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Structure of 2,2′;4,4′-Bis(*p*-phenylenedioxy)bis(2,4,6,6-tetrachloro-1,3,5,$2\lambda^5$,$4\lambda^5$,$6\lambda^5$-triazatriphosphorine)

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Abstract. $C_{12}H_8Cl_8N_6O_4P_6$, $M_r = 769\cdot70$, monoclinic, $P2_1/c$, $a = 8\cdot959$ (1), $b = 18\cdot666$ (2), $c = 17\cdot124$ (1) Å, $\beta = 102\cdot01$ (1)°, $V = 2800\cdot9$ (6) Å^3, $Z = 4$, $D_x = 1\cdot825$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 11\cdot8$ cm^{-1}, $F(000) = 1520$, $T = 130$ K, $R = 0\cdot026$ for 4629 observed reflections with $I > 2\cdot5\sigma(I)$. Molecules of the title compound consist of two, nearly parallel [angle 11·03 (5)°], N_3P_3 rings linked to each other by two non-geminal *p*-phenylenedioxy units. The angles between the inorganic and organic rings vary from 84·15 (7) to 89·80 (7)°. Endocyclic parameters are: P—N = 1·579 (1), C—C = 1·379 (2) Å (mean values); N—P—N varies from 116·4 (1) to 119·5 (1)°, P—N—P = 120·9 (1), C—C—C(O) = 118·8 (1), C—C(O)—C = 122·4 (2)° (mean values). The phenylene ring [C(1)–C(6)] is rotated around the C(1)–C(4) axis by short intermolecular contacts.

Introduction. Polycondensation of the hexafunctional trimer $(NPCl_2)_3$ and hydroquinone leads to a broad range of cyclolinear and cyclomatrix polymers (Allcock, 1972). We found that when the polycondensation is carried out in a THF–aqueous NaOH solvent system the process can be governed by suitable reaction conditions and thus the composition of the product formed (Brandt, 1986). In order to obtain some insight into the structure of the polymers the condensation process was allowed to proceed for short periods (3 to 5 min). Analysis of the reaction mixtures showed that the absence or presence of a phase-transfer catalyst in the heterogeneous solvent mixture determines the structure of the oligomers formed in the beginning of the reaction (Brandt, Jekel, Meetsma & van de Grampel, 1988). In the absence of a catalyst single-bridged compounds, *e.g.* $N_3P_3Cl_5$—(*p*-OC_6H_4O)—$N_3P_3Cl_5$, are formed; in the presence of a catalyst low yields (about 2%) of double-bridged derivatives are found besides appreciable amounts of polymeric material. The structure of one of these derivatives is described in this paper.

Experimental. A suitable colourless block-shaped crystal (0·28 × 0·30 × 0·20 mm) was glued on the top of a glass fibre and transferred into the cold nitrogen stream (130 K) of the low-temperature unit mounted on an Enraf–Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Graphite-monochromated Mo $K\bar{\alpha}$ radiation used to obtain 11 653 reflections (h 0→11, k −22→22, l −21→20); $1\cdot09 < \theta < 26\cdot0°$; $(\sin\theta)_{\max}/\lambda = 0\cdot6168$ Å^{-1}; $\omega/2\theta$ scan, $\Delta\omega = (0\cdot70 + 0\cdot35\mathrm{tg}\theta)°$. Three reference reflections measured every 2·5 h ($\bar{4}\bar{9}2$: r.m.s.d. 1·5%; $\bar{3}8\bar{5}$: r.m.s.d. 2·0%; $3\bar{5}5$: r.m.s.d. 1·8%) showed no indication of crystal decomposition and/or movement during the 269·7 h of X-ray exposure time. Unit-cell parameters and their standard deviations were derived from the angular settings of 25 reflections in the range $11\cdot56 < \theta < 14\cdot77°$. Reduced-cell calculations did not indicate any higher lattice symmetry (Le Page, 1982). The net intensities of the data were corrected for scale variation and Lorentz and polarization effects. In view of the observed intensity variation (7%) for a 360° ψ scan of the close-to-axial reflection (211) correction for absorption was judged to be unnecessary. Variance $\sigma^2(I)$ was calculated based on counting statistics and the term (P^2I^2) where P (= 0·038) is the instability constant as derived from the excess variance in the reference reflections (McCandlish, Stout & Andrews, 1975). Data set averaged in a set of 5480 unique reflections. The structure was solved by direct methods (*GENTAN;* Stewart & Hall, 1983) and refined on F by full-matrix least-squares techniques with anisotropic thermal parameters for non-H atoms. H atoms were located on a difference Fourier map and included in the final refinement with isotropic temperature factors. Convergence reached at $R = 0\cdot026$, $wR = 0\cdot034$, $w = 1/\sigma^2(F)$, $S = 1\cdot411$; 4629 observed reflections with $I > 2\cdot5\sigma(I)$; 358 parameters refined; average Δ/σ

