Structure of 2,2′-(2,4-Pyrimidinediyldioxy)bis(2,4,4,6,6-pentachloro-1,3,5,2λ⁵,4λ⁵,6λ⁵-triazatriphosphorine) at 130 K

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Abstract. $C_4H_2Cl_{10}N_8O_2P_6$, $M_r = 734.48$, monoclinic, $P2_1/a$, $a = 8.365\ (8)$, $b = 22.654\ (2)$, $c = 13.436\ (5)$ Å, $\beta = 107.70\ (5)°$, $V = 2426\ (3)$ Å^3, $Z = 4$, $D_x = 2.011$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0.71073$, $\mu = 15.7$ cm^{-1}, $F(000) = 1432$, $T = 130$ K, $R_F = 0.026$ for 3530 unique reflections with $I \geq 3\sigma(I)$ and 279 parameters. The molecule consists of two $N_3P_3Cl_5$ fragments coupled together by a pyrimidinediyldioxy group *via* P—O—C bridges. The mean P—N bond length is 1.579 (1) Å, the P—Cl bond lengths vary from 1.976 (2) to 2.003 (2) Å. The lengths of the N—C bonds [1.316 (5)–1.343 (5) Å] and C—C bonds [mean value 1.380 (7) Å] reflect the aromatic character of the organic heterocycle.

Introduction. During our investigations of the polycondensation of $(NPCl_2)_3$ with bifunctional reagents (Brandt, Jekel, Meetsma & van de Grampel, 1989) we extended our studies to the system $(NPCl_2)_3$–monosodium salt of uracil–Bu$_4$NBr. From that reaction mixture three products could be isolated, the title compound and two hydrolysis products, $(N_3P_3Cl_5)$—O—$(N_3P_3Cl_5)$ and $[N_3P_3Cl_5$-O]$^-$[NBu$_4$]$^+$ (Brandt, van de Grampel, Meetsma & Jekel, 1991). All three products can be easily discerned by their ^{31}P NMR spectra. For the oxygen-bridged product a complex $A_2A_2'XX'$ spin system is observed; the salt-like product exhibits a simple A_2X system [δ^{31}P 20.5, -3.4 p.p.m., ^2J(PP) 40.2 Hz], which is in accordance with the molecular structure (Meetsma, van der Lee, Jekel, van de Grampel & Brandt, 1990). The title compound shows two independent A_2X spin systems [δ^{31}P 23.6, 23.6, 13.6, 13.5 p.p.m., ^2J(PP) 60.0, 62.3 Hz]. Here we report on the crystal and molecular structure of this compound.

Experimental. A colourless block-shaped crystal (0.50 × 0.50 × 0.40 mm) was glued on the top of a

glass fiber and transferred into the cold nitrogen stream of the low-temperature unit (van Bolhuis, 1971; van Nes & van Bolhuis, 1978) mounted on an Enraf–Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Graphite-monochromated Mo $K\bar{\alpha}$ radiation ($\lambda = 0.71073$ Å) was used. Unit-cell parameters were derived from the setting angles of 25 reflections in the range $9.68 \leq \theta \leq 16.85°$. The space group was derived from the observed systematic absences. The monoclinic unit cell was checked for the presence of higher lattice symmetry (Spek, 1988); the observed pseudo-orthorhombic lattice was found to be inconsistent with the symmetry of the reflection data. Examination of the final atomic coordinates of the structure did not yield extra lattice symmetry elements (Le Page, 1987). Intensities of 4238 unique reflections were collected [h $0 \to 9$, k $0 \to 26$, l $-15 \to 15$; $1.00 \leq \theta \leq 25°$; $\omega/2\theta$ scan, $\Delta\omega = (0.90 + 0.35\tan\theta)°$], 3530 satisfying a $3.0\sigma(I)$ criterion of observability. Three standard reflections (392, 3,11,$\bar{2}$, 37$\bar{2}$) monitored at regular intervals showed negligible change during the data-collection period. The intensities were corrected for Lorentz–polarization effects and for absorption (min. transmission coefficient 0.5625, max. 0.9048). The structure was solved by direct methods and refined on F by block-diagonal least-squares procedures with anisotropic thermal parameters for all non-H atoms. H atoms were located on a difference Fourier map and included in the final refinement with isotropic temperature factors. Convergence was reached at $R = 0.026$, $wR = 0.030$ ($w = 1$), $S = 3.1$; 3530 observed reflections; 279 parameters refined; maximum $\Delta/\sigma = 0.03$. The final difference Fourier map did not show any significant residual features (maximum peak height 0.376 e Å^{-3}). Atomic scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Structure determination and refinement performed on a PDP-11/23 computer with the CAD-4 *SDP* program package (Frenz, 1985); other calculations

