centrosymmetric model. Hydroxy H atoms were located from difference maps and refined isotropically, while other H atoms were placed in calculated positions with a C—H distance of 0.95 Å and B_{iso} = 1.3 B_{eq} for the bonded C atom. The structure was solved using *SHELXS*86 (Sheldrick, 1985) and refined using *MolEN* (Fair, 1990).

(2): The crystal was mounted in a capillary for data collection. The structure was solved using *MULTAN*80 (Main *et al.*, 1980). H atoms were refined isotropically, except for those attached to C4, C7 and C16. Those on C4 and C7 did not refine well and were included as fixed contributions with a C—H distance of 0.95 Å. The methyl group involving C16 is disordered and was modeled as two half-populated rotamers with six half-populated H atoms in fixed positions.

(3): The compound is isomorphous with the hexachloro analog (4). Heavy-atom positions from (4), with the exception of Cl5 and Cl6, were successfully used as a beginning phasing model.

(4): The crystal was mounted in a capillary for data collection. The structure was solved using *MULTAN*80 (Main *et al.*, 1980).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, torsion angles for (1)-(4) and C—H bonds for (2) and (4) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71468 (155 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1071]

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2,2,4,4,6,6-Tris(2,3-naphthylenedioxy)cyclotriphosphazene

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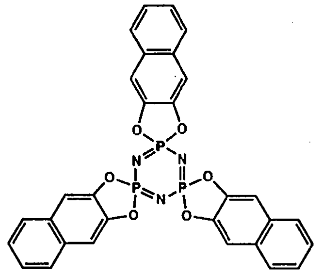
Abstract

The molecular structure of the title compound, $C_{30}H_{18}N_3O_6P_3$, is distorted from that observed in related clathrate compounds. The central phosphazene core takes a boat conformation. The peripheral naphthalene rings are not planar and the five-membered exocyclic rings are bent appreciably at the O-atom positions. The packing of the distorted molecules is governed predominantly by van der Waals forces in the crystal.

Comment

Tris(2,3-naphthylenedioxy)cyclotriphosphazene (TNDOCTP), (I), functions as a host in clathration



(I)

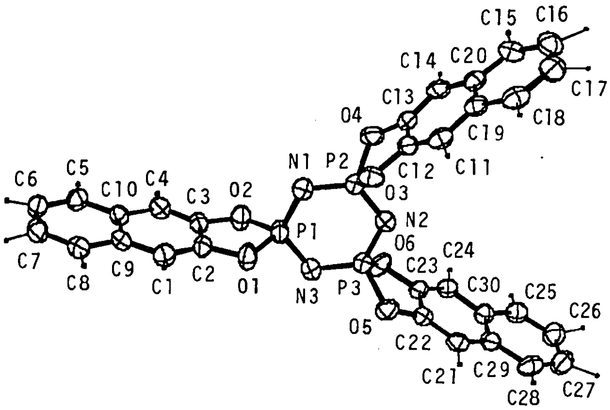


Fig. 1. Atomic numbering scheme and thermal ellipsoids at 50% probability.

and forms channel-type clathrates of isomorphous structures with benzene, chloroform, *etc.* (Allcock & Stein, 1974; Allcock, 1984) or a cage-type clathrate with *p*-xylene (Kubono, Asaka, Isoda, Kobayashi & Taga, 1993), but the structure of guest-free TNDOCTP has not yet been established. The guest-free crystals of TNDOCTP, synthesized as described by Allcock & Kugel (1966), were obtained by sublimation under vacuum (10^{-4} Pa). Although most of the crystals were twins, a single crystal was also found and analyzed. The molecule of TNDOCTP is significantly distorted from the symmetrical structure previously observed in the host–guest compounds of TNDOCTP (Allcock & Stein, 1974; Kubono, Asaka, Isoda, Kobayashi & Taga, 1993). The phosphazene core is almost planar with displacements of atoms P1, N1, P2, N2, P3 and N3 from the mean plane of the phosphazene ring by −0.035 (3), +0.068 (7), −0.043 (3), −0.011 (7), +0.041 (3) and −0.019 (10) Å, respectively. The deviations of the C atoms in the naphthalene ring branching out from the mean plane at P2 range from +0.047 (10) to −0.058 (10) Å, and in the naphthalene ring at P3 from +0.049 (10) to −0.041 (10) Å. For the naphthalene ring at P1 the deviations are relatively small: +0.021 (10) to −0.028 (10) Å. The non-planarity of the naphthalene rings reflects the diversity in the C—C bond lengths; for example, C11—C12 = 1.320 (8) and C19—C20 = 1.448 (9) Å. The five-membered exocyclic rings are also nonplanar and are bent at the O atoms: the torsion angles P1—O1—C2—C3, P2—O3—C12—C13 and P3—O5—C22—C23 are 8.4 (6), 18.6 (6) and −16.3 (5)°, respectively.

