Crystal Structure of Compounds with (N–P)$_n$ Rings. Part 12.[1] Decafluorocyclopentaphosphazene

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Three monoclinic crystal modifications of the title compound (m.p. −50 °C) have been obtained by low-temperature crystallization. The crystallographic data are: (1), space group $P2_1/c$, a = 11.098(19), b = 14.459(6), c = 11.784(19) Å, β = 142.4(5)°; (2), space group $P2_1/a$, a = 15.785(12), b = 15.237(10), c = 4.919(6) Å, β = 97.4(2)°; and (3), space group $P2_1/n$, a = 14.02, b = 16.02, c = 5.24 Å, β = 99.5°. The crystal structures of modifications (1) and (2) have been determined from low-temperature diffractometer data by the symbolic addition method and refined by block-diagonal least-squares analysis [(1), 1 598 reflections, R 0.59; (2), 1 919 reflections, R 0.74]. The unit cell in both structures contains four molecules in a general position. In (1) the (N–P)$_5$ ring of the molecule is somewhat boat-shaped and the molecule has a pseudo-two-fold rotation axis passing through an N and a P atom. In (2) the molecule has a rather irregular shape, which resembles to some extent the structure of $N_5P_5Br_{10}$. Mean P–N bond lengths are 1.549(5) in (1) and 1.546(5) Å in (2). The mean P–F bond length is the same in (1) and (2) [1.528(4) Å]. The P–N–P angles range from 132.7 to 151.6° [means 137.4(3) for (1) and 140.6(4)° for (2)]. The N–P–N angles range from 119.1 to 123.9° [means 121.4(2) in (1) and 120.9(3)° in (2)]. The mean value of the F–P–F angles in (1) and (2) is 99.4(2)°.

CRYSTAL structures of several homogeneously substituted halogenocyclophosphazenes have previously been described. These include the chlorides [2-4] $N_nP_nCl_{2n}$ and bromides [5-7] $N_nP_nBr_{2n}$ with n = 3—5, and the fluorides [8,9] $N_nP_nF_{2n}$ with n = 3 or 4. The crystal structure of the pentameric fluoride $N_5P_5F_{10}$ has not been reported, perhaps because of the fact that this compound is a liquid at room temperature.

A crystal-structure determination of $N_5P_5F_{10}$, however, seemed of interest to us for two reasons. First, among all the cyclophosphazenes with $n > 3$ the tetrameric fluoride is rather unique in that the molecule $N_4P_4F_8$ has a planar ring structure in the crystalline state; it would be of interest, therefore, to know the ring structure of the next higher member of the fluoride series, the pentamer $N_5P_5F_{10}$. Secondly, cyclophosphazenes with medium-sized rings are known to show various conformations in the solid state; [4,7,10-13] it seemed worthwhile to determine the crystal structure of $N_5P_5F_{10}$ in order to enlarge the experimental data on the structures and ring conformations of this group of compounds.

In this paper the results of the X-ray diffraction study of $N_5P_5F_{10}$ are reported. Three different crystalline modifications have been observed and the crystal structures of two of them have been determined.

EXPERIMENTAL

The preparation and characterization of decafluorocyclopentaphosphazene $N_5P_5F_{10}$ has been described previously.[14] The compound has a melting point of −50 °C. Crystals of

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[1] Part 11, M. B. Peterson and A. J. Wagner, *J.C.S. Dalton*, 1973, 106.

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

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

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[12] M. W. Dougill and N. L. Paddock, *J.C.S. Dalton*, 1974, 1022.

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

[14] A. C. Chapman, N. L. Paddock, D. H. Paine, H. T. Searle, and D. R. Smith, *J. Chem. Soc.*, 1960, 3608.

$N_5P_5F_{10}$ were grown at low temperature (*ca.* −80 °C) by moving a sealed glass gube containing liquid $N_5P_5F_{10}$ slowly into a stream of cold nitrogen gas. The cold gas stream was enveloped by a warm stream of dry nitrogen gas in order to avoid deposition of moisture and ice on the glass tube.[15] The crystallization process was observed through a polarizing microscope. Single crystals were obtained by first solidifying the whole contents of the glass tube, then melting the crystal mass except for a tiny crystal at the end of the glass tube, and finally recrystallizing the liquid into one single crystal using the tiny crystal as a nucleus. The crystals obtained were cylindrical with a diameter of 0.3 mm and a length of *ca.* 0.3 mm. The crystals were characterized by low-temperature Weissenberg photographs and diffractometer measurements. Three different modifications have been observed, the crystallographic data of which are as follows.