Table 1. *Final fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (Å²)
Cl(1)	0.4508 (1)	0.28799 (4)	0.77528 (6)	0.0259 (3)
Cl(2)	0.7244 (1)	0.49812 (4)	1.01678 (6)	0.0207 (2)
Cl(3)	0.5945 (1)	0.39584 (4)	1.12325 (6)	0.0235 (3)
Cl(4)	0.9999 (1)	0.26041 (4)	1.06577 (7)	0.0270 (3)
Cl(5)	1.1504 (1)	0.35540 (4)	0.95634 (7)	0.0290 (3)
Cl(6)	0.7180 (1)	0.52193 (4)	0.29846 (6)	0.0202 (2)
Cl(7)	0.3224 (1)	0.34588 (4)	0.24650 (6)	0.0237 (3)
Cl(8)	0.3646 (1)	0.35277 (4)	0.48131 (6)	0.0237 (3)
Cl(9)	0.9718 (1)	0.31670 (5)	0.56218 (8)	0.0385 (3)
Cl(10)	0.9304 (1)	0.30926 (4)	0.32602 (8)	0.0315 (3)
P(1)	0.6280 (1)	0.34790 (4)	0.82841 (6)	0.0149 (2)
P(2)	0.7013 (1)	0.41044 (4)	1.01135 (6)	0.0149 (2)
P(3)	0.9337 (1)	0.33352 (4)	0.97920 (7)	0.0170 (2)
P(4)	0.7110 (1)	0.46249 (4)	0.40558 (6)	0.0136 (2)
P(5)	0.4918 (1)	0.36914 (4)	0.38160 (6)	0.0163 (2)
P(6)	0.8297 (1)	0.34826 (4)	0.42525 (7)	0.0185 (2)
O(1)	0.6145 (3)	0.3777 (1)	0.7184 (2)	0.0182 (6)
O(2)	0.7562 (3)	0.5073 (1)	0.5026 (2)	0.0177 (6)
N(1)	0.6944 (3)	0.4397 (1)	0.6122 (2)	0.0148 (6)
N(2)	0.7928 (3)	0.4534 (1)	0.7973 (2)	0.0186 (8)
N(3)	0.5711 (3)	0.3904 (1)	0.9045 (2)	0.0162 (6)
N(4)	0.8840 (4)	0.3829 (1)	1.0474 (2)	0.0196 (8)
N(5)	0.8033 (4)	0.3163 (1)	0.8713 (2)	0.0212 (10)
N(6)	0.5262 (3)	0.4376 (1)	0.3768 (2)	0.0158 (6)
N(7)	0.6445 (4)	0.3252 (1)	0.4035 (3)	0.0253 (12)
N(8)	0.8596 (3)	0.4169 (1)	0.4219 (2)	0.0166 (6)
C(1)	0.7076 (4)	0.4263 (1)	0.7108 (3)	0.0164 (12)
C(2)	0.8711 (4)	0.5027 (2)	0.7817 (3)	0.0187 (12)
C(3)	0.8658 (4)	0.5233 (1)	0.6850 (3)	0.0167 (12)
C(4)	0.7726 (4)	0.4888 (1)	0.6026 (2)	0.0152 (12)
H(2)†	0.923 (5)	0.524 (2)	0.836 (3)	0.025 (8)
H(3)†	0.921 (4)	0.558 (2)	0.674 (3)	0.017 (9)

† These atoms were refined isotropically.

