is most probably filled with disordered water. The electron count in the solvent channel, as obtained with the *BYPASS* procedure (van der Sluis & Spek, 1990), yielded 90·0 electrons which is equivalent to 4·5 water molecules in the asymmetric unit. The corresponding calculated density of 1·39 Mg m^{-3} is in agreement with the experimental ρ_{obs} = 1·36 (2) Mg m^{-3}. The hydrophobic nature of the interior of the channel may be the cause for the disorder of the water molecules. The nearly continuous density observed suggests a possible incommensurate ordering of the water molecules in the channel.

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Structure of Ethyl 2,4,4,6,6-Pentachloro-1,3,5,2λ^5,4λ^5,6λ^5-triazatriphosphinine-2-carbamate

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Abstract. $C_3H_6Cl_5N_4O_2P_3$, M_r = 400·29, orthorhombic, *Pnnm*, a = 9·195 (2), b = 14·348 (3), c = 11·351 (1) Å, V = 1497·5 (5) Å^3, Z = 4, D_x = 1·775 g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, μ = 12·8 cm^{-1}, $F(000)$ = 792, T = 298 K, R_F = 0·042 for 1035 reflections with $I \geq 2{\cdot}5\sigma(I)$. The crystal structure consists of dimers arising from hydrogen-bond bridges. The organic moiety is located close to the NP ring. The endocyclic N—P bond lengths average to 1·570 (5) Å; N—P (exocyclic) = 1·662 (6) Å. The P—Cl bond lengths vary from 1·974 (2) to 2·007 (3) Å.

Introduction. Although for reactions of $(NPCl_2)_3$ with alkali metal cyanates hardly any product formation is observed, addition of one or more equivalents of alcohol to these reaction mixtures leads to high yields of the corresponding carbamato derivatives (Buwalda, 1989; van de Grampel, Buwalda, van der Huizen, Wilting, Meetsma & van Bolhuis, 1987). In that way the title compound could be prepared in 80% yield from a 1:1:1 mixture of $(NPCl_2)_3$, NaOCN, and ethanol in dry acetonitrile. In order to examine the position of the organic group with respect to the inorganic ring, and its influence on the endocyclic bonding, a structure determination by X-rays was carried out.

Experimental. Transparent, colourless, needle-shaped crystals were obtained by recrystallization from petroleum ether 60–80. A block-shaped fragment (0·23 × 0·25 × 0·30 mm) cleaved from a larger crystal was glued on the top of a glass fibre. Enraf–Nonius CAD-4F diffractometer was interfaced to a Micro-

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VAX 2000 computer. Graphite-monochromated Mo $K\bar{\alpha}$ radiation used to obtain 1385 reflections ($h\,0\rightarrow10$, $k\,0\rightarrow16$, $l\,-12\rightarrow0$); $1{\cdot}42 < \theta < 23{\cdot}99°$; $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}5721$ Å^{-1}; $\omega/2\theta$ scan, $\Delta\omega = (1{\cdot}00 + 0{\cdot}35\tan\theta)°$. Cell dimensions derived from the angular settings of 25 reflections with $7{\cdot}81 < \theta < 20{\cdot}16°$. Reduced-cell calculations did not indicate any higher lattice symmetry (Spek, 1988). Three reference reflections measured every two hours (420: r.m.s.d. = 0·9%; 332: r.m.s.d. = 0·8%; 30$\bar{3}$: r.m.s.d. = 0·8%) showed a linear decay of 7% during the 24·8 h of X-ray exposure time. Intensities corrected accordingly, and for Lorentz and polarization effects. No absorption correction applied. Variance $\sigma^2(I)$ calculated on the basis of counting statistics plus the term (P^2I^2), where P (= 0·014) is the instability constant as derived from the excess variance in the reference reflections (McCandlish, Stout & Andrews, 1975). The systematic extinctions ($0kl$: $k + l = 2n + 1$; $h0l$: $2n + 1$) pointed to *Pnnm* or *Pnn*2 as possible space groups of which the former was finally chosen [with *Pnn*2 convergence reached at $R_F = 0{\cdot}034$, $wR = 0{\cdot}033$, $S = 1{\cdot}117$ and 172 parameters refined; molecular symmetry and coordinate equivalence within their e.s.d.'s suggested a centrosymmetric space group (Marsh & Herbstein, 1988)]. The structure was solved by Patterson and Fourier methods using *SHELXS*86 (Sheldrick, 1986) and refined on F by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms, using 1035 reflections with $I \geq 2{\cdot}5\sigma(I)$. Hydrogen atoms were located on a difference Fourier map and included in the final refinement with one common isotropic temperature factor. Convergence was reached at $R_F = 0{\cdot}042$; $wR = 0{\cdot}039$; $w = 1$; $S = 1{\cdot}276$; 102 parameters refined; maximum $\Delta/\sigma = 0{\cdot}351$. A final difference Fourier map did not show residual peaks outside ± 0·415 e Å^{-3}. Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 1.* Scattering factors from Cromer & Mann (1968). Anomalous-dispersion factors were taken from Cromer & Liberman (1970). All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages *XTAL* (Hall & Stewart, 1987), *EUCLID* (Spek, 1982; calculation of geometric data) and a locally modified version of *PLUTO* (Meetsma, 1986; Motherwell & Clegg, 1978; preparation of illustrations).