Crystal Data.—$N_5P_5F_{10}$, $M = 415.0$, Monoclinic, $Z = 4$, $F(000) = 800$, $\lambda(\text{Mo-}K_\alpha) = 0.710\ 7$ Å. (1), $a = 11.098(19)$, $b = 14.459(6)$, $c = 11.784(19)$ Å, $\beta = 142.4(5)°$, $U = 1\ 154$ Å^3, $D_c = 2.40$ g cm^{-3}, space group $P2_1/c$, $\mu(\text{Mo-}K_\alpha) = 9.4$ cm^{-1}. (2), $a = 15.785(12)$, $b = 15.237(10)$, $c = 4.919(6)$ Å, $\beta = 97.4(2)°$, $U = 1\ 173.2$ Å^3 ,$D_c = 2.35$ g cm^{-3}, space group $P2_1/a$, $\mu(\text{Mo-}K_\alpha) = 9.3$ cm^{-1}. (3), $a = 14.02$, $b = 16.02$, $c = 5.24$ Å, $\beta = 99.5°$, $U = 1\ 162$ Å^3, $D_c = 2.38$ g cm^{-3}, space group $P2_1/n$, $\mu(\text{Mo-}K_\alpha) = 9.3$ cm^{-1}.

Measurements.—The unit-cell dimensions of modifications (1) and (2) were obtained by a least-squares procedure from the $\sin^2\theta$ values of 15 reflections measured on a computer-operated four-circle single-crystal diffractometer (Enraf–Nonius CAD-4) at 110 K. The unit-cell dimensions of modification (3) were derived from Weissenberg photographs. The experimental density of $N_5P_5F_{10}$ in the solid state is not known, but the calculated densities, computed on the assumption of four molecules of $N_5P_5F_{10}$ per unit cell, compare well with the density observed[14] at room temperature for $N_3P_3F_6$ and $N_4P_4F_8$ (2.24 g cm^{-3}).

Only once was a crystal of modification (3) obtained suitable for intensity measurements. However, this crystal melted prematurely due to a failure of the cooling equipment. Insufficient intensity data had been collected at the time of melting and, unfortunately, no structure determination of (3) could be undertaken.

The intensities of the reflections of modifications (1) and (2) were measured on the Enraf–Nonius CAD-4 diffractometer at 110 K using zirconium-filtered molybdenum radiation. The mosaic spread of the crystals was estimated to be *ca.* 1.4° and the ω-scanning method was used with a scanning angle of 1.7—2.0°. The intensity of one of a few standard reflections was measured every 20 min, and decreased slowly during the data collection. The intensities of the reflections were corrected for this effect. For modification (1), 3 642 independent reflections were measured in the range θ 0—30°. Of these, 2 231 had a non-zero net intensity. For (2), 3 504 independent reflections were measured in the same θ range, 1 925 of which had non-zero net intensity. The intensities were corrected for Lorentz and polarization effects, but no correction for absorption was applied.

Structure Analysis.—The crystal structures were solved by direct methods. A scale factor and an average isotropic temperature factor were determined by Wilson's statistical method[16] and used in the calculation of $|E|$ values from observed $|F|$ values. Some quantities characterizing the distribution of the $|E|$ values are collected in a Table which has been included in Supplementary Publication No. SUP 22297 (23 pp.).* On the basis of these data a centrosymmetric crystal structure was suggested for both modifications. Signs of the $|E|$ values were determined by the symbolic addition method,[17] first by hand and in later stages with the aid of a program. 190 Reflections having a minimum $|E|$ value of 1.7 were used in the case of (1); for (2) the corresponding numbers are 202 and 1.8. Relevant information about the starting set used in the sign-determining process and the sign indications derived is given in the SUP 22297. An E map was calculated using the sign indications having the highest probability and, for both crystal structures (1) and (2), the positions of all the independent atoms could be found in this map.

