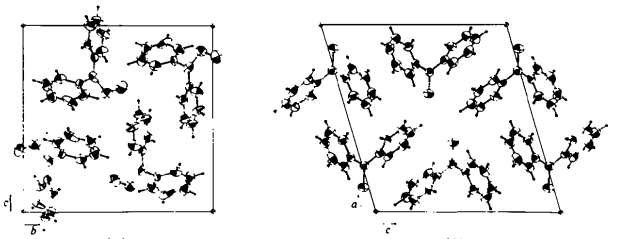

(*a*) (*b*)

Fig. 3. (*a*) $\overline{1}$BPSO viewed along the *a* axis; (*b*) $\overline{1}\overline{1}$BP viewed along the *b* axis.

between the torsion angles S–C(7)–C(1)–C(2) (42·7°) and S–C(7)–C(1′)–C(2′) (31·9°) must be the result of the crystallographic packing. The dihedral angle between the two phenyl rings is 68·6°.

The crystal packing for both molecules is shown in Fig. 3.

The excellent agreement between the experimental results given above and the theoretical predictions concerning the twist angle of the phenyl ring in TBPSO demonstrates the applicability of the CNDO/S-CI procedure to the thiocarbonyl *S*-oxide system, justifying its further use on the unknown carbonyl *O*-sulfide system.

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The Crystal Structure of a New Antitumour Agent: 2,2,4,4,6,6,8,8-Octapyrrolidinylcyclotetra(phosphazene), $N_4P_4(NC_4H_8)_8$

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Abstract

2,2,4,4,6,6,8,8-Octapyrrolidinylcyclotetra(phosphazene), $C_{32}H_{64}N_{12}P_4$, $N_4P_4(NC_4H_8)_8$, $M_r = 740$, crystallizes in the tetragonal system, space group $P\bar{4}2_1c$, with the unit-cell parameters $a = 14{\cdot}218\ (\bar{2})$, $c = 9{\cdot}675\ (2)$ Å, $V = 1956$ Å^3, $Z = 2$, $d_m = 1{\cdot}25\ (2)$, $d_x = 1{\cdot}257$ Mg m^{-3}. The unit cell contains two discrete molecules. The data were collected using an automatic X-ray diffractometer (Cu $K\alpha$ radiation). The structure analysis followed by anisotropic least-squares refinement reduced the R value to 0·058. The saddle-shaped eight-membered $(N-P)_4$ ring has $\bar{4}$ symmetry. Within the ring the two valence angles P–N–P and N–P–N are different [118·8 (4) and 131·7 (4)°]. The two short endocyclic bond lengths are equal [1·575 (6) and 1·574 (6) Å]. The p_π–d_π electron delocalization

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(Dewar's islands model) can be assumed for the molecular configuration of $N_4P_4(NC_4H_8)_8$.

Introduction

It has recently been shown (Cros *et al.*, 1979) that some aminocyclophosphazenes have significant antitumour activity against murine L 1210 and P 388 ascites leukaemiae and against B 16 melanoma. The first drug to be identified is $N_4P_4(NC_4H_8)_8$. Crystals were prepared by pyrrolidinolysis of $N_4P_4Cl_8$ in benzene. Its activity against P 388 leukaemia was found to be moderate, the corresponding ILS being 38% (25% is considered to be significant) in a mono-injection schedule.

The antitumour tests so far performed are consistent with an explanation based on a DNA dialkylating process by means of (at least) one pair of cyclic amino groups which are opened *in vivo*. The maximal activity is observed when this dialkylation is symmetric, *i.e.* when the two cyclic amino ligands are symmetric with respect to the phosphazene ring. Consequently, the moderate activity of $N_4P_4(NC_4H_8)_8$ could be due to puckering of the phosphazene ring since this would induce asymmetry within the pair of pyrrolidinyl groups on a given endocyclic P atom.

Table 1. *Conditions for data collection and structure refinement*

(1) Conditions for data collection

Temperature: 293 K
Radiation: Cu $K\alpha_1$; $\lambda = 1{\cdot}5405$ Å
Monochromator: graphite crystal
Distance between crystal and detector: 208 mm
Aperture of the detector: horizontal = 4 mm, vertical = $(3{\cdot}50 + 0{\cdot}75 \text{ tg } \theta)$ mm
Take-off angle: 4·0°
Scan mode: θ–2θ
Maximum Bragg angle: 78°
Scan width: $\Delta\theta = (1{\cdot}10 + 0{\cdot}15 \text{ tg } \theta)°$
Scan-speed parameters:* $\sigma_{pre} = 0{\cdot}40$, $\sigma = 0{\cdot}018$, $V_{pre} = 10°$ min^{-1}, $T_{max} = 130$ s

