atoms range from 119·6 (7) to 121·7 (6)° (*A*) and from 119·6 (5) to 121·6 (5)° (*B*).

There is no difference in the conformations of the symmetrically independent molecules. The geometry of the present molecules can be considered in two ways: (1) by dividing the ring part into two moieties, cyclohexane and cyclohexene, or (2) as a cyclooctene ring. C(5), C(6), C(7), C(8), C(9), C(11) form a cyclohexane ring in a chair conformation. C(5), C(11), C(9), C(10), C(12), C(13) are in a cyclohexene ring with a typical half-chair conformation. C(5), C(10), C(12), C(13) form plane I (Table 5) and atoms C(9) and C(11) are displaced from this plane by 0·313 and −0·496 Å in *A* and 0·346 and −0·467 Å in *B*. C(5), C(6), C(8), C(9) lie in plane II (Table 5) and C(7) and C(11) are displaced from it by −0·599 and 0·742 Å in *A* and −0·615 and 0·737 Å in *B*. Thus the conformation can be described by means of *cis*-fused six-membered rings. Dihedral angles of 74·9 (2) (*A*) and 75·4 (2)° (*B*) define the relative orientation of fused cyclohexane and cyclohexene rings and also the puckering of a cyclooctene ring. The number of possible cyclooctene ring conformations is limited due to the bridging C(11) atom. The conformation of the cyclooctene ring with corresponding torsion angles is shown in Fig. 3.

The symmetrically independent molecules (*A* and *B*) are hydrogen bonded by N—H···O contacts of 2·870 (4) and 2·857 (4) Å between carboxamide groups, forming dimers.

The authors thank Dr S. Mutak for suggesting the problem and providing the crystals.

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The First Example of a Cyclophosphazene 'Anticlathrate Structure': Geometry of 2,2,4,4,6,6-Hexa(1-aziridinyl)cyclotri(phosphazene), $N_3P_3az_6$, from an X-ray Investigation of the Complex $N_3P_3az_6 . 3CCl_4$

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Abstract

The molecular structure of hexaaziridinylcyclotri(phosphazene), $N_3P_3(NC_2H_4)_6$ (*i.e.* $N_3P_3az_6$), a powerful antitumor agent, was determined from an X-ray single-crystal analysis of the complex $N_3P_3az_6 . 3CCl_4$, $M_r = 849$. This complex crystallizes in the monoclinic system, space group $C2/c$, with the parameters a = 15·609 (5), b = 18·748 (4), c = 12·208 (6) Å, β = 106·40 (3)°, and $Z = 4$, $V = 3428$ Å^3, $d_m = 1·5$ (2), $d_x = 1·645$ Mg m^{-3}, μ(Mo $K\alpha$) = 1·13 mm^{-1}. Each $N_3P_3az_6$ is inserted in a monocapped icosahedron formed by 13 CCl_4 molecules and directly connected to six of them by a 'bent halogen bond' (N···Cl = 3·144 Å; ∠N···Cl—C = 157°); so far as is known, such a bond is described here for the first time. The crystal network is a 'bee's nest net' where the host lattice is built up from CCl_4 molecules, and the $N_3P_3az_6$ guest

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molecules are inserted within the hexagonal channels of the lattice. Consequently, this is the first example of a cyclophosphazene 'anticlathrate' structure, as defined by reference to the well known cyclophosphazene clathrates [Allcock (1978). *Acc. Chem. Res.* **11**, 51–87].

Introduction

We recently reported the discovery of antitumor properties exhibited by some aminocyclophosphazenes, namely $N_3P_3az_6$ (az = 1-aziridinyl), $N_4P_4az_8$ and $N_4P_4pyrro_8$ (pyrro = pyrrolidinyl), against murine L 1210 and P 388 leukemias and B16 melanoma (Labarre *et al.*, 1978; Labarre, Faucher, Levy, Sournies, Cros & Francois, 1979); in each case the most active appeared to be – as well as against line 26 colon carcinoma, Lewis lung carcinoma, ependymoblastoma, P 815 mastocytoma (Spreafico & Labarre, 1978) and Yoshida sarcoma (Fox & Labarre, 1978) – the title compound $N_3P_3az_6$ and, consequently, we were urged to investigate the X-ray crystal structure of this new antitumor agent, particularly inasmuch as the Ames tests, performed within the series (Lecointe & Labarre, unpublished), had proved that the origin of the activity could be reasonably searched for within a 'two-body' (drug *versus* target) assumption: $N_3P_3az_6$ was indeed found to be slightly mutagenic *either with or without microsomes*, supporting the idea that the drug does not need any intermediate metabolization to be effective.