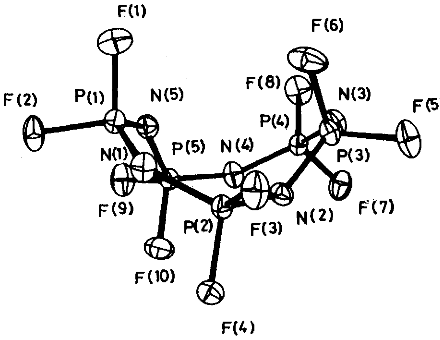

FIGURE 1 View of molecule (1)

Structure Refinement.—The crystal structures were refined by a block-diagonal least-squares procedure,[18] in which the function $\Sigma w(|F_o| - k|F_c|)^2$ was minimized. The positional co-ordinates and the anisotropic thermal parameters of all the atoms were refined. For (1) only the reflections in the range θ 0—25°, 1 598 in number, were used in the later stages of the refinement, those in the higher range θ 25—30° being considered less accurate. For (2) six reflections suspected of extinction were omitted and the remaining 1 919 were used in the refinement. The scattering factors used were taken from Doyle and Turner.[19] The weightings w were calculated from the relation $w = (w_c^{-1} + p|F_o|^2)^{-1}$ in which w_c is the weighting from counting statistics and p is a factor chosen to make $\langle w|\Delta F|^2\rangle$, averaged over groups of reflections of nearly the same $|F_o|$, approximately independent of $|F_o|$. The value 0.000 5 was given to p for (1) and 0.000 4 for (2). Refinement was terminated when the changes in the atomic co-ordinates were $<0.1\sigma$. Final values of the factors $R = (\Sigma|\Delta F|^2/\Sigma|F_o|^2)^{\frac{1}{2}}$ and $R' = (\Sigma w|\Delta F|^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$ were 0.59 and 0.65 for (1) and 0.74 and 0.86 for (2). The final atomic co-ordinates with standard deviations as determined from the least-squares residuals are given in Table 1. Anisotropic temperature factors and observed and calculated structure factors are listed in SUP 22297.

Description of the Structures.—Both modifications (1) and (2) have a monoclinic unit cell containing four molecules of

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[15] F. van Bolhuis, *J. Appl. Cryst.*, 1971, **4**, 263.

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

$N_5P_5F_{10}$, one of which is independent. In Figures 1 and 2 a molecule of each modification is shown, and in 3 and 4 stereoviews of the unit cells are given. The molecular conformations will be discussed later, but the difference in ring conformation of the molecules and the difference in crystal environment of the two modifications is already apparent from the Figures.

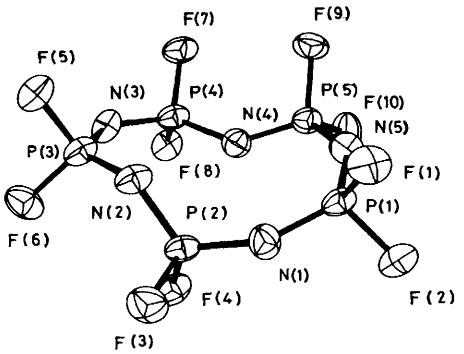

FIGURE 2 View of molecule (2)

TABLE 1

Fractional atomic co-ordinates of (1) with standard deviations in parentheses. The values for (2) follow those for (1)