Experimental

Crystal data

$C_{30}H_{18}N_3O_6P_3$
$M_r = 609.41$
Monoclinic
$C2/c$
$a = 32.265$ (6) Å
$b = 5.825$ (1) Å
$c = 27.518$ (4) Å
$\beta = 95.25$ (1)°
$V = 5150$ (2) Å^3
$Z = 8$
$D_x = 1.572$ Mg m^{-3}
$D_m = 1.56$ Mg m^{-3}
Density measured by flotation in n-C_6H_{14}/CCl_4

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 9.7$- 17.6°
$\mu = 2.597$ mm^{-1}
$T = 296$ K
Prism
0.2 × 0.2 × 0.1 mm
Colourless

Data collection

Rigaku AFC-5*RU* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4401 measured reflections
4299 independent reflections
2913 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.0309$
$\theta_{\rm max} = 60°$
$h = -36 \rightarrow 36$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 30$
3 standard reflections monitored every 150 reflections intensity variation: 4%

Refinement

Refinement on F
$R = 0.0618$
$wR = 0.0524$
$S = 5.79$
2913 reflections
452 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + (0.023F_o)^2]$

$(\Delta/\sigma)_{\rm max} = 0.69$
$\Delta\rho_{\rm max} = 0.212$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.200$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
P1	0.11850 (6)	1.3875 (4)	−0.11331 (6)	3.45 (4)
P2	0.16214 (5)	1.4935 (3)	−0.02632 (6)	3.21 (3)
P3	0.08881 (5)	1.2452 (3)	−0.02818 (6)	3.18 (3)
N1	0.1582 (1)	1.481 (1)	−0.0827 (2)	3.8 (2)
N2	0.1273 (1)	1.366 (1)	0.0012 (2)	3.2 (2)
N3	0.0837 (2)	1.263 (1)	−0.0849 (2)	3.8 (2)
O1	0.0970 (1)	1.5858 (8)	−0.1476 (1)	3.7 (2)
O2	0.1321 (1)	1.2286 (8)	−0.1572 (1)	3.6 (2)
O3	0.1677 (1)	1.7543 (8)	−0.0071 (1)	3.5 (2)
O4	0.2072 (1)	1.4066 (8)	−0.0032 (2)	3.4 (1)
O5	0.0459 (1)	1.3295 (8)	−0.0066 (1)	3.4 (1)
O6	0.0858 (1)	0.9832 (8)	−0.0106 (1)	3.5 (2)
C1	0.0991 (2)	1.708 (1)	−0.2320 (2)	3.2 (2)
C2	0.1065 (2)	1.561 (1)	−0.1949 (2)	3.0 (2)
C3	0.1273 (2)	1.351 (1)	−0.2009 (2)	2.8 (2)
C4	0.1414 (2)	1.290 (1)	−0.2429 (2)	3.0 (2)
C5	0.1499 (2)	1.399 (1)	−0.3284 (2)	3.2 (2)
C6	0.1434 (2)	1.546 (1)	−0.3669 (2)	3.8 (2)
C7	0.1213 (2)	1.751 (1)	−0.3616 (2)	3.6 (2)
C8	0.1067 (2)	1.803 (1)	−0.3181 (2)	3.1 (2)
C9	0.1126 (2)	1.655 (1)	−0.2774 (2)	2.9 (2)
C10	0.1349 (2)	1.444 (1)	−0.2832 (2)	2.6 (2)
C11	0.2009 (2)	1.917 (1)	0.0684 (2)	3.2 (2)
C12	0.1960 (2)	1.758 (1)	0.0342 (2)	2.9 (2)
C13	0.2199 (2)	1.552 (1)	0.0361 (2)	2.8 (2)
C14	0.2486 (2)	1.510 (1)	0.0727 (2)	3.1 (2)
C15	0.2815 (2)	1.633 (1)	0.1532 (2)	3.7 (2)