Thus, the situation was appropriate for looking at an eventual relationship between the *in vitro* geometric (or electronic) structure and the *in vivo* antitumor activity of the drugs in question, whatever the target might be.

The X-ray crystal structure of $N_4P_4pyrro_8$ was investigated as a first step (Bovin, Galy, Labarre & Sournies, 1978; Bovin, Labarre & Galy, 1979) without any particular difficulty, this compound spontaneously giving suitable single crystals. On the other hand, the two aziridinyl compounds, mainly $N_3P_3az_6$, are obtained in an amorphous state upon aziridinolysis of $N_3P_3Cl_6$ or $N_4P_4Cl_8$ (Ratz, Kober, Grundmann & Ottmann, 1964), and we spent months, using several tricks, in an attempt to obtain single crystals of them. We describe below how we succeeded in the case of $N_3P_3az_6$ and how successful was the structure determination.

Experimental section

1. *Synthesis of* $N_3P_3az_6$

$N_3P_3az_6$ was prepared using the procedure of Ratz *et al.* (1964) by aziridinolysis of $N_3P_3Cl_6$ in the presence of Et_3N. Its purity was checked by infrared spectroscopy, ^{31}P NMR ($\delta = -37{\cdot}0$ p.p.m.; 85% H_3PO_4 as standard), HPLC and mass spectrometry. The last technique was found to be a very powerful tool for testing the purity of aminocyclophosphazenes for biological or clinical uses (Labarre, Sournies, Montsarrat, Prome & van de Grampel, 1979).

2. *Crystal growth*

Crystals were grown from a saturated carbon tetrachloride solution of $N_3P_3az_6$ by adding a few drops of *n*-hexane (in which $N_3P_3az_6$ is hardly soluble). The crystals grow at the interface between the two solvents and stay perfectly colorless as long as they are in contact with some CCl_4 (liquid *or* vapor) (Sournies, Levy & Labarre, 1979). When CCl_4 evaporates, the crystals start to decompose giving rise to a white powder. To avoid this, 'carbon tetrachloride-wet' single crystals were readily mounted in a Lindemann capillary with a little extra drop of CCl_4; the capillary was then sealed.

3. *Crystal morphology*

Crystal shapes were close to perfect hexagonal prisms more or less elongated. The crystal used in the present study had the following dimensions: 0·45 mm in length and 0·25 mm between opposite faces of the hexagonal section.

4. *X-ray analysis*

Preliminary investigations, using a Weissenberg camera and Ni-filtered Cu $K\alpha$ radiation, allowed the assignment of a hexagonal cell to the crystal. The parameters were $a = 18{\cdot}75$ and $c = 16{\cdot}88$ Å, the c axis being directed along the prism. A careful study conducted by photographic methods, using a Stoe 'reciprocal-lattice explorer' camera and Zr-filtered Mo $K\alpha$ radiation, revealed that the title compound in fact crystallized in the monoclinic system; systematic absences gave space groups $C2/c$ or Cc. Precise data are given in the *Abstract*.

The matrix indicated below permits the transformation of the hexagonal cell into the monoclinic one. It also permits the index of face boundaries of the pseudohexagonal crystal in the monoclinic system to be found:

$$\text{hexagonal} \rightarrow \text{monoclinic} \quad \begin{vmatrix} \bar{1} & \bar{2} & \bar{2} \\ \bar{3} & 0 & 0 \\ 1 & 2 & \bar{1} \end{vmatrix}.$$

It was difficult to obtain an accurate determination of the specific mass of the crystal; it is very soluble in almost any solvent and decomposes very quickly; thus, an approximate measurement was performed by a flotation method in dibromobenzene.