Atom	*x*	*y*	*z*
P(1)	0.007 4(2)	0.235 4(1)	0.180 3(2)
	−0.029 6(1)	0.151 3(1)	0.002 9(3)
P(2)	0.238 1(2)	0.343 2(1)	0.200 1(2)
	−0.009 6(1)	0.337 4(1)	0.184 8(3)
P(3)	0.542 7(2)	0.361 1(1)	0.596 7(2)
	0.158 9(1)	0.411 2(1)	0.305 2(3)
P(4)	0.404 8(2)	0.439 7(1)	0.704 5(2)
	0.222 9(1)	0.257 2(1)	0.595 2(3)
P(5)	0.007 9(2)	0.393 2(1)	0.332 3(2)
	0.130 1(1)	0.107 2(1)	0.333 7(3)
N(1)	0.079 4(7)	0.270 5(3)	0.117 4(6)
	−0.042 9(3)	0.248 7(4)	0.070 9(12)
N(2)	0.370 8(6)	0.390 6(3)	0.389 3(6)
	0.079 9(3)	0.370 1(4)	0.133 1(11)
N(3)	0.549 2(6)	0.395 7(3)	0.724 5(6)
	0.219 4(3)	0.355 6(4)	0.514 0(11)
N(4)	0.178 0(7)	0.444 4(3)	0.519 1(6)
	0.147 4(3)	0.194 9(4)	0.487 6(11)
N(5)	0.035 7(7)	0.292 7(3)	0.311 5(6)
	0.048 8(3)	0.097 9(4)	0.124 2(11)
F(1)	0.096 9(5)	0.140 5(2)	0.269 8(5)
	−0.038 4(3)	0.141 4(3)	−0.310 7(8)
F(2)	−0.208 5(5)	0.206 9(2)	0.004 9(4)
	−0.109 3(2)	0.101 7(3)	0.056 7(8)
F(3)	0.363 9(5)	0.299 8(2)	0.199 8(4)
	−0.075 5(2)	0.406 1(3)	0.072 8(8)
F(4)	0.137 7(5)	0.420 0(2)	0.058 8(4)
	−0.018 3(2)	0.343 8(3)	0.492 5(7)
F(5)	0.739 9(5)	0.387 3(3)	0.688 6(5)
	0.211 9(2)	0.453 2(3)	0.103 3(8)
F(6)	0.562 9(5)	0.255 7(2)	0.612 0(5)
	0.136 1(3)	0.492 9(3)	0.459 3(8)
F(7)	0.474 7(5)	0.537 5(2)	0.781 9(5)
	0.308 2(2)	0.218 7(3)	0.537 3(8)
F(8)	0.450 6(5)	0.395 0(3)	0.853 2(5)
	0.236 6(2)	0.253 1(3)	0.909 9(7)
F(9)	−0.168 6(5)	0.397 0(2)	0.280 6(5)
	0.207 1(2)	0.079 9(3)	0.195 3(8)
F(10)	−0.070 3(5)	0.454 3(2)	0.177 6(5)
	0.131 1(3)	0.033 1(2)	0.541 2(8)

The bond lengths and valence angles of the molecules (1) and (2) are given in Table 2. The mean value of the P–N bond lengths is 1.549(5) Å in (1) and 1.546(5) Å in (2). In no case is there a significant deviation of an individual P–N bond length from the mean. Also the P–F bond lengths are equal within experimental error [mean 1.528(4) Å in both (1) and (2)]. As usual in cyclophosphazene structures, the P–N–P angles show a range of values [132.7—151.6°; means 137.4(3) for (1) and 140.6(4)° for (2)]. Also as usual, the range of N–P–N angles is much smaller [119.1—123.9°; means 121.4(2) in (1) and 120.9(3)° in (2)]. All the F–P–F angles are approximately equal [overall mean 99.4(2)°].

TABLE 2

Bond lengths (Å) and valence angles (°) with standard deviations in parentheses

(*a*) Bond lengths

	Molecule (1)	Molecule (2)
P(1)–N(1)	1.546(4)	1.541(6)
P(1)–N(5)	1.551(5)	1.537(5)
P(1)–F(1)	1.528(3)	1.538(4)
P(1)–F(2)	1.529(3)	1.520(4)
P(2)–N(1)	1.561(4)	1.530(5)
P(2)–N(2)	1.552(4)	1.549(5)
P(2)–F(3)	1.533(3)	1.528(4)
P(2)–F(4)	1.519(3)	1.540(4)
P(3)–N(2)	1.552(4)	1.546(5)
P(3)–N(3)	1.534(5)	1.560(6)
P(3)–F(5)	1.534(4)	1.520(4)
P(3)–F(6)	1.530(3)	1.524(4)
P(4)–N(3)	1.559(5)	1.551(6)
P(4)–N(4)	1.550(5)	1.561(5)
P(4)–F(7)	1.521(3)	1.529(4)
P(4)–F(8)	1.529(3)	1.536(4)
P(5)–N(4)	1.542(5)	1.543(5)
P(5)–N(5)	1.544(5)	1.546(5)
P(5)–F(9)	1.524(3)	1.525(4)
P(5)–F(10)	1.533(3)	1.521(4)

