuals are given in Table 3. Parameters of the anisotropic and isotropic temperature factors are given in Tables 4 and 5, respectively. Observed and calculated structure-factors are listed in Supplementary Publication No SUP 20339 (18 pages, 1 microfiche).*

TABLE 3

Fractional atomic co-ordinates with standard deviations in parentheses

Atom	*x*	*y*	*z*
P(1)	0·4053(5)	0·7912(6)	0·0911(6)
P(2)	0·3387(5)	0·6459(6)	0·2966(6)
P(3)	0·1425(5)	0·3368(6)	0·1352(6)
P(4)	0·1682(5)	0·3355(6)	−0·1263(6)
P(5)	0·2476(5)	0·5980(6)	−0·2318(6)
N(1)	0·3382(14)	0·6732(16)	0·1485(17)
N(2)	0·2669(17)	0·4666(20)	0·2764(21)
N(3)	0·1021(16)	0·3191(18)	−0·0399(19)
N(4)	0·1574(15)	0·4655(17)	−0·2156(18)
N(5)	0·3739(15)	0·7202(18)	−0·0776(19)
Br(1)	0·6079(2)	0·8849(3)	0·2563(3)
Br(2)	0·3617(3)	0·9958(3)	0·0882(3)
Br(3)	0·5247(2)	0·7210(3)	0·5154(3)
Br(4)	0·2566(3)	0·7898(3)	0·3456(3)
Br(5)	−0·0129(2)	0·3499(3)	0·1313(3)
Br(6)	0·1542(2)	0·1218(2)	0·2014(3)
Br(7)	0·0768(2)	0·1119(2)	−0·3053(3)
Br(8)	0·3627(2)	0·3544(2)	0·0276(3)
Br(9)	0·1327(2)	0·7120(2)	−0·3877(3)
Br(10)	0·3016(2)	0·5005(2)	−0·3678(3)

TABLE 4

Parameters (Å^2 $\times 10^{-4}$) of the anisotropic temperature factors $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$ with standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
P(1)	177(28)	59(22)	183(26)	85(41)	110(39)	298(48)
P(2)	191(28)	90(23)	128(25)	87(42)	85(39)	218(46)
P(3)	132(26)	77(22)	135(25)	74(41)	124(38)	156(44)
P(4)	181(28)	77(23)	136(25)	91(42)	39(38)	200(46)
P(5)	162(27)	83(23)	87(23)	81(41)	44(36)	146(43)
Br(1)	193(12)	305(12)	175(11)	−34(19)	−42(18)	227(19)
Br(2)	584(18)	184(11)	478(15)	500(23)	393(21)	877(29)
Br(3)	239(12)	211(11)	173(10)	29(18)	142(17)	163(19)
Br(4)	550(17)	233(11)	372(13)	519(23)	332(20)	762(27)
Br(5)	229(12)	435(14)	283(12)	331(22)	300(21)	393(22)
Br(6)	250(12)	124(9)	238(11)	97(18)	211(17)	187(20)
Br(7)	340(14)	112(10)	221(11)	43(18)	−30(16)	341(21)
Br(8)	190(11)	132(9)	262(11)	190(17)	178(16)	314(19)
Br(9)	214(11)	175(10)	227(10)	178(17)	257(16)	288(19)
Br(10)	282(12)	225(10)	212(11)	225(19)	122(17)	379(20)

TABLE 5

Parameters (Å^2) of the isotropic temperature factors $\exp[-B(\sin^2\theta)/\lambda^2]$ with standard deviations in parentheses

Atom	*B*	Atom	*B*
N(1)	0·4 (0·2)	N(4)	0·8 (0·3)
N(2)	1·7 (0·3)	N(5)	1·0 (0·3)
N(3)	1·2 (0·3)		

A comparison of the estimated standard deviations of the structural parameters with those obtained in the structure analysis of $N_4P_4Br_8$ [1] indicates that the errors are higher in the case of $N_5P_5Br_{10}$ by a factor 2 or 3. Although the number of reflexions measured in proportion to the number of parameters adjusted (47 : 1 for $N_4P_4Br_8$, 21 : 1 for $N_5P_5Br_{10}$) is much larger for $N_4P_4Br_8$, the ratio for $N_5P_5Br_{10}$

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[10] D. W. J. Cruickshank, 'Computing Methods and the Phase Problem in *X*-ray Crystal Analysis,' Pergamon Press, Oxford, 1961.