Table 1. *Conditions for data collection and refinement*

(1) Data collection
Temperature: 292 K
Radiation: molybdenum ($\lambda K\bar{\alpha} = 0{\cdot}71069$ Å)
Monochromatization: oriented graphite crystal
Crystal–detector distance: 208 mm
Detector window: height = 4 mm, width = 4 mm
Take-off angle: 3·5°
Scan mode: $\theta,2\theta$
Maximum Bragg angle: $\theta = 27°$
Scan angle: $\Delta\theta = \Delta\theta_0 + B\tan\theta$; $\Delta\theta = 0{\cdot}85$, $B = 0{\cdot}35$
Values determining the scan-speed: $\sigma_{pre}{}^* = 0{\cdot}500$, $\sigma^* = 0{\cdot}018$, $V_{pre}{}^* = 20°\ \text{min}^{-1}$, $T_{max}{}^* = 45\text{s}$
Intensity control: reflections $24\bar{4}$, $51\bar{3}$, 004; periodicity: 3600s
Orientation control: reflections $33\bar{4}$, $26\bar{7}$, 0,10,0; periodicity: 200 reflections

(2) Conditions for refinement
Reflections for the refinement of cell dimensions: 25
Recorded reflections: 3997
Independent reflections: 3762
Utilized reflections: 2265
Refined parameters: 179
Reliability factors: $R = \sum(k|F_o| - |F_c|)/\sum k|F_o| = 0{\cdot}0424$
$R_w = [\sum w(k|F_o| - |F_c|)^2/\sum wk^2F_o^2]^{1/2} = 0{\cdot}0427$

* Defined by Mosset, Bonnet & Galy (1977).

5. *Data collection and computer treatment*

The intensity measurements were performed on a CAD-4 Enraf–Nonius PDP 8/M computer-controlled single-crystal diffractometer after optimization of the unit-cell parameters. Conditions for the data collection are summarized in Table 1.

The intensities of selected reflections [$I > 3\sigma(I)$] were corrected for Lorentz and polarization factors. The calculation of the transmission factor shows that its value is between 0·77 and 0·79. Thus, no absorption corrections were applied.

Atomic scattering factors corrected for anomalous dispersion were obtained from Cromer & Waber (1974) and Cromer & Liberman (1970).

6. *Structure solution – single-crystal formula – refinement*

The initial solution of the structure in space group $C2/c$ was difficult because the real content of the cell was not precisely known. The full structure was solved by a combination of the Patterson function and direct methods, using the *MULTAN* program of Germain, Main & Woolfson (1971). The content of the cell was finally shown to be $N_3P_3az_6.3CCl_4$.

At the first attempt, the cyclophosphazene molecule was obtained and centered on the twofold axis of the cell. From Patterson and subsequent Fourier syntheses, two independent CCl_4 molecules were found:

– one, centered on the same twofold axis as the cyclophosphazene molecule (four equivalents),

– the other in a general position (eight equivalents).

Such peculiarities are in perfect agreement with the formula given above.

Refinement of the model, using isotropic thermal parameters for all the atoms, gave a reliability index of 0·203; the introduction of anisotropy in the atomic vibrations reduced the index to 0·080. Difference syntheses permitted the location of the H atoms in their expected positions. They were positioned geometrically following the indications concerning the bonding of such H atoms in aziridinyl groups, *i.e.* C–H = 0·97 Å and ∠H–C–H = 116°, according to Dermer & Ham (1969), and included in the structure factor calculations.

In the last cycles all non-hydrogen atoms were refined, the positions of the H atoms being con-

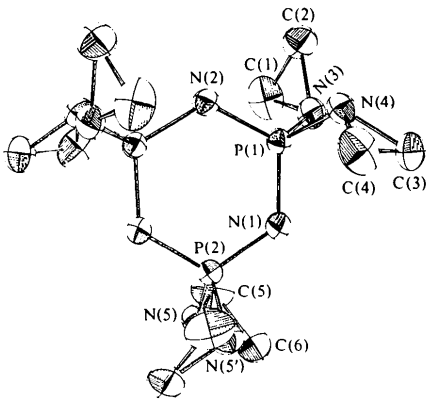


Fig. 1. A perspective view of an $N_3P_3(NC_2H_4)_6$ molecule. Thermal ellipsoids are scaled to include 50% probability. Hydrogen atoms are omitted.