(*b*) Bond angles

P(1)–N(1)–P(2)	132.7(3)	151.6(4)
P(1)–N(5)–P(5)	138.8(3)	140.2(4)
P(2)–N(2)–P(3)	136.5(3)	136.7(4)
P(3)–N(3)–P(4)	137.9(3)	133.9(4)
P(4)–N(4)–P(5)	141.0(3)	140.5(4)
N(1)–P(1)–N(5)	122.0(2)	123.5(3)
N(1)–P(2)–N(2)	120.8(2)	120.2(3)
N(2)–P(3)–N(3)	119.9(2)	121.5(3)
N(3)–P(4)–N(4)	123.9(2)	120.0(3)
N(4)–P(5)–N(5)	120.4(3)	119.1(3)
F(1)–P(1)–N(1)	109.0(2)	108.4(3)
F(1)–P(1)–N(5)	106.6(2)	107.5(3)
F(2)–P(1)–N(1)	107.0(2)	107.6(3)
F(2)–P(1)–N(5)	110.8(2)	108.2(3)
F(3)–P(2)–N(1)	107.6(2)	106.7(3)
F(3)–P(2)–N(2)	110.8(2)	108.3(3)
F(4)–P(2)–N(1)	108.8(2)	110.3(3)
F(4)–P(2)–N(2)	106.8(2)	109.8(3)
F(5)–P(3)–N(2)	109.4(2)	106.6(3)
F(5)–P(3)–N(3)	107.1(2)	108.5(3)
F(6)–P(3)–N(2)	110.0(2)	112.2(3)
F(6)–P(3)–N(3)	108.7(2)	106.3(3)
F(7)–P(4)–N(3)	108.3(2)	109.0(3)
F(7)–P(4)–N(4)	107.0(2)	110.8(3)
F(8)–P(4)–N(3)	106.6(2)	107.2(3)
F(8)–P(4)–N(4)	109.2(2)	108.6(3)
F(9)–P(5)–N(4)	106.7(2)	110.8(3)
F(9)–P(5)–N(5)	109.0(2)	108.5(3)
F(10)–P(5)–N(4)	108.7(2)	109.1(3)
F(10)–P(5)–N(5)	110.5(2)	108.3(3)
F(1)–P(1)–F(2)	99.1(2)	98.9(2)
F(3)–P(2)–F(4)	100.2(2)	99.7(2)
F(5)–P(3)–F(6)	99.8(2)	99.6(3)
F(7)–P(4)–F(8)	99.0(2)	99.2(2)
F(9)–P(5)–F(10)	99.6(2)	99.1(3)

In Table 3 the shortest intermolecular F · · · F distances in (1) and (2) are given. These distances are less than the shortest F · · · F distance in $N_3P_3F_6$ (2.95 Å)[8] and $N_4P_4F_8$ (3.01 Å).[9] They are also shorter than the F · · · F van der

Waals distance (3.00 Å) given by Bondi.[20] In the crystal structures of (1) and (2) no non-bonded F · · · N, F · · · P, or P · · · N distances are present that are shorter than the corresponding van der Waals distances.[21]

DISCUSSION

Conformations.—As seen in Figure 1 the $(N-P)_5$ ring in the molecule (1) is somewhat boat-shaped. The molecule has a pseudo-two-fold rotation axis passing through the atoms N(1) and P(4). This may be seen from the data in Figure 5, where the molecule is projected on to the best (least-squares) plane through the 10 ring atoms. At each atom the upper number gives the distance of the atom to the least-squares plane, whereas the lower number gives the distance of the atom to a second plane passing through N(1) and P(4) and orientated perpendicular to the first plane. The italicized numbers are the dihedral angles associated with the ring bonds.

Molecule (2) (Figure 2) has a rather irregular shape. The ring conformation is to some extent similar to that in $N_5P_5Br_{10}$.[7] Thus, as in $N_5P_5Br_{10}$, the $(N-P)_5$ ring in (2) has one re-entrant angle P–N–P and the phosphorus atom opposing this angle is the ring atom having the largest distance to the least-squares plane through the ring. However, whereas the structure of $N_5P_5Br_{10}$ has a pseudo-mirror plane normal to the ring,[7] there are no indications of pseudo-symmetry in the case of (2). This may be seen in Figure 6, where the molecule is projected on to the least-squares plane through the ring and the atomic distances to this plane and the ring dihedral angles are given.