[11] P. A. Doyle and P. S. Turner, *Acta Cryst.*, 1968, **A24**, 390.

is still a reasonable number. We think, therefore, that the main origin of the relatively low accuracy of the present structure is the occurrence of many weak reflexions and the difficulties experienced in obtaining accurate values for their intensities. Also, the complex shape of the crystal presented difficulties in connection with the absorption correction.

DESCRIPTION AND DISCUSSION

In the crystal structure two molecules occupy a general position in the triclinic unit-cell of space-group $P\bar{1}$. A view of one molecule is shown in Figure 1.

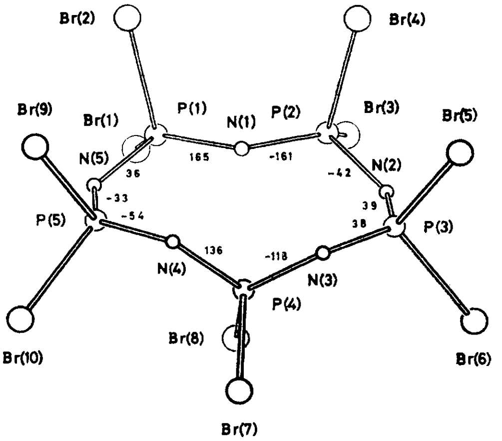

FIGURE 1 View of a molecule projected along a line having direction cosines $-0{\cdot}96593$, 0, and $-0{\cdot}25882$ with respect to the orthogonal axes $\vec{a}^{*}$, $\vec{c} \times \vec{a}^{*}$, and $\vec{c}$

The central part of the molecule is formed by a puckered ten-membered ring of alternately phosphorus and nitrogen atoms. Data on least-squares planes through various sets of ring atoms are given in Table 6. The most interesting point is the position of the atom P(4), which deviates 0·54 Å from the best plane through all ring atoms, or 0·75 Å from the best plane through the remaining nine atoms. As a consequence of the location of P(4), the bromine atom Br(8) has short non-bonded distances to three of the ring atoms, *viz.* 3·33, 3·64, and 3·71 Å to the atoms N(1), P(5), and P(3). These contacts are shorter than the usually accepted van der Waals distances[12] (3·45 Å Br · · · N, 3·85 Å Br · · · P). The special location of P(4) is also reflected in the dihedral angles * which can be assigned to the ring bonds and which are included in Figure 1. These angles further indicate that the $(N{-}P)_5$ ring has a re-entrant angle at the atom N(1).

The bond lengths and valence angles with their standard deviations are given in Figure 2. The ten independent P–Br bonds vary from 2·156 to 2·195 Å, and, on the basis of the least-squares standard deviations (0·006 Å) do not all have the same length. The variation of the P–Br bond lengths around the molecule is rather irregular. No correlation has been found with the positions and orientations of particular atoms or groups of atoms of surrounding molecules, *i.e.* the longer P–Br bonds cannot be explained by intermolecular bonding interactions, as has been possible for the crystal structure of $N_3P_3Br_6$.[5]

The P–N bond lengths vary from 1·541—1·606 Å, mean 1·571(17) Å. The largest deviations from the mean are shown by the P–N bonds at either side of the atom N(2), but the mean length of the bonds P(2)–N(2) and P(3)–N(2) (1·574 Å) is the same as the mean length (1·570 Å) of the eight remaining bonds. N(2) has a relatively large temperature factor (Table 5) and, apparently, its position could not be determined very accurately. We believe, therefore, that all P–N bonds may be considered as being equal.

The valence angles (Figure 2) inside the ring have a very regular pattern. There are two different groups of N–P–N angles [means 114·3 (9) and 120·5(9)°] and three groups of P–N–P angles [means 131·2(11), 136·6(11), and 143·8(10)°]. It follows from the equivalence of all P–N bond lengths that there is no dependence of the length of a P–N bond on the value of the P–N–P angle adjacent to it. Such a correlation has been described by Schlueter and Jacobson[4] for the structure of the related compound $N_5P_5Cl_{10}$. They found a decrease in the P–N bond length accompanying an increase in the angle P–N–P. However, it was shown by Zoer and Wagner[1] that a relationship between angle P–N–P and P–N bond length in cyclophosphazenes cannot be postulated in general. The bond lengths and valence angles in the $N_5P_5Br_{10}$ molecule further support this latter point of view.