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

	x	y	z	U_{eq}(Å^2)*
Cl(1)	0·98941 (7)	−0·13244 (3)	0·16136 (3)	0·0285 (2)
Cl(2)	1·35524 (6)	0·02369 (3)	0·24953 (3)	0·0342 (2)
Cl(3)	0·99597 (6)	0·00983 (3)	0·40109 (3)	0·0255 (2)
Cl(4)	0·77429 (7)	0·12009 (3)	0·30316 (3)	0·0314 (2)
Cl(5)	0·25543 (6)	0·30974 (3)	−0·09460 (3)	0·0322 (2)
Cl(6)	0·37092 (6)	0·39658 (3)	0·17009 (3)	0·0286 (2)
Cl(7)	0·59171 (8)	0·27352 (4)	0·23065 (3)	0·0415 (2)
Cl(8)	0·63685 (7)	0·45724 (3)	−0·03659 (3)	0·0310 (2)
P(1)	0·92587 (6)	−0·02953 (3)	0·15608 (3)	0·0171 (1)
P(2)	1·15523 (6)	0·06917 (3)	0·20342 (3)	0·0181 (2)
P(3)	0·93644 (6)	0·05065 (3)	0·29196 (3)	0·0160 (1)
P(4)	0·43441 (6)	0·26869 (3)	−0·01938 (3)	0·0195 (2)
P(5)	0·50883 (6)	0·32751 (3)	0·13062 (3)	0·0182 (2)
P(6)	0·67419 (6)	0·36295 (3)	0·01783 (3)	0·0195 (2)
O(1)	0·7927 (2)	−0·03508 (7)	0·08010 (8)	0·0210 (4)
O(2)	1·2161 (2)	0·13596 (8)	0·16368 (8)	0·0221 (4)
O(3)	0·4164 (2)	0·18839 (8)	−0·04852 (8)	0·0233 (4)
O(4)	0·8506 (2)	0·35748 (8)	0·02040 (8)	0·0207 (4)
N(1)	1·0592 (2)	0·01856 (9)	0·13747 (9)	0·0194 (5)
N(2)	0·8632 (2)	−0·01110 (9)	0·23327 (9)	0·0199 (5)
N(3)	1·0745 (2)	0·0940 (1)	0·27242 (9)	0·0224 (5)
N(4)	0·4088 (2)	0·2749 (1)	0·0692 (1)	0·0230 (5)
N(5)	0·5866 (2)	0·3017 (1)	−0·0368 (1)	0·0209 (5)
N(6)	0·6433 (2)	0·3699 (1)	0·1055 (1)	0·0251 (6)
C(1)	0·7047 (2)	0·0265 (1)	0·0522 (1)	0·0186 (5)
C(2)	0·7269 (2)	0·0571 (1)	−0·0178 (1)	0·0210 (6)
C(3)	0·6314 (3)	0·1131 (1)	−0·0502 (1)	0·0235 (6)
C(4)	0·5207 (2)	0·1360 (1)	−0·0117 (1)	0·0199 (6)
C(5)	0·5016 (2)	0·1058 (1)	0·0598 (1)	0·0217 (6)
C(6)	0·5955 (2)	0·0497 (1)	0·0918 (1)	0·0210 (6)
C(7)	1·1134 (2)	0·1901 (1)	0·1284 (1)	0·0189 (6)
C(8)	1·0918 (3)	0·2484 (1)	0·1734 (1)	0·0252 (6)
C(9)	1·0016 (2)	0·3040 (1)	0·1379 (1)	0·0247 (6)
C(10)	0·9351 (2)	0·2989 (1)	0·0577 (1)	0·0187 (6)
C(11)	0·9561 (2)	0·2399 (1)	0·0125 (1)	0·0234 (6)
C(12)	1·0469 (3)	0·1847 (1)	0·0483 (1)	0·0239 (6)

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

$= 0·65 \times 10^{-4}$, maximum $\Delta/\sigma = 0·0017$. Minimum and maximum residual densities in final Fourier map −0·74 and 0·38 e Å^{-3}. Correction for isotropic secondary extinction applied (Zachariasen, 1967), $g = 6·8\ (8) \times 10^{-4}$. Neutral-atom scattering factors from Cromer & Mann (1968). Anomalous-dispersion factors (for the non-H atoms) from Cromer & Liberman (1970). All calculations carried out on the CDC Cyber 170/760 computer of the University of Groningen with the program packages *XTAL* (Stewart & Hall, 1983), *EUCLID* (Spek, 1982; calculation of geometric data) and a locally modified version of *PLUTO* (Meetsma, 1986; Motherwell & Clegg, 1978; preparation of illustrations).

Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1.*

Discussion. As shown in Fig. 1 the molecules consist of four cyclic parts connected to each other by P—O—C linkages in a non-geminal way. This structure is consistent with its AB_2-type $^{31}P\{^1H\}$ NMR spectrum [$\delta(PCl_2) = 26·6$, $\delta(PClO) = 18·8$, $^2J(PP) = 64·2$ Hz]. Whereas the inorganic rings are nearly parallel – the two ring planes subtending an angle of only 11·03 (5)° – the phenylene rings exhibit a mutual angle of 49·80 (1)°. This observation can be explained by a rotation of the C(1)–C(6) ring around the C(1)–C(4) axis caused by hydrogen bonding (Berkovitch-Yellin & Leiserowitz, 1984) between H(2)···N(1)($2-x,-y,-z$) = 2·47 (2) Å [sum of the van der Waals radii is 2·75 Å (Bondi, 1964)] and H(5)···O(2)($x-1,y,z$) = 2·54 (2) Å (sum of the van der Waals radii is 2·72 Å); angles C(2)–H(2)···N(1) and C(5)–H(5)···O(2) are 162 (2) and 173 (2)°, respectively. The rotation of the C(1)–C(6) ring is also reflected by the values of the C—C—O—P torsion angles (Table 2): for the C(1)–C(6)

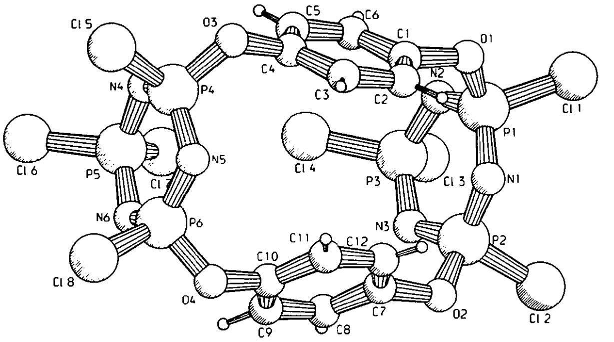

Fig. 1. *PLUTO* drawing of the molecule illustrating the puckering and the adopted numbering scheme.

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

Cl(1)–P(1)	2·0002 (8)	P(3)–N(3)	1·571 (2)
Cl(2)–P(2)	1·9915 (8)	P(4)–O(3)	1·577 (2)
Cl(3)–P(3)	1·9856 (8)	P(4)–N(4)	1·585 (2)
Cl(4)–P(3)	1·9857 (9)	P(4)–N(5)	1·580 (2)
Cl(5)–P(4)	1·9894 (8)	P(5)–N(4)	1·575 (2)
Cl(6)–P(5)	1·9983 (8)	P(5)–N(6)	1·574 (2)
Cl(7)–P(5)	1·9929 (8)	P(6)–N(5)	1·579 (2)
Cl(8)–P(6)	1·9870 (8)	P(6)–N(6)	1·587 (2)
P(1)–O(1)	1·575 (2)	P(6)–O(4)	1·575 (2)
P(1)–N(1)	1·579 (2)	O(1)–C(1)	1·419 (2)
P(1)–N(2)	1·578 (2)	O(2)–C(7)	1·415 (2)
P(2)–N(1)	1·582 (2)	O(3)–C(4)	1·408 (2)
P(2)–O(2)	1·571 (2)	O(4)–C(10)	1·406 (2)
P(2)–N(3)	1·578 (2)		
P(3)–N(2)	1·579 (2)	C–C (mean value)	1·379 (2)
N(1)–P(1)–N(2)	117·46 (9)	P(5)–N(6)–P(6)	120·7 (1)
N(1)–P(2)–N(3)	116·4 (1)	Cl(1)–P(1)–O(1)	97·68 (6)
N(2)–P(3)–N(3)	118·78 (9)	Cl(2)–P(2)–O(2)	98·35 (7)
N(4)–P(4)–N(5)	117·0 (1)	Cl(5)–P(4)–O(3)	98·37 (7)
N(4)–P(5)–N(6)	119·5 (1)	Cl(8)–P(6)–O(4)	98·08 (6)
N(5)–P(6)–N(6)	117·2 (1)	Cl(3)–P(3)–Cl(4)	102·60 (3)
P(1)–N(1)–P(2)	121·1 (1)	Cl(6)–P(5)–Cl(7)	100·46 (3)
P(1)–N(2)–P(3)	121·3 (1)		
P(2)–N(3)–P(3)	120·8 (1)	C–C–C(O) (mean value)	118·8 (1)
P(4)–N(4)–P(5)	120·6 (1)	C–C(O)–C (mean value)	122·4 (2)
P(4)–N(5)–P(6)	120·8 (1)		
C(2)–C(1)–O(1)–P(1)	108·3 (2)	C(8)–C(7)–O(2)–P(2)	93·3 (2)
C(6)–C(1)–O(1)–P(1)	−76·3 (2)	C(12)–C(7)–O(2)–P(2)	−91·2 (2)
C(3)–C(4)–O(3)–P(4)	−103·0 (2)	C(9)–C(10)–O(4)–P(6)	−90·3 (2)
C(5)–C(4)–O(3)–P(4)	81·3 (2)	C(11)–C(10)–O(4)–P(6)	93·2 (2)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms and an *ORTEP* plot (Johnson, 1965) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44808 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