Table 2. *Selected data on the geometry: bond distances (Å) and angles (°)*

Standard deviations in the last decimal place are given in parentheses.

P(1)—N(3)	1.579 (3)	P(4)—N(6)	1.579 (3)
P(1)—N(5)	1.575 (4)	P(4)—N(8)	1.579 (3)
P(2)—N(3)	1.582 (3)	P(5)—N(6)	1.582 (3)
P(2)—N(4)	1.584 (4)	P(5)—N(7)	1.575 (4)
P(3)—N(4)	1.580 (3)	P(6)—N(7)	1.576 (4)
P(3)—N(5)	1.575 (3)	P(6)—N(8)	1.578 (3)
Cl(1)—P(1)	1.976 (2)	Cl(6)—P(4)	1.985 (2)
Cl(2)—P(2)	1.995 (2)	Cl(7)—P(5)	2.004 (2)
Cl(3)—P(2)	1.996 (2)	Cl(8)—P(5)	1.983 (2)
Cl(4)—P(3)	2.003 (2)	Cl(9)—P(6)	1.995 (2)
Cl(5)—P(3)	1.991 (2)	Cl(10)—P(6)	1.988 (2)
P(1)—O(1)	1.597 (3)	P(4)—O(2)	1.604 (3)
N(3)—P(1)—N(5)	118.1 (2)	N(6)—P(4)—N(8)	118.1 (1)
N(3)—P(2)—N(4)	119.9 (2)	N(6)—P(5)—N(7)	118.7 (2)
N(4)—P(3)—N(5)	118.6 (2)	N(7)—P(6)—N(8)	118.5 (2)
P(1)—N(3)—P(2)	120.2 (2)	P(4)—N(6)—P(5)	121.1 (2)
P(2)—N(4)—P(3)	120.1 (2)	P(5)—N(7)—P(6)	121.4 (2)
P(1)—N(5)—P(3)	122.1 (2)	P(4)—N(8)—P(6)	121.6 (2)
Cl(1)—P(1)—O(1)	97.0 (1)	Cl(6)—P(4)—O(2)	96.2 (1)
Cl(2)—P(2)—Cl(3)	101.42 (7)	Cl(7)—P(5)—Cl(8)	100.71 (7)
Cl(4)—P(3)—Cl(5)	101.04 (7)	Cl(9)—P(6)—Cl(10)	101.78 (8)
O(1)—C(1)	1.370 (4)	C(2)—C(3)	1.369 (6)
O(2)—C(4)	1.374 (4)	C(3)—C(4)	1.385 (4)
N(1)—C(1)	1.331 (4)	C(2)—H(2)	0.87 (4)
N(2)—C(2)	1.343 (5)	C(3)—N(3)	0.95 (4)
N(1)—C(4)	1.316 (4)		
N(2)—C(1)	1.316 (5)		
C(1)—N(1)—C(4)	113.4 (2)	N(2)—C(2)—C(3)	123.7 (3)
C(1)—N(2)—C(2)	114.1 (3)	C(2)—C(3)—C(4)	114.5 (3)
N(1)—C(1)—N(2)	129.2 (3)	N(1)—C(4)—C(3)	125.0 (2)

carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program package *EUCLID* (Spek, 1982; geometric data) and a locally modified version of *PLUTO* (Meetsma, 1986; Motherwell & Clegg, 1978; illustrations). The fractional atomic coordinates and equivalent isotropic parameters of the atoms are presented in Table 1.* Molecular-geometry data are given in Table 2.