	Intensity control	Orientation control
Reflections	880, 416, 008	880, 064, 245
Periodicity	3600 s	100 reflections

(2) Refinement conditions

Number of reflections:	1249
Number of independent reflections:	1194
Number of reflections used ($\lvert F_o\rvert^2 > 1\sigma\lvert F_o\rvert^2$):	1042
Number of variables:	110

Reliability factors:
$R = \sum\lvert k\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum k\lvert F_o\rvert = 0{\cdot}058$
$R_w = [\sum w(k\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum wk^2F_o^2]^{1/2} = 0{\cdot}071$
$w = 4F_c^2/\sigma^2(F_o)^2$

* For definitions see Mosset, Bonnet & Galy (1977).

Structure determination and refinement

A colourless single crystal was used for preliminary studies conducted by photographic methods using a Stoe 'reciprocal-lattice explorer' camera and Zr-filtered Mo $K\alpha$ radiation. Three sets of photographic data revealed that $N_4P_4(NC_4H_8)_8$ crystallizes in the tetragonal system. Systematic absences gave the space group $P\bar{4}2_1c$.

The crystal [0·15 × 0·15 × 0·9 mm, $\mu(\lambda \text{ Cu}) = 2{\cdot}2$ mm^{-1}] was mounted on a CAD-4 Enraf–Nonius PDP 8/M computer-controlled single-crystal diffractometer and the unit-cell parameters were refined by optimizing the settings for 25 reflections. Conditions for the data collection and refinements are summarized in Table 1.

The intensities of selected reflections [$I > 3\sigma(I)$] were corrected for Lorentz and polarization factors and absorption corrections were applied. Atomic scattering factors of Cromer & Waber (1965) for the non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for spherical H atoms were used. Real and imaginary dispersion corrections given by Cromer (1965) were used.

The coordinates of the N and P atoms were solved from a three-dimensional Patterson function. The C atoms were located by successive refinements and Fourier syntheses. The structure refinements were performed using full-matrix least-squares techniques. Difference Fourier maps enabled the positions of the H atoms to be determined, but in the refinement they were fixed at 0·97 Å from the nearest C atom with an H—C—H or H—C—C angle of 109°. All non-hydrogen atoms were then refined with anisotropic thermal parameters, a fixed isotropic thermal parameter of $B_H = (B_{eqC} + 1)$ Å^2 being assigned to the H atoms [B_{eqC} is the equivalent isotropic temperature factor of the C to which the H is bonded: $B_{eqC} = \frac{4}{3}\sum_{ij}(\mathbf{a}_i.\mathbf{a}_j)B_{ij}$]. The final difference map showed no peaks greater than 0·4 e Å^{-3}.

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters, with e.s.d.'s in parentheses*

	x	y	z	B_{eq} (Å^2)
P	1390 (1)	164 (1)	302 (2)	3·2
N(1)	828 (4)	927 (4)	−543 (6)	4·0
N(2)	2427 (4)	121 (5)	−527 (6)	4·2
N(3)	1716 (5)	497 (4)	1871 (7)	4·6
C(1)	3161 (6)	−501 (6)	0 (10)	6·0
C(2)	2521 (6)	252 (6)	−2000 (8)	4·8
C(3)	3474 (7)	−51 (8)	−2331 (10)	6·2
C(4)	3781 (7)	−754 (8)	−1250 (14)	9·6
C(5)	1431 (7)	41 (8)	3147 (8)	6·8
C(6)	2257 (6)	1325 (7)	2099 (9)	5·7
C(7)	1973 (10)	615 (9)	4224 (12)	9·3
C(8)	2208 (9)	1475 (10)	3669 (11)	8·3

Atomic coordinates and equivalent isotropic temperature factors are given in Table 2.*

Description of the structure

The crystal structure of $N_4P_4(NC_4H_8)_8$ is shown in a (001) projection in Fig. 1. The molecular packing arrangement is very similar to those reported for $N_4P_4[N(CH_3)_2]_8$ (Bullen, 1962), $N_4P_4Cl_8$ (the *K* form) (Ketalaar & De Vries, 1939; Hazekamp, Migchelsen & Vos, 1962) and $N_4P_4Cl_8$ (the *T* form) (Wagner & Vos, 1968). The positions of the phosphazene rings are almost identical in these structures, the only difference being that the unit-cell dimensions increase owing to the increase in volume of the exocyclic ligand.