moiety the torsion angles are quite different from 90°, whereas for C(7)–C(12) this difference amounts to 3° at the most. The double-bridged compound somewhat resembles a rectangular cage by the almost perpendicular position of the organic and inorganic rings: angle [P(1)–N(2)]–[C(1)–C(6)] = 84·15 (7), [P(1)–N(2)]–[C(7)–C(12)] = 88·92 (8), [P(4)–N(4)]–[C(1)–C(6)] = 89·80 (7), [P(4)–N(4)]–[C(7)–C(12)] = 85·79 (8)°. The observed conformations of both inorganic rings can be described as envelopes (Boeyens, 1978), with torsion angles ranging from −24·5 (2) to 21·1 (2)° and lowest asymmetry parameter value ΔC_s[P(2)] = 4·5 (2)° (Duax, Weeks & Rohrer, 1976) for [P(1)–N(2)], and with torsion angles ranging from −23·8 (2) to 22·1 (2)° and lowest asymmetry parameter value ΔC_s[P(5)] = 2·4 (2)° for [P(4)–N(4)]. Puckering parameters (Cremer & Pople, 1975; e.s.d.'s following Norrestam, 1981) are: Q = 0·195 (1) Å, θ = 128·0 (3)°, φ = 285·7 (5)° and Q = 0·187 (1) Å, θ = 134·1 (3)°, φ = 128·6 (6)°, respectively. Although belonging to a heterogeneously substituted N_3P_3 system, the P—N bond lengths appear to be equal within experimental error [mean value 1·579 (1) Å*], due to the small difference in electronegativity between the groups linked to phosphorus (Hinze & Jaffé, 1962; Huheey, 1966; Winter, van de Grampel, de Boer, Meetsma & Spek, 1987). From the structure of the title compound another isomer can be derived in which the PCl_2 groupings are in the *trans* position. The presence of a second oligomer in the reaction mixture of $(NPCl_2)_3$, hydroquinone and a phase-transfer catalyst (Brandt *et al.*, 1988) with similar $^{31}P\{^1H\}$ NMR data [AB_2 type, $\delta(PCl_2) = 25{\cdot}7$, $\delta(PClO) = 17{\cdot}2$, $^2J(PP) = 67{\cdot}8$ Hz] supports this assumption.

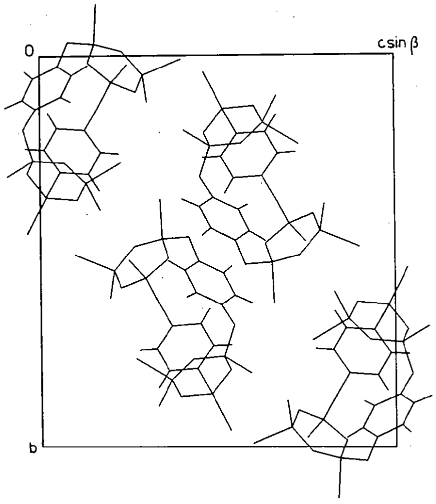

Fig. 2. Projection of the structure down the *a* axis.

Apart from the hydrogen bonding another short intermolecular contact is observed, *viz* Cl(5)···N(3)(x−1, $\frac{1}{2}$−y, z−$\frac{1}{2}$) = 3·082 (2) Å [sum of the van der Waals radii is 3·30 Å (Bondi, 1964)]. No alterations in the local geometry, caused by this contact, are observed.

Fig. 2 shows the arrangement of the compound in the unit cell viewed down **a**.

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* Throughout this paper the mean values and their standard deviations have been calculated using the formulae given by Domenicano, Vaciago & Coulson (1979).

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