Table 2. *Fractional atomic coordinates and equivalent thermal parameters for the non-hydrogen atoms, with e.s.d.'s in parentheses*

	x	y	z	$B_{eq.}$ (Å²)
P(1)	0·04303 (7)	0·29306 (5)	0·16388 (8)	2·30
P(2)	0	0·16388 (7)	¼	2·28
N(1)	0·0416 (2)	0·2082 (2)	0·1667 (3)	2·70
N(2)	0	0·3332 (2)	¼	2·74
N(3)	−0·0020 (2)	0·3189 (2)	0·0284 (3)	3·15
N(4)	0·1465 (2)	0·3252 (2)	0·1835 (3)	3·16
N(5)	−0·0773 (2)	0·1058 (2)	0·1789 (3)	3·11
C(1)	*−0·0979 (3)*	*0·3350 (3)*	*−0·0077 (4)*	*5·08*
C(2)	−0·0326 (3)	0·3930 (3)	0·0074 (4)	4·23
C(3)	0·2096 (3)	0·2837 (3)	0·1396 (5)	4·27
C(4)	0·2204 (3)	0·2875 (3)	0·2627 (5)	5·04
C(5)	−0·1352 (4)	0·1274 (3)	0·0668 (4)	5·09
C(6)	−0·0660 (3)	0·0734 (3)	0·0744 (4)	4·34
C(7)	0	−0·1393 (4)	¼	4·03
C(8)	0·3052 (3)	0·0555 (3)	0·1392 (4)	3·96
Cl(1)	0·0909 (1)	−0·0845 (1)	0·2481 (1)	6·34
Cl(2)	−0·0247 (1)	−0·1932 (1)	0·1292 (1)	8·39
Cl(3)	0·3512 (2)	−0·0197 (1)	0·2178 (1)	8·34
Cl(4)	0·2056 (1)	0·0765 (1)	0·1685 (1)	8·38
Cl(5)	0·2882 (1)	0·0362 (1)	−0·0062 (1)	6·37
Cl(6)	0·3772 (1)	0·1291 (1)	0·1754 (1)	6·33

Table 3. *Molecular parameters with e.s.d.'s in parentheses*

Symmetry code: superscript: none x,y,z; (i) $\bar{x}$, y, $\frac{1}{2}-z$; (ii) $x,\bar{y},\frac{1}{2}+z$; (iii) $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$.

P(1)–N(1)	1·592 (3) Å	P(1)–N(1)–P(2)	123·2 (2)°
P(1)–N(2)	1·588 (2)	P(1)–N(2)–P(1^{i})	123·4 (2)
P(1)–N(3)	1·676 (4)	N(1)–P(1)–N(2)	116·6 (2)
P(1)–N(4)	1·677 (3)	N(1)–P(1)–N(3)	107·8 (2)
P(2)–N(1)	1·587 (3)	N(1)–P(1)–N(4)	112·0 (2)
P(2)–N(5)	1·675 (4)	N(2)–P(1)–N(3)	112·2 (2)
N(3)–C(1)	1·468 (6)	N(2)–P(1)–N(4)	107·8 (2)
N(3)–C(2)	1·467 (6)	N(3)–P(1)–N(4)	99·0 (2)
N(4)–C(3)	1·469 (5)	N(1)–P(2)–N(5)	107·9 (2)
N(4)–C(4)	1·461 (6)	N(1)–P(2)–N(1^{i})	116·8 (2)
N(5)–C(5)	1·463 (6)	P(1)–N(3)–C(1)	117·7 (3)
N(5)–C(6)	1·468 (6)	P(1)–N(3)–C(2)	118·1 (3)
C(1)–C(2)	1·465 (7)	P(1)–N(4)–C(3)	118·4 (3)
C(3)–C(4)	1·466 (7)	P(1)–N(4)–C(4)	118·0 (3)
C(5)–C(6)	1·464 (8)	P(2)–N(5)–C(5)	117·8 (3)
C(7)–Cl(1)	1·757 (4)	P(2)–N(5)–C(6)	118·2 (3)
C(7)–Cl(2)	1·739 (4)	N(3)–C(1)–C(2)	60·0 (3)
C(8)–Cl(3)	1·741 (5)	C(1)–C(2)–N(3)	60·0 (3)
C(8)–Cl(4)	1·736 (5)	C(1)–N(3)–C(2)	59·9 (3)
C(8)–Cl(5)	1·757 (5)	N(4)–C(3)–C(4)	59·7 (3)
C(8)–Cl(6)	1·756 (5)	C(3)–C(4)–N(4)	60·2 (3)
Cl(1)–Cl(2)	2·835 (2)	C(3)–N(4)–C(4)	60·1 (3)
Cl(3)–Cl(4)	2·829 (2)	N(5)–C(5)–C(6)	60·1 (3)
Cl(4)–Cl(5)	2·887 (3)	C(5)–C(6)–N(5)	60·1 (3)
Cl(5)–Cl(6)	2·854 (3)	C(5)–N(5)–C(6)	59·8 (3)
Cl(3)–Cl(6)	2·886 (3)	Cl(1)–C(7)–Cl(2)	108·4 (1)
Cl(1)–Cl(1^{i})	2·852 (3)	Cl(1)–C(7)–Cl(1^{i})	108·4 (4)
Cl(1)–Cl(2^{i})	2·888 (5)	Cl(1)–C(7)–Cl(2^{i})	111·4 (1)
Cl(2)–Cl(2^{i})	2·829 (3)	Cl(3)–C(8)–Cl(4)	108·9 (3)
N(3^{i})...Cl(2^{ii})	3·143 (4)	Cl(3)–C(8)–Cl(5)	108·1 (3)
N(4)···Cl(3^{iii})	3·145 (4)	Cl(3)–C(8)–Cl(6)	111·3 (3)
N(5^{i})...Cl(4)	3·144 (4)	Cl(4)–C(8)–Cl(5)	111·5 (3)
		Cl(4)–C(8)–Cl(6)	108·5 (3)
		Cl(5)–C(8)–Cl(6)	108·7 (3)
		C(7)–Cl(2^{i})–N(3^{ii})	156·8 (2)
		C(8)–Cl(3)–N(4)	156·6 (2)
		C(8)–Cl(4)–N(5^{i})	156·7 (2)