Table 1. *Final fractional atomic coordinates and equivalent isotropic thermal parameters for non*-H *atoms, with their e.s.d.'s in parentheses*

	x	y	z	U_{eq}(Å^2)*
Cl(1)	0·4096 (2)	0·0929 (1)	0·0000	0·0841 (8)
Cl(2)	0·1613 (2)	0·4150 (1)	0·2258 (1)	0·1017 (7)
Cl(3)	0·4838 (1)	0·3625 (1)	0·2059 (1)	0·0934 (6)
P(1)	0·2462 (2)	0·1857 (1)	0·0000	0·0493 (6)
P(2)	0·2963 (1)	0·34805 (9)	0·1201 (1)	0·0555 (4)
O(1)	−0·1351 (5)	0·0838 (3)	0·0000	0·058 (1)
O(2)	−0·0488 (5)	0·2303 (3)	0·0000	0·062 (1)
N(1)	0·2541 (4)	0·2427 (2)	0·1187 (3)	0·056 (1)
N(2)	0·3065 (8)	0·4017 (4)	0·0000	0·076 (2)
N(3)	0·1067 (6)	0·1121 (4)	0·0000	0·054 (1)
C(1)	−0·0363 (8)	0·1382 (5)	0·0000	0·054 (3)
C(2)	−0·195 (1)	0·2682 (6)	0·0000	0·081 (4)
C(3)	−0·187 (1)	0·3667 (8)	0·0000	0·131 (7)

$*U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

Cl(1)—P(1)	2·007 (3)	P(2)—N(2)	1·570 (3)
Cl(2)—P(2)	1·974 (2)	O(1)—C(1)	1·198 (9)
Cl(3)—P(2)	1·991 (2)	O(2)—C(1)	1·326 (8)
P(1)—N(3)	1·662 (6)	O(2)—C(2)	1·45 (1)
P(1)—N(1)	1·578 (3)	N(3)—C(1)	1·367 (9)
P(2)—N(1)	1·561 (3)	C(2)—C(3)	1·42 (1)
N(1)—P(1)—N(1*A*)	117·3 (1)	P(1)—N(3)—C(1)	124·6 (5)
N(1)—P(2)—N(2)	118·7 (2)	N(3)—C(1)—O(2)	110·9 (6)
P(1)—N(1)—P(2)	121·5 (2)	C(1)—O(2)—C(2)	117·0 (6)
P(2)—N(2)—P(2*A*)	120·8 (4)	O(2)—C(2)—C(3)	109·2 (8)
Cl(1)—P(1)—N(3)	99·0 (2)	N(3)—C(1)—O(1)	123·4 (7)
Cl(2)—P(2)—Cl(3)	101·38 (9)	O(1)—C(1)—O(2)	125·7 (7)
N(1*A*)—P(1)—N(1)—P(2)	−10·9 (4)	N(1)—P(2)—N(2)—P(2*A*)	−8·4 (6)
N(2)—P(2)—N(1)—P(1)	9·8 (5)		

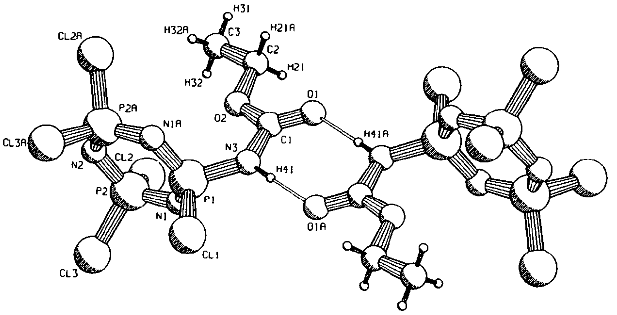

Fig. 1. *PLUTO* drawing of the dimer molecule illustrating the conformation and the adopted numbering scheme.

Discussion. Fig. 1 gives a view of the title compound including the adopted numbering scheme. Selected data on the geometry are given in Table 2. In the unit cell dimeric units of the title compound are present, situated around crystallographic twofold

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances, angles and torsion angles, and three figures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52602 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

axes. Linkages in these dimers take place *via* hydrogen bonding between the nitrogen-bonded hydrogen and the double-bonded oxygen. The H(41)···O(1*A*) distance is 1·85 (9) Å (sum of the van der Waals radii is 2·72 Å; Bondi, 1964). The angle N(3)—H(41)···O(1*A*) is 179 (7)°, whereas the angle H(41*A*)···O(1)—C(1) is 126 (3)°. The organic side group is in close contact with the NP ring. Probably this type of orientation of the organic substituent, which was first reported by Ritchie, Harris & Allcock (1980) for $(NPCl_2)_2NP(H)$-*i*-C_3H_7, renders the molecule more compact, allowing an efficient molecular packing in the unit cell. As imposed by symmetry the dihedral angle between the plane formed by Cl(1), P(1), N(3), C(1), O(1), C(2) and C(3) and the least-squares plane through the NP ring is 90·0°. The ring is slightly puckered with torsion angles varying from − 10·9 (4) to 9·8 (5)°. The substitution of a chloro ligand by an ethyl carbamato group has little influence on π bonding in the ring as the differences between the endocyclic NP bonds [mean value 1·570 (5) Å] are small (Winter, van de Grampel, de Boer, Meetsma & Spek, 1987). The endocyclic angles are all close to 120° with mean values* NPN = 117·6 (6) and PNP = 121·4 (3)°. The exocyclic N(3)—P(1) bond length [1·662 (6) Å] is shorter than the so-called single σ bond in the phosphoramidate ion [1·77 (2) Å; Cruickshank, 1960], indicating that some additional π bonding is present between N(4) and P(1).

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* Throughout this paper the mean values and their standard deviations have been calculated according to Domenicano, Vaciago & Coulson (1975).

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