TABLE 6

Equations of least-squares planes through various sets of ring atoms and distances (Å) from these planes

Equations of planes:*

(I) All ring atoms included in the calculation:
$$-0{\cdot}6804X + 0{\cdot}7212Y + 0{\cdot}1306Z = 0{\cdot}6661$$

(II) All ring atoms, except P(4):
$$-0{\cdot}6297X + 0{\cdot}7602Y + 0{\cdot}1599Z = 0{\cdot}9704$$

(III) Phosphorus atoms only:
$$-0{\cdot}7464X + 0{\cdot}6598Y + 0{\cdot}0870Z = 0{\cdot}3082$$

(IV) Nitrogen atoms only:
$$-0{\cdot}5777X + 0{\cdot}7936Y + 0{\cdot}1910Z = 1{\cdot}1151$$

Distances from planes

	(I)	(II)	(III)	(IV)
P(1)	0·048	0·104	−0·107	0·289
P(2)	0·127	0·185	−0·034	0·382
P(3)	0·114	−0·013	0·213	0·009
P(4)	−0·544	−0·746	−0·329	−0·805
P(5)	0·145	0·014	0·257	0·011
N(1)	0·115	0·137	0·005	0·295
N(2)	−0·266	−0·286	−0·313	−0·160
N(3)	0·225	0·034	0·417	−0·013
N(4)	0·324	0·139	0·510	0·088
N(5)	−0·289	−0·314	−0·326	−0·209

* The equations are referred to the orthogonal axes $\vec{a}^{*}$, $\vec{c} \times \vec{a}^{*}$, and $\vec{c}$; X, Y, Z are expressed in Å.

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* For sign convention, see Ref. 1.

[12] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960.

Mean values of bond lengths and valence angles in three bromocyclophosphazene molecules are compared in Table 7. There is a good agreement between the P–N bond lengths, the P–Br bond lengths, and the angles Br–P–Br, but, as expected, there are some variations among the angles N–P–N or P–N–P.

TABLE 7

Mean values (and individual standard deviations) of bond lengths (Å) and valence angles (°) in bromocyclophosphazenes

	P–N	P–Br	Br–P–Br	N–P–N	P–N–P
$N_3P_3Br_6$ *	1·576 (8)	2·162 (4)	102·1 (1)	118·5 (5)	121·4 (5)
$N_4P_4Br_8$ †	1·575 (6)	2·171 (2)	103·9 (1)	120·1 (4)	131·0 (4)
$N_5P_5Br_{10}$	1·571 (17)	2·175 (6)	103·3 (2)	116·8 (9)	135·9 (11)

* Ref. 5. † Ref. 1.

It is clear from the data presented in Figures 1 and 2 that the molecule $N_5P_5Br_{10}$ has a pseudo-mirror plane, passing through the atoms N(1) and P(4) and orientated perpendicular to the ring. The corresponding chlorophosphazene $N_5P_5Cl_{10}$ [4] also has a pseudo-mirror plane normal to the $(N–P)_5$ ring, but, apart from this, the two molecular conformations are entirely different. The ring in $N_5P_5Cl_{10}$ is nearly planar and is characterized by two re-entrant P–N–P angles, situated at either side of the pseudo-mirror plane.

The bonding in cyclophosphazenes has been discussed by Craig and Paddock [13,14] and by Cruickshank.[15] The model of a double system of d_π–p_π bonds, extending throughout the cyclophosphazene ring and constructed from mutually perpendicular and equally strong components in each particular P–N bond, is generally accepted now. Owing to the double π bonding system the total π overlap in a P–N bond will be highly independent of the dihedral angle of that bond, and energy differences between different conformations of a cyclophosphazene ring may be assumed to be small. As a consequence, the molecular conformation of a cyclophosphazene compound, as realized in its crystal structure, will be the result of very subtle intra- and inter-molecular energy effects (neglecting entropy effects).

The foregoing argument gives, in a qualitative sense, the reason why two such closely related compounds as $N_5P_5Br_{10}$ and $N_5P_5Cl_{10}$ have so different crystal and molecular structures. In this case, it would be difficult to determine precisely what energy effects are responsible for the different structures. It can be shown, however, that these effects are not of a simple intramolecular steric nature. The $N_5P_5Br_{10}$ ring conformation can be combined with chlorine atoms as substituents (P–Cl 1·98 Å, in the direction of the P–Br bonds) without obtaining too close Cl · · · Cl contacts. Conversely, the $N_5P_5Cl_{10}$ conformation with bromine atoms as substituents (P–Br 2·17 Å) also leads to a sterically acceptable structure.