tinuously readjusted after each cycle and an isotropic thermal parameter, $B(H_i) = B_{eq}(C_i) + 1$ Å^2, being attributed to them.

In the final stages of refinement, an overall extinction parameter ($0{\cdot}737 \times 10^{-8}$) was automatically calculated.

The final R value ($R = 0{\cdot}042$) for 2265 reflections and 179 adjusted variables justifies the structural description in the chosen space group $C2/c$. The final difference map showed no peaks greater than 0·3 e Å^{-3}.

Atomic positional parameters and equivalent isotropic thermal parameters are given in Table 2 and bond lengths and bond angles, with e.s.d.'s calculated from the variance–covariance matrix, in Table 3.*

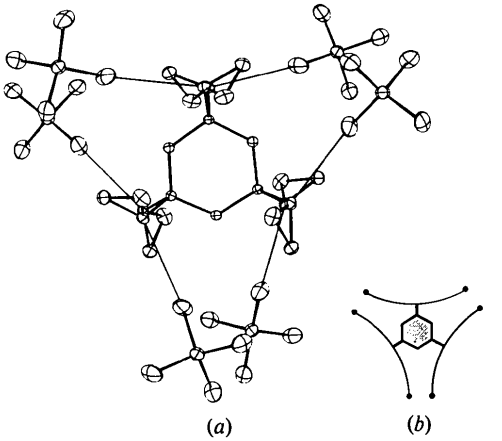
* Lists of structure factors, anisotropic thermal parameters and atomic coordinates of the hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34849 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Description of the structure and discussion

A perspective view of the hexaaziridinylcyclotri(phosphazene) molecule, $N_3P_3az_6$, is shown in Fig. 1, on which the numbering of the atoms is indicated.

The molecule has a twofold symmetry axis. The six-membered phosphazene ring is almost perfectly planar. The endocyclic P–N distances are equal within experimental error and similar to those found by Rettig & Trotter (1973) in the homologous compound $N_3P_3[N(CH_3)_2]_6$. The bond angles around the P and N atoms of the ring are classically smaller and larger respectively than 120°. The exocyclic P–N distances are equal and longer than the previous ones. The aziridinyl groups are remarkably regular (Table 3). N(3), N(4) and N(5) are at the apices of trigonal pyramids, the basal planes being formed by one P and two C atoms; these basal planes are perpendicular to the phosphazene ring (90·9, 91·0, 91·2°), the N atoms being 0·69 Å away from these planes.