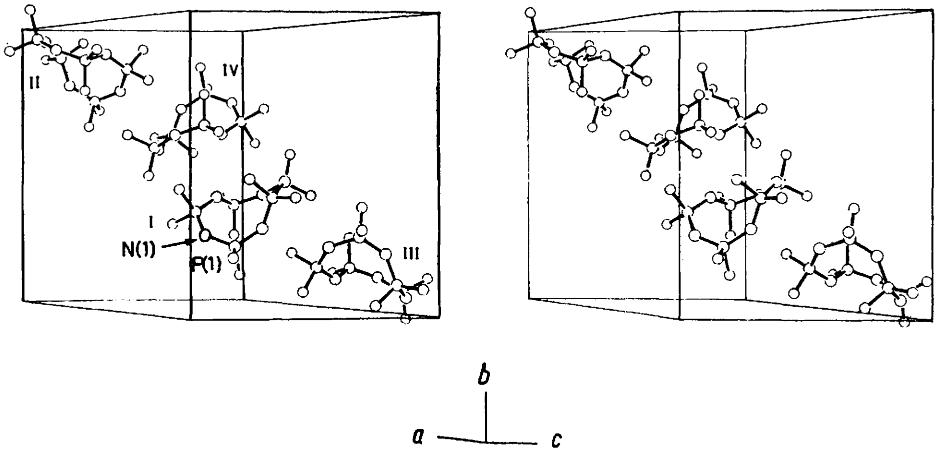

FIGURE 3 Stereoview of the unit cell of (1)

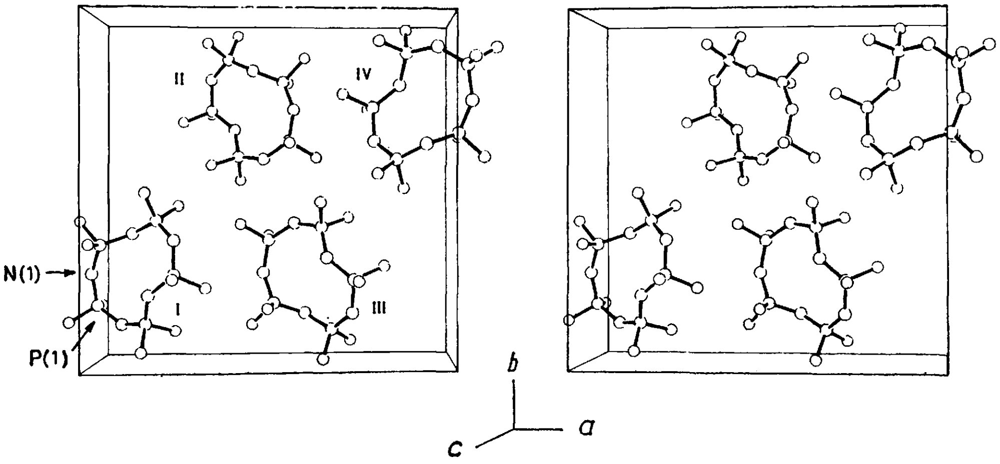

FIGURE 4 Stereoview of the unit cell of (2)

The molecular structure of the fourth known pentameric halogenocyclophosphazene, $N_5P_5Cl_{10}$,[4] is characterized by a relatively planar $(N-P)_5$ ring with two re-entrant P–N–P angles. Comparing the four molecular structures $N_5P_5X_{10}$ (X = F, Cl, or Br), the most striking feature is the large variation shown by the ring conformations. This is, for example, borne out by the following data, where $\Sigma\Delta^2$ is the sum of the squares of the distances

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[20] A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

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

of the ring atoms to the best plane through the $(N-P)_5$ ring:

Molecule	$\Sigma\Delta^2/\text{Å}^2$
(1)	3.05
(2)	1.16
$N_5P_5Br_{10}$	0.67
$N_5P_5Cl_{10}$	0.09

Theoretically, the large variation in ring conformation may be understood on the basis of the π-bonding theory[22] of the cyclophosphazenes. Experimentally, there is (apart from the variability of ring conformation in the crystalline state) evidence for a considerable flexibility of cyclophosphazene rings in the liquid state. In particular, the vibrational spectra of the fluorides $N_nP_nF_{2n}$ (n = 3—17)[14,23] indicate the quite flexible nature of the larger rings in the liquid. It may be inferred that this flexibility is one of the important factors accounting for the different crystal modifications that have been obtained in the low-temperature crystallization of $N_5P_5F_{10}$, as described above.