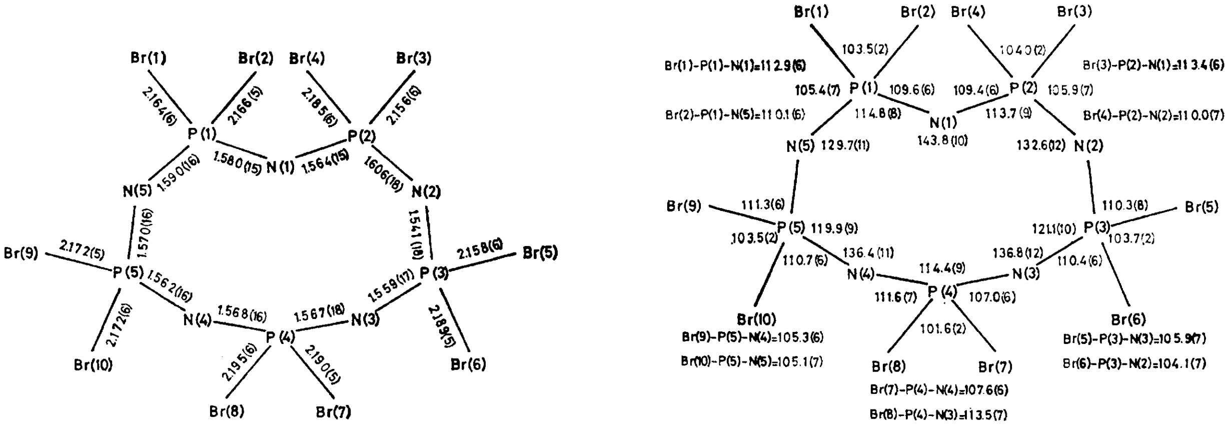

FIGURE 2 Bond lengths (Å) and valence angles (°) with standard deviations are given in parentheses

Some short intermolecular Br · · · N and Br · · · Br distances are tabulated in Table 8. The three shortest Br · · · Br distances (3·45, 3·45, 3·48 Å) suggest a van der Waals radius for bromine of *ca.* 1·73 Å, *i.e.* 0·2 Å smaller than that radius given by Pauling.[12] It may be noted that the intramolecular non-bonded contacts

TABLE 8

Short intermolecular distances (Å) between bromine atoms of the standard molecule and nitrogen or bromine atoms of surrounding molecules (Br · · · N < 3·70 Å, Br · · · Br < 3·90 Å)

Br(3) · · · $N(2^{I})$	3·57	Br(3) · · · $Br(6^{I})$	3·45
Br(5) · · · $N(4^{II})$	3·38	Br(4) · · · $Br(6^{VII})$	3·85
Br(9) · · · $N(4^{III})$	3·61	Br(5) · · · $Br(9^{II})$	3·80
Br(10) · · · $N(2^{IV})$	3·42	Br(6) · · · $Br(6^{VIII})$	3·81
Br(1) · · · $Br(8^{V})$	3·84	Br(7) · · · $Br(7^{IX})$	3·48
Br(1) · · · $Br(9^{VI})$	3·86	Br(7) · · · $Br(9^{III})$	3·84
Br(2) · · · $Br(8^{VII})$	3·45	Br(8) · · · $Br(10^{V})$	3·70

Roman numerals as superiors refer to the following equivalent positions, relative to the reference molecule at x, y, z:

I $-x + 1, -y + 1, -z + 1$
II $-x, -y + 1, -z$
III $-x, -y + 1, -z - 1$
IV $x, y, z - 1$
V $-x + 1, -y + 1, -z$
VI $-x + 1, -y + 2, -z$
VII $x, y + 1, z$
VIII $-x, -y, -z$
IX $-x, -y, -z - 1$

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[13] D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 1962, 4118.
[14] N. L. Paddock, *Quart. Rev.*, 1964, **18**, 168.
[15] D. W. J. Cruickshank, *J. Chem. Soc.*, 1961, 5486.

in $N_5P_5Br_{10}$, as well as the intermolecular Br · · · Br distances in the crystal structure of $N_4P_4Br_8$,[1] are consistent with the small value of 1·73 Å.

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