In other words, the exocyclic N atoms exhibit a *very pronounced tetragonal character* – quite unusual in P–N chemistry (Barthelat, Mathis, Mathis & Labarre, 1975) – in contrast to the 'normal' trigonal situation we observed previously in $N_4P_4pyrro_8$ (Bovin *et al.*, 1978, 1979). As a consequence, we could predict that $N_3P_3az_6$ would be a very strong Lewis base, mainly upon coordination with transition-metal complexes. This is actually the case, $N_3P_3az_6$ being able to chelate in a quantitative way at room temperature, and in a few hours, various metals from their chloride aqueous solutions, namely Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, Pt^{2+} (Levy & Labarre, unpublished). Even if the structures of these complexes have not yet been completely elucidated, preliminary investigations support the idea that complexation of metals would occur through the three pairs of tetragonal aziridinyl N atoms, each pair chelating one metal atom. From this point of view, $N_3P_3az_6$ could be suitable for new developments within the field of analytical chemistry, in the way that has



(*a*) (*b*)

Fig. 2. (*a*) A perspective view of $N_3P_3(NC_2H_4)_6$ and the six closest CCl_4 molecules. (*b*) Condensed scheme.

been hexakis(*S*-thiosemicarbazido)cyclo(triphosphazene) (Janik, Ryeszutko & Pel'char, 1967).

Incidentally, it may be noticed that owing to the very pronounced tetragonal character of the aziridinyl N atoms, the P—N exocyclic bond lengths would be expected to be extremely long (high 'single' character) when compared to P—N_{sp^2} lengths: indeed, in such a case, the classically invoked p_π–d_π back-bonding of N lone pairs towards P 3*d* orbitals – responsible for the shortening of the corresponding P—N bonds – may presumably be very small. However, no unusual lengthening is observed in $N_3P_3az_6$ (1·589 *versus* 1·575 Å in $N_4P_4pyrro_8$), lessening in some way the absolute validity of a direct relationship between the sp^2 character of N atoms and the length of their linkages to a P atom.

In a first approach, it is possible to consider each molecule of $N_3P_3az_6$ as being inserted in a 'sphere' of 13 CCl_4 molecules, twelve of them occupying the corners of a slightly distorted icosahedron, the last (on the twofold axis) capping the polyhedron above an edge, and *directly connected to six of them by a* N···Cl–C *bridge* (Fig. 2). Indeed, the mean N···Cl distance is 3·144 (4) Å, which is significantly shorter than the sum (3·30 Å) of the van der Waals radii for a N,P couple. The C—Cl···N angle is 157°. This spatial arrangement is, to our knowledge, the first example where a 'halogen bond' between a CCl_4 moiety and an 'amine-like' entity is visualized in an unambiguous way and the most striking result is the *'non-linearity' of the* C—Cl···N *interaction.* Many investigations of the existence and nature of such a 'halogen bond' in several CX_4 amine adducts have been performed previously (Groth & Hassel, 1963) by indirect techniques (IR and Raman spectroscopy, dipole moments,...) and *the assumption of a linear* C–*X*···N *interaction* has been systematically made to interpret the experimental data so obtained. Thus, we think that the X-ray structure presented here may be of some help in re-analyzing in a more real way the observations made by using these other approaches.

Moreover, it appears that within each CCl_4 of the crystal structure, *two* Cl *atoms only are bound to* N *atoms.* The corresponding C—Cl bond lengths are 1·741 (5) and 1·736 (5) Å (Table 3), the two others being 1·757 (5) and 1·756 (5) Å. Even if these two sets cannot be considered as definitively different, we may say, however, that the two C—Cl bonds interacting with N atoms seem to be slightly shorter than the other two. Such a trend does not support the general idea that a N···Cl_4C interaction would proceed from a $n \rightarrow t_2^*$ charge transfer from the N lone pair towards the LUMO t_2^* level of the T_d CX_4 molecule, this charge transfer inducing a slight lengthening of the C—Cl bonds involved. In fact, the reverse situation seems to occur: the two 'free' C—Cl bonds appear to be slightly longer than the other two.