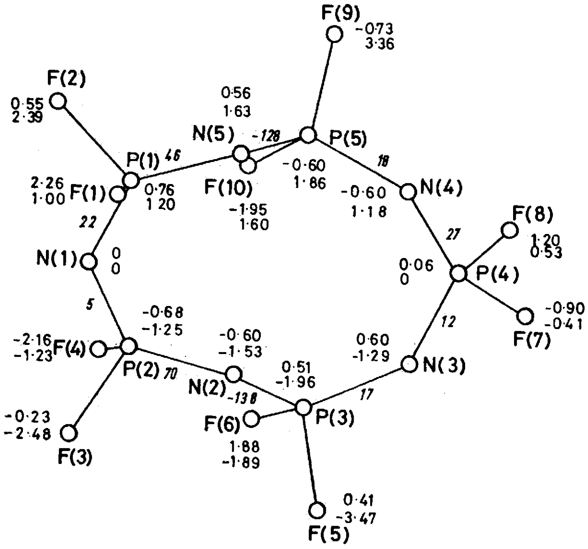

FIGURE 5 Projection of molecule (1) on the least-squares plane through the ring atoms. The numbers are the distances of the atoms to the least-squares plane (upper values), the distances of the atoms to the plane through N(1) and P(4) perpendicular to the least-squares plane (lower values), and the dihedral angles of the ring bonds (italicized values)

TABLE 3

Shortest intermolecular F · · · F distances (Å) in the crystal structures of (1) and (2) between a molecule at x,y,z and surrounding molecules

(*a*) Molecule (1)	
F(1) · · · F(10, $-x$, $y-\frac{1}{2}$, $-z+\frac{1}{2}$)	2.83
F(3) · · · F(7, $-x+1$, $-y+1$, $-z+1$)	2.86
F(2) · · · F(3, $x-1$, $-y+\frac{1}{2}$, $z-\frac{1}{2}$)	2.90
F(6) · · · F(9, $x+1$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$)	2.88
F(4) · · · F(10, $-x$, $-y+1$, $-z$)	2.88
F(4) · · · F(5, $x-1$, y, $z-1$)	2.87
(*b*) Molecule (2)	
F(2) · · · F(10, $-x$, $-y$, $-z$)	2.91
F(5) · · · F(9, $-x+\frac{1}{2}$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$)	2.84

Molecular Geometry.—Some *X*-ray diffraction data on the molecular geometry of the fluorides $N_nP_nF_{2n}$ (n = 3—5) are given in Table 4. For the trimer and the tetramer the electron-diffraction data on the molecular structures in the gaseous state are also included. In general, bond lengths and valence angles of a certain type compare well in different structures. The most striking exception is $N_4P_4F_8$ in the crystalline state, where a planar $(N-P)_4$ ring has been observed with a short P-N bond and a large P-N-P angle. Furthermore, in both modifications of $N_5P_5F_{10}$ not one value but a range of values has been found for the P-N-P angle. A similar situation applies to the N-P-N angle.

TABLE 4

Molecular geometry of fluorocyclophosphazenes. Mean values (and individual standard deviations) of bond lengths and angles or ranges of angles are given

	Bond distance/Å	
Compound	P–N	P–X
$N_3P_3F_6$	1.56(1)	1.52(1)
$N_3P_3F_6$ [a]	1.590(5)	1.543(5)
$N_4P_4F_8$	1.51(2)	1.51(2)
$N_4P_4F_8$ [b]	1.56(1)	1.55(1)
$N_5P_5F_{10}$ (1)	1.549(5)	1.528(3)
(2)	1.546(5)	1.528(4)

	Angle/°		
Compound	N–P–N	P–N–P	X–P–X
$N_3P_3F_6$	119.4(8)	120.4(8)	99.1(7)
$N_3P_3F_6$ [a]	121.3(9)	118.7(9)	98.1(8)
$N_4P_4F_8$	123(1)	147(1)	99(1)
$N_4P_4F_8$ [b]	121(2)	137(2)	102(2)
$N_5P_5F_{10}$ (1)	119.9—123.9(2)	132.7—141.0(3)	99.5(2)
(2)	119.1—123.5(3)	133.9—151.6(4)	99.3(3)

[a] Electron diffraction data (J. W. Paul, Thesis, University of Texas, Austin, 1969; M. I. Davis and J. W. Paul, *J. Mol. Structure*, 1971, **9**, 476). [b] Electron diffraction data (first ref. in footnote *a*).