The discrete molecule, $N_4P_4(NC_4H_8)_8$, with $\bar{4}$ symmetry, has a phosphazene ring (*cf.* Fig. 2) with a saddle shape (*cf.* Fig. 3), as in the structure of $N_4P_4[N(CH_3)_2]_8$. The P and N atoms of the puckered eight-membered ring are alternately (and respectively) 0·29 and 0·59 Å above and below the mean plane of the ring [(001) plane]. The value of 0·29 Å for the P atom can be compared with corresponding values in other structures: 0·35 Å in $N_4P_4Cl_8$ (the *K* form), 0·21 Å in $N_4P_4(CH_3)_8$ (Dougill, 1961), 0·18 Å in $N_4P_4[N(CH_3)_2]_8$ and 0·004 Å in $N_4P_4F_8$ (McGeachin & Tromans, 1961). The two short endocyclic bond lengths [P–N(1) in Table 3] are equal within experimental error, involving a classical p_π–d_π bond type of Dewar's islands model (Faucher, Devanneaux, Leibovici & Labarre, 1971). The lengths found for these P–N bonds are similar to those of other phosphonitrile molecules, as can be seen in Table 4. The valency angles, N(1)–P–N(1) = 118·8° and P–N(1)–P = 131·7°, of the ring are very close to the corresponding mean values of the six- and eight-membered rings given in Table 4 (121 and 132°).

The exocyclic P–N(2) and P–N(3) bonds, 1·679 (6) and 1·656 (7) Å, are not equal within experimental errors. They are close to those found in $N_4P_4[N(CH_3)_2]_8$. They clearly have a different bond order from the cyclic P–N bonds and are considerably shorter than the length of a P–N single bond (1·77 Å) (Hobbs, Corbridge & Raistrick, 1953; Cruickshank, 1964). It has been suggested by Bullen (1962) that the shortening of the bond is due to a back-donation of the lone pair of electrons from the exocyclic N atom. In support of this, Bullen (1962) mentions the planarity of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34253 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Intramolecular distances* (Å) *and angles* (°)

P–N(1)	1·575 (6)	C(1)–C(4)	1·54 (1)
P–N(1)*	1·574 (6)	C(2)–C(3)	1·46 (1)
P–N(2)	1·679 (6)	C(3)–C(4)	1·51 (1)
P–N(3)	1·656 (7)	C(5)–C(7)	1·53 (1)
N(2)–C(1)	1·461 (9)	C(6)–C(8)	1·54 (1)
N(2)–C(2)	1·443 (9)	C(7)–C(8)	1·38 (2)
N(3)–C(5)	1·453 (9)		
N(3)–C(6)	1·423 (9)		

N(1)–P–N(2)	102·9 (3)	N(2)–C(1)–C(4)	106·0 (8)
N(1)–P–N(3)	114·9 (4)	N(2)–C(2)–C(3)	105·4 (8)
N(2)–P–N(3)	101·7 (3)	C(1)–C(4)–C(3)	102·9 (8)
N(1)*–P–N(1)	118·8 (4)	C(2)–C(3)–C(4)	108·2 (8)
N(1)*–P–N(2)	113·9 (4)	N(3)–C(6)–C(8)	104·2 (9)
N(1)*–P–N(3)	103·7 (3)	N(3)–C(5)–C(7)	101·5 (8)
P–N(1)–P	131·7 (4)	C(5)–C(7)–C(8)	109 (1)
		C(6)–C(8)–C(7)	106 (1)
P–N(2)–C(1)	118·9 (6)		
P–N(2)–C(2)	123·6 (6)		
P–N(3)–C(5)	125·0 (6)		
P–N(3)–C(6)	122·0 (6)		
C(1)–N(2)–C(2)	110·9 (7)		
C(5)–N(3)–C(6)	112·8 (7)		

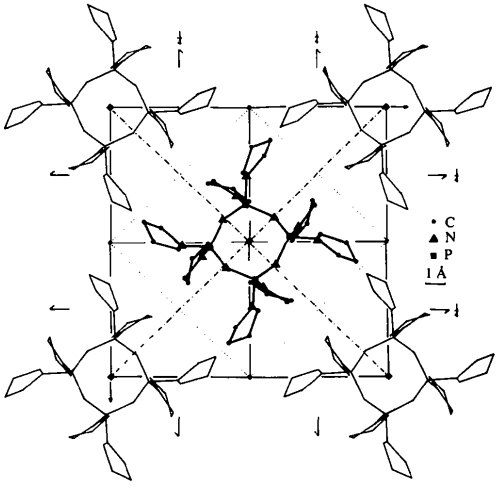

Fig. 1. Projection on to the plane (001) showing the molecular packing in the structure of $N_4P_4(NC_4H_8)_8$.