C16	0.2850 (2)	1.780 (1)	0.1917 (2)	4.3 (2)
C17	0.2609 (2)	1.985 (1)	0.1891 (2)	4.2 (2)
C18	0.2352 (2)	2.029 (1)	0.1487 (2)	3.7 (2)
C19	0.2298 (2)	1.879 (1)	0.1088 (2)	2.9 (2)
C20	0.2545 (2)	1.671 (1)	0.1110 (2)	2.9 (2)
C21	0.0134 (2)	1.218 (1)	0.0665 (2)	3.0 (2)
C22	0.0382 (2)	1.180 (1)	0.0313 (2)	2.8 (2)
C23	0.0619 (2)	0.976 (1)	0.0298 (2)	2.8 (2)
C24	0.0618 (2)	0.811 (1)	0.0628 (2)	3.0 (2)
C25	0.0363 (2)	0.684 (1)	0.1404 (2)	3.4 (2)
C26	0.0143 (2)	0.721 (1)	0.1792 (2)	4.2 (2)
C27	−0.0101 (2)	0.924 (1)	0.1817 (2)	4.3 (2)
C28	−0.0110 (2)	1.079 (1)	0.1445 (2)	4.0 (2)
C29	0.0124 (2)	1.050 (1)	0.1036 (2)	3.0 (2)
C30	0.0367 (2)	0.843 (1)	0.1015 (2)	2.9 (2)

Table 2. *Selected geometric parameters* (Å, °)