Discussion. As shown in Fig. 1 the molecules of the title compound consist of two cyclophosphazene units connected to each other by a dioxypyrimidine group. The central heterocycle is almost perpendicular to both phosphazene planes; angles between the least-squares planes are 88.8 (1)° [for the P(1)–N(5) ring] and 81.3 (1)° [for the P(4)–N(8) ring]. The phosphazene groups exhibit a mutual angle of 59.3 (9)°. As may be seen from the bond angles (Table 2), the P(4)–N(8) ring, which resembles a

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, torsion angles and an *ORTEP* plot (Johnson, 1965) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54563 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0272]
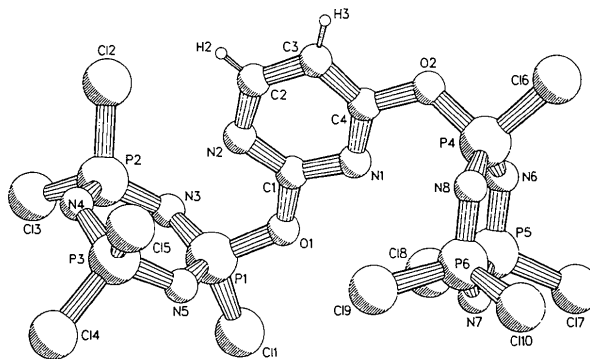

Fig. 1. *PLUTO* drawing of the molecule illustrating the adopted atom-numbering scheme.

half-chair, is more symmetric than the P(1)–N(5) ring (skew-boat). Deviations from planarity, however, are small with a maximum value for P(1) of 0.074 (1) Å. The P—N bond lengths are equal within the experimental error with a mean value of 1.579 (1) Å.* This observation is in line with the small difference in electronegativity between the PClO and PCl₂ centers (Winter, van de Grampel, de Boer, Meetsma & Spek,

* Throughout this paper the mean values and their standard errors have been calculated using the formulae given by Domenicano, Vaciago & Coulson (1975).

1987). The pyrimidine ring is almost planar. The mean value of 1.380 (7) Å for the C—C bond length is in agreement with the average bond length [1.387 (18) Å] reported for C-substituted pyrimidines (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The N—C bonds can be divided into two groups, those having a mean length of 1.336 (6) Å and those with a mean value of 1.316 (3) Å. Whereas the former length agrees with that given for H—C—N—C—H in N-containing aromatic rings, the latter differs significantly and corresponds to the N(3)—C(2) bond in imidazole (Allen *et al.*, 1987). From the molecular structure a straightforward explanation can be given for the observed ^{31}P NMR spectrum: the chemical environments of C(1) and C(4) are different as a result of the asymmetry of the pyrimidine ring. This results in small differences in chemical shifts and coupling constants. From the number of bonds between P(1) and P(4) no coupling can be expected between these atoms.

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Structure of D,L-Iditol

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Abstract. C$_6$H$_{14}$O$_6$, M_r = 182.17, monoclinic, $P2_1/n$, a = 5.209 (1), b = 20.217 (1), c = 7.987 (1) Å, β = 103.45 (1)°, V = 818.0 (2) Å^3, Z = 4, D_x = 1.479 g cm^{-3}, λ(Cu $K\alpha_1$) = 1.54051 Å, μ = 11.1 cm^{-1}, $F(000)$ = 392, T = 293 K, R = 0.047 for 1704 observed reflexions. The title compound crystallizes as a racemate. The molecules adopt a twisted conformation, thus avoiding 1,3-parallel interactions between O(2) and O(4) as well as O(3) and O(5). All six hydroxyl groups are involved as donors and acceptors in a complex pattern of intermolecular hydrogen bonds.

Introduction. Hexitols (sugar alcohols with a central chain of six C atoms) occur as six diastereomers, of which two are *meso* forms. Together with the most recently determined X-ray structure of D-altritol ('D-talitol') (Kopf, Bischoff & Köll, 1991) all the *meso* compounds and all the pure enantiomers of the four possible chiral isomers have been reported. The