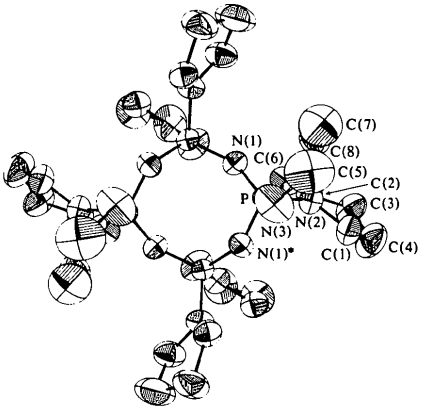

Fig. 2. View of a $N_4P_4(NC_4H_8)_8$ molecule along the *c* axis.

Table 4. *Comparison of bond lengths and bond angles in some phosphonitrile molecules (X being the exocyclic ligand)*

	Symmetry	Cyclic P–N (Å)	Cyclic N–P–N (°)	Cyclic P–N–P (°)	Exocyclic P–X (Å)	Exocyclic X–P–X (°)	References
$N_3P_3F_6$	m	1·56 (1), 1·57 (1) 1·55 (1), 1·56 (1)	120 (1)	119 (1)	1·52 (1), 1·53 (1) 1·52 (1), 1·52 (1)	100 (1) 99 (1)	Dougill (1963)
$N_3P_3Cl_6$	m	1·61 (2) 1·57 (2)	121 (1) 118 (1)	120 (1) 118 (1)	1·98 (1), 1·97 (1) 1·98 (1), 1·97 (1)	102 (1) 102 (1)	Wilson & Carroll (1960)
$N_4P_4F_8$	$\bar{1}$	1·52 (2), 1·49 (2) 1·51 (2), 1·51 (2)	122 (1) 123 (1)	147 (1) 147 (1)	1·53 (2), 1·50 (1) 1·53 (2), 1·50 (1)	100 (1) 100 (1)	McGeachin & Tromans (1961)
$N_4P_4Cl_8$ (K form)	$\bar{4}$	1·57 (1) 1·57 (1)	121·2 (5)	131·3 (6)	1·985 (4) 1·993 (4)	102·8 (2)	Hazekamp, Migchelsen & Vos (1962)
$N_4P_4Cl_8$ (T form)	$\bar{1}$	1·56 (1), 1·56 (1) 1·56 (1), 1·56 (1)	119·3 (7) 121·7 (7)	133·6 (8) 137·6 (8)	1·989 (4), 1·988 (4) 1·990 (4), 2·002 (4)	103·3 (2) 102·9 (2)	Wagner & Vos (1968)
$N_4P_4(CH_3)_8$	$\bar{4}$	1·591 (5) 1·601 (5)	119·8 (3)	132·0 (2)	1·802 (6)	104·1 (2)	Dougill (1961)
$N_4P_4[N(CH_3)_2]_8$	$\bar{4}$	1·58 (1) 1·58 (1)	120·1 (5)	130·0 (6)	1·69 (1) 1·67 (1)	103·8 (5)	Bullen (1962)
$N_4P_4(NC_4H_8)_8$	$\bar{4}$	1·575 (6) 1·574 (6)	118·8 (4)	131·7 (4)	1·679 (6) 1·656 (7)	101·7 (3)	This work
$N_6P_6[N(CH_3)_2]_{12}$	$\bar{3}$	1·57 1·56	120	147	1·67	103	Wagner & Vos (1965)

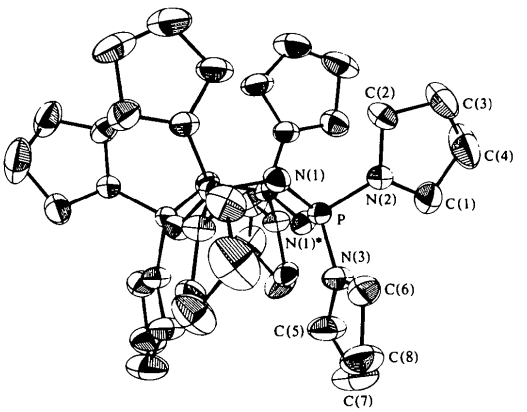

Fig. 3. View of a $N_4P_4(NC_4H_8)_8$ molecule perpendicular to the c axis.

the P–N–C_2 grouping and, indeed, the three bonds from N(2) and N(3) in $N_4P_4(NC_4H_8)_8$ are very nearly coplanar, the sum of the three bond angles around N being close to 360° (*cf.* Table 3).