P1—N1	1.565 (5)	P1—N3	1.600 (7)
P1—O1	1.608 (4)	P1—O2	1.614 (4)
P2—N1	1.547 (6)	P2—N2	1.595 (5)
P2—O3	1.613 (5)	P2—O4	1.614 (4)
P3—N2	1.583 (5)	P3—N3	1.558 (6)
P3—O5	1.631 (4)	P3—O6	1.607 (5)
O1—C2	1.372 (6)	O2—C3	1.394 (6)
O3—C12	1.391 (6)	O4—C13	1.405 (8)
O5—C22	1.398 (7)	O6—C23	1.410 (7)
C1—C2	1.337 (8)	C1—C9	1.395 (8)
C2—C3	1.412 (8)	C3—C4	1.329 (8)
C4—C10	1.427 (8)	C5—C6	1.363 (8)
C5—C10	1.400 (8)	C6—C7	1.405 (9)
C7—C8	1.360 (8)	C8—C9	1.412 (8)
C9—C10	1.440 (9)	C11—C12	1.320 (8)
C11—C19	1.402 (8)	C12—C13	1.425 (8)
C13—C14	1.327 (8)	C14—C20	1.411 (8)
C15—C16	1.359 (8)	C15—C20	1.404 (8)
C16—C17	1.423 (8)	C17—C18	1.349 (8)
C18—C19	1.402 (8)	C19—C20	1.448 (9)
C21—C22	1.330 (9)	C21—C29	1.417 (8)
C22—C23	1.416 (9)	C23—C24	1.322 (8)
C24—C30	1.408 (9)	C25—C26	1.352 (9)
C25—C30	1.416 (8)	C26—C27	1.426 (9)
C27—C28	1.363 (8)	C28—C29	1.422 (9)
C29—C30	1.442 (9)		
N1—P1—N3	118.1 (3)	C4—C10—C5	122.3 (5)
N1—P1—O2	109.7 (2)	C5—C10—C9	118.4 (5)
N3—P1—O2	110.9 (3)	O3—C12—C11	128.3 (6)
N1—P2—N2	117.2 (3)	C11—C12—C13	122.4 (5)
N1—P2—O4	111.7 (3)	O4—C13—C14	127.4 (5)
N2—P2—O4	108.4 (3)	C13—C14—C20	118.8 (6)
N2—P3—N3	119.2 (3)	C15—C16—C17	118.9 (5)
N2—P3—O6	109.5 (2)	C17—C18—C19	123.4 (6)
N3—P3—O6	111.2 (3)	C11—C19—C20	119.3 (5)
P1—N1—P2	123.0 (3)	C14—C20—C15	123.0 (5)
P1—N3—P3	120.3 (4)	C15—C20—C19	117.6 (5)
P1—O2—C3	109.6 (4)	O5—C22—C21	126.8 (5)
P2—O4—C13	107.6 (4)	C21—C22—C23	121.6 (5)
P3—O6—C23	108.5 (4)	O6—C23—C24	126.8 (6)
O1—C2—C1	128.1 (6)	C23—C24—C30	117.4 (6)
C1—C2—C3	121.3 (5)	C25—C26—C27	120.2 (5)
O2—C3—C4	126.4 (5)	C27—C28—C29	122.6 (6)
C3—C4—C10	118.1 (6)	C21—C29—C30	120.0 (5)
C5—C6—C7	119.8 (5)	C24—C30—C25	122.1 (6)
C7—C8—C9	122.0 (6)	C25—C30—C29	118.3 (5)
N1—P1—O1	110.7 (3)	C8—C9—C10	117.7 (5)
N3—P1—O1	109.2 (3)	C4—C10—C9	119.3 (5)
O1—P1—O2	96.0 (2)	C12—C11—C19	118.8 (6)
N1—P2—O3	111.7 (3)	O3—C12—C13	109.2 (5)
N2—P2—O3	110.2 (3)	O4—C13—C12	111.1 (5)
O3—P2—O4	95.6 (2)	C12—C13—C14	121.4 (5)
N2—P3—O5	109.4 (2)	C16—C15—C20	123.1 (6)
N3—P3—O5	109.2 (3)	C16—C17—C18	119.5 (5)
O5—P3—O6	95.7 (2)	C11—C19—C18	123.3 (6)
P2—N2—P3	121.2 (4)	C18—C19—C20	117.4 (5)
P1—O1—C2	111.1 (4)	C14—C20—C19	119.3 (5)
P2—O3—C12	109.1 (4)	C22—C21—C29	117.7 (6)
P3—O5—C22	107.4 (4)	O5—C22—C23	111.6 (5)
C2—C1—C9	119.6 (6)	O6—C23—C22	109.5 (5)
O1—C2—C3	110.6 (5)	C22—C23—C24	123.7 (6)
O2—C3—C2	111.0 (5)	C26—C25—C30	122.3 (6)
C2—C3—C4	122.5 (5)	C26—C27—C28	119.1 (6)
C6—C5—C10	122.1 (6)	C21—C29—C28	122.5 (5)
C6—C7—C8	120.0 (5)	C28—C29—C30	117.5 (5)
C1—C9—C8	123.0 (5)	C24—C30—C29	119.6 (5)
C1—C9—C10	119.2 (5)		

Corrections were made for Lorentz and polarization effects. Since the structure could not be solved by direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), it was solved by the Patterson method and subsequent Fourier methods. Refinement was performed by block-diagonal least squares. H atoms were determined from difference Fourier syntheses. All computations were performed on a FACOM M382 computer at the Data Processing Center of Kyoto University, using *KPPXRAY* (Taga, Masuda, Higashi & Iizuka, 1991).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71481 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1057]

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