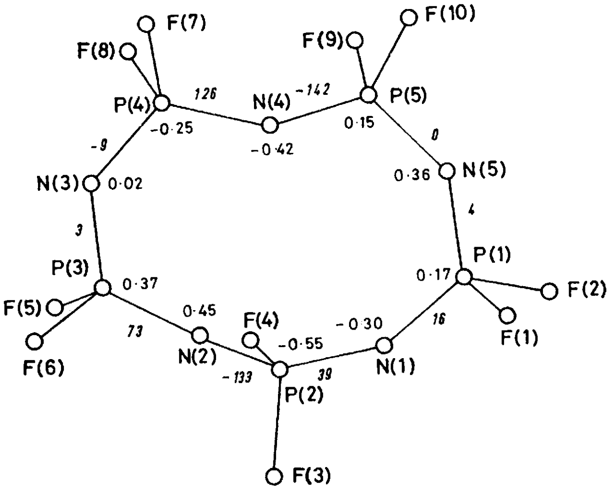

FIGURE 6 Projection of molecule (2) on the least-squares plane through the ring atoms. The numbers are the distances of the atoms to the least-squares plane, and the dihedral angles of the ring bonds (italicized values)

An interesting point may be made concerning the

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[22] D. P. Craig and N. L. Paddock in ' Nonbenzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1971, vol. 2, p. 273.

[23] A. C. Chapman and N. L. Paddock, *J. Chem. Soc.*, 1962, 635.

angles X–P–X and N–P–N in tri-, tetra-, and penta-meric halogenocyclophosphazenes. Mean values of these angles are given in Table 5. It is seen that the angles X–P–X and N–P–N are systematically larger in the tetrameric than in the tri- and penta-meric molecules. Thus, F–P–F and N–P–N in the tetrameric fluoride are larger than in the tri- and penta-meric fluoride and the same is true for the chlorides and bromides.

TABLE 5

Mean values * of X–P–X and N–P–N angles (°) in compounds $N_nP_nX_{2n}$

	X = F		Cl		Br	
n	F–P–F	N–P–N	Cl–P–Cl	N–P–N	Br–P–Br	N–P–N
3	98.6	120.3	101.6	118.3	102.1	118.5
4	100.3	121.7	102.9	120.9	103.9	120.1
5	99.4	121.4	102.1	118.4	103.3	116.8

* For $N_3P_3F_6$ and $N_4P_4F_8$ both *X*-ray diffraction and electron-diffraction data were considered.

A possible explanation for this behaviour may be given in terms of the π-bonding theory of the cyclophosphazenes, provided the π overlap from a phosphorus atom to the neighbouring ring-nitrogen atoms as well as to the exocyclic atoms is considered.[24] There is evidence [25] from ionization-potential measurements and from Hückel-type molecular-orbital calculations that the two π systems distinguished in the theory (homo- and hetero-morphic) are comparable in energy in tri- and penta-meric molecules, but that (due to the alternation of π-electron energy in the homomorphic system) the heteromorphic system is the more favourable one energetically in the tetramers. It may be expected, therefore, that, as far as there is an effect of the π-bonding systems on the geometry of the molecules, the effect of the heteromorphic system is more pronounced in a tetrameric than in a tri- or penta-meric molecule. Now it may be verified,[26] using in the π-bonding systems the atomic orbitals as given in refs. 24 and 25, that overlap in the homomorphic system increases as the angles X–P–X and N–P–N decrease, and is a maximum when these angles are 90°. In the heteromorphic system, on the other hand, the overlap increases when these angles increase, and would become maximal when the angles become 180°. From these considerations it may be inferred that the effect of the heteromorphic π system on the molecular geometry, which would be especially operative in tetrameric cyclophosphazenes (and in hexameric, *etc.*, systems), is to enlarge the angles X–P–X and N–P–N. Although there are of course other factors which influence molecular geometry, the data in Table 5 are in agreement with this conclusion and may be explained in this way.

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[26] J. G. Pauzenga-Hartsuiker, Thesis, University of Groningen, 1975.