In the present structure the valency angle N(2)–P–N(3) is 101·7 (3)°, very close to the mean value (102°) of the corresponding angles of the phosphonitrile molecules in Table 4. The striking similarity of the corresponding angles within the PN_2X_2 group (*cf.* Table 3) makes it possible to describe all the phosphonitrile molecules by means of corner-sharing distorted PN_2X_2 tetrahedra making up three-, four- and six-tetrahedra-membered rings. The orientation of the tetrahedra *versus* the N–N edge of the tetrahedra is of course a function of the shape and volume of the X ligand.

In Fig. 3 it can clearly be seen that the four pyrrolidinyl entities, viewed down the z direction above the mean plane of the ring, are opened like the petals of a flower, whereas the other four, viewed in the opposite direction, are coiled around the fourfold axis like faded sepals. Such a coiling makes the four 'below' pyrrolidinyl groups quite different, from a geometrical point of view, from the four 'above'. The two pyrrolidinyl entities also show different shapes according to the distances and angles given in Table 3. The most remarkable difference is shown between the two terminal C–C bonds, 1·51 (1) and 1·38 (2) Å. In other words, the terminal C–C bond of each 'below' pyrrolidinyl group has a definite 'ethylene-like' character, probably due to the packing of the four pyrrolidinyl groups in question. Therefore, this intramolecular packing within the pair of pyrrolidinyl groups linked to a given P atom induces the real asymmetry which was expected on the basis of our explanation of the moderate antitumour activity for $N_4P_4(NC_4H_8)_8$: owing to the difference between the C(3)–C(4) and C(7)–C(8) bond lengths, each 'below' pyrrolidinyl group will be much more stable (and, consequently, much more difficult to open) than the corresponding 'above' one. Thus, the DNA dialkylation by the cyclophosphazene studied here will be slightly symmetric and of low efficiency from the antitumour point of view.

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The Crystal and Molecular Structure of 2,4-Dihydroxybenzophenone (HHB)

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Abstract

2,4-Dihydroxybenzophenone (HHB), $C_{13}H_{10}O_3$, is monoclinic, $P2_1/c$, $a = 7{\cdot}272\ (4)$, $b = 19{\cdot}121\ (15)$, $c = 7{\cdot}595\ (6)$ Å, $\beta = 94{\cdot}1\ (1)°$, $U = 1053{\cdot}4$ Å^3, $Z = 4$, $M_r = 214{\cdot}1$, $D_x = 1{\cdot}35$ Mg m^{-3}, $F(000) = 448$. The counter technique, direct methods and least-squares refinement were used to give $R = 5{\cdot}4\%$ ($R_w = 3{\cdot}8\%$) for 1064 reflexions measured at 293 K. An intramolecular hydrogen bond with O(1)···O(2) = 2·550 (4) Å and an intermolecular hydrogen bond with O(2)···O(3) = 2·735 (4) Å are present. The significant distortions observed in the ring formed by the intramolecular hydrogen bond as well as in the adjacent benzene ring are discussed.

Introduction

2,4-Dihydroxybenzophenone (HHB), also called Uvinul 400, is used in a similar way to several other *ortho*-substituted benzophenones as 'sunscreen agents' added to numerous synthetic materials such as plastics, fibres and even to such preparations as suntan lotions. These substances, which combine a high absorption in the UV range with an outstanding photostability, have been shown to prevent undesirable photochemical degradation.

Beckett & Porter (1963), studying the surprisingly low photochemical reactivity of HHB, showed that it depended on the presence on benzophenone of a hydroxy group in the *ortho* and/or *para* position. Previously Yang & Rivas (1961) had observed that photo-enolization takes place in 2-methylbenzophenone. The mechanism of this reaction was established later by flash photolysis on 2,4-dimethylbenzophenone (Porter & Tchir, 1970), showing the presence of several transients, the photo-enol reverting by dark reaction to the initial form.

As with 2-hydroxy-4-methoxybenzophenone (HMB) and 2-hydroxy-4-methoxy-4′-chlorobenzophenone (HMCB), HHB forms complexes with H_3BO_3 in concentrated H_2SO_4 but, due to weaker fluorescence, is less suitable as a reagent for the determination of traces of boron (Liebich, 1971). The structure of HHB was determined after those of HMB (Liebich & Parthé, 1974*a*) and HMCB (Liebich, 1976) to provide further data on the nature of the hydrogen bonds found in this family of compounds.

Experimental

Pale-yellow, plate-like crystals of HHB were grown from alcohol solutions (EGA-CHEMIE KG). Precession photographs of the crystal indicated the centro-

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