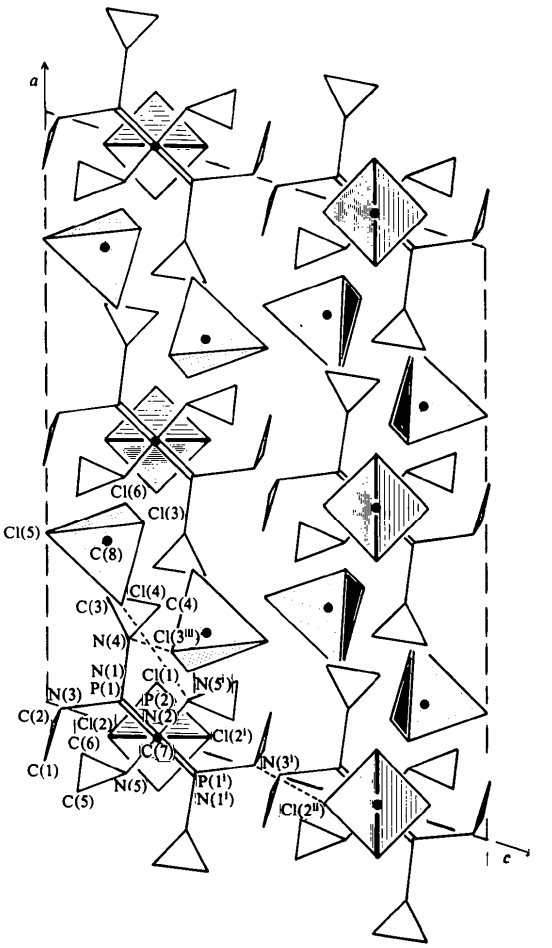


Fig. 3. Projection on to the (010) plane of the $N_3P_3(NC_2H_4)_6 \cdot 3CCl_4$ structure.

A projection of the crystal structure on to the (010) plane is given in Fig. 3. Geometrically, the $N_3P_3az_6$ molecule can be inscribed in a 'cylinder', the axis of which is directed towards the [101] direction with average values of 5·5 Å for the radius and 3·5 Å for the height. Cyclophosphazene rings, with periodicity $\frac{1}{2}[11\bar{1}]$, lie on (201) planes. The whole cell can be described with such planar units by the repetition $\frac{1}{6}[101](201)$, which is close to the 'hexagonal repetition' which was implied by the crystal morphology.

Fig. 4, based on idealized units of Fig. 2, shows the remarkable network which appears to an observer looking at the structure along the [101] direction. Such a structure may be called a 'cyclophosphazene anticlathrate structure' by reference to the well known 'cyclophosphazene clathrates' (Allcock, 1978). Such clathrates were indeed defined by Allcock as 'crystalline solids in which guest molecules (*i.e.* 'solvents') occupy cavities, channels or tunnels in the host cyclophosphazenic lattice'.

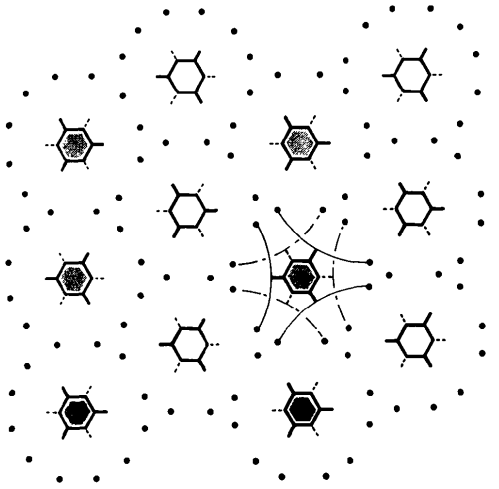


Fig. 4. The 'bee's nest net' packing. Black dots represent CCl_4 molecules and the curved lines the N···Cl–C bonds.

In contrast, the host lattice in our case is built up from CCl_4 entities, the $N_3P_3az_6$ molecules being inserted within the hexagonal channels of this lattice *to stabilize* the 'bee's nest net' in Fig. 4.

It should be mentioned that further investigations have shown that $N_3P_3az_6$ actually gives many stable charge-transfer complexes with several other solvents; the X-ray crystal structure determinations of some of these are now in progress.

In addition to local programs, the following were used on the CICT CII Iris 80 system: A. Zalkin's Fourier program; *NUCLS* (J. A. Ibers and R. J. Doedens); *ORFFE* (Busing, Martin & Levy, 1964); and *ORTEP* (Johnson, 1965).

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