The Crystal and Molecular Structure of 2,4,6-Tris-(2,2′-dioxybiphenyl)cyclotriphosphazene

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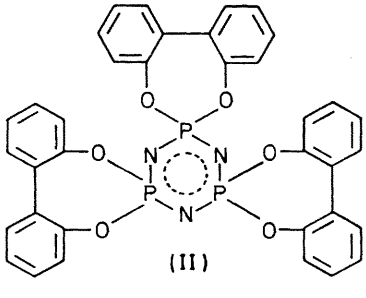
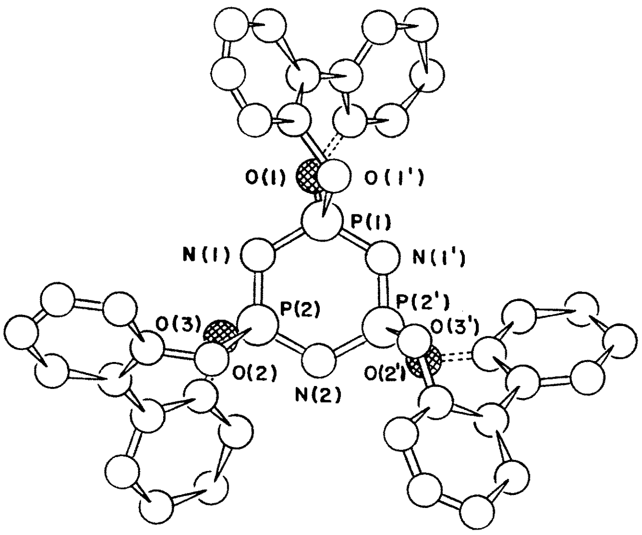
Summary The crystal and molecular structure of the title compound has been determined from single-crystal *X*-ray data: the results explain the absence of molecular-inclusion adducts with this compound.

CERTAIN cyclotriphosphazenes (phosphonitriles), such as tris-(*o*-phenylenedioxy)cyclotriphosphazene, $(NPO_2C_6H_4)_3$ (I), which have bulky aromatic side units can form crystalline molecular-inclusion adducts with organic molecules and polymerize when heated.[1,2] However, the related derivative, 2,4,6-tris-(2,2′-dioxybiphenyl)cyclotriphosphazene (II) forms no comparable inclusion adducts and cannot be induced to undergo thermal polymerization.[2] We believe that these differences are closely related to the different spatial arrangements of the side groups and to the different crystal structures found in the two cases.



(II)

We have completed an *X*-ray single-crystal structure determination of (II) and have compared its structural parameters with the published values recorded for (I).[3] Crystals of (II) are monoclinic with the space group $C2/c$. The unit cell determined from Cr-K_α powder data has the dimensions $a = 15{\cdot}377(2)$ $b = 10{\cdot}810(1)$, $c = 20{\cdot}152(7)$ Å, $\beta = 108{\cdot}8°(1')$, $Z = 4$. A total of 1600 non-zero reflections were collected with a four-circle Syntex automatic diffractometer, using Cu-K_α radiation. The P–P–P triangle was found readily from the Patterson map, and an initial structure factor calculation, including all phosphorus atoms all nitrogen atoms, and one oxygen, gave an R factor of 60%. The remaining atoms, except the hydrogens, were found from a difference Fourier. With isotropic least-squares refinement, R dropped to 14%, and total anisotropic refinement reduced the R factor to 7·8%. A representation of the molecular structure is shown in the Figure.



FIGURE

In the crystal, P(1) and N(2) lie on the two-fold axis at $x = 0$, $z = \frac{1}{4}$. Thus, only half of the molecule is in the asymmetric unit. The phosphazene ring is approximately planar with a slight distorted boat deformation. The greatest deviations from the least-squares plane are for P(2′) and N(1), which are 0·076 Å above the plane, and for N(1′) and P(2), which are 0·076 Å below the plane. Bond lengths and angles of interest are shown in the Table. Of the three crystallographically independent P–N bond distances, two [P(1)–N(1) and P(2)–N(2)] are essentially identical, but the third [P(2)–N(1)] is longer by an amount which marginally exceeds the standard deviation. The average P–N distance of 1·572 Å is in good agreement with the value for (I) and for hexachlorocyclotriphosphazene (III).[4] The O–P–O angle in (II) is the same as the Cl–P–Cl angle in (III), and this probably corresponds to an unstrained external ring angle. In contrast to this, the O–P–O angle in the five-membered ring of (I) is 97°.[3] The average angle of twist between the phenyl rings in (II) is 41°, and the long axis of each biphenyl group is twisted 48° to the phosphazene ring plane with the biphenyl unit at P(1) twisted in the opposite direction to the other two units.

Bond lengths (Å)

P(1)–N(1) = 1·568(7)	P(1)–O(1) = 1·581(4)
P(2)–N(1) = 1·582(6)	P(2)–O(2) = 1·584(5)
P(2)–N(2) = 1·566(4)	P(2)–O(3) = 1·586(5)

Bond angles (°)

N(1)–P(1)–N(1′) = 118·6(0·3)	O(1)–P(1)–O(1i) = 103·0(0·2)
N(2)–P(2)–N(1) = 118·3(0·2)	O(2)–P(2)–O(3) = 102·4(0·3)
P(1)–N(1)–P(2) = 120·8(0·3)	N(1)–P(1)–O(1) = 104·1(0·3)
P(2)–N(2)–P(2′) = 121·2(0·2)	N(1)–P(2)–O(2) = 105·9(0·3)
	N(2)–P(2)–O(3) = 106·8(0·2)

The most striking differences between (I) and (II) are the greater bulkiness of the side units in (II) and the different orientations of the side groups. In (I), the *o*-dioxyphenyl groups are oriented nearly perpendicular to the phosphazene ring, whereas the seven-membered rings in (II) are appreciably twisted. In the crystal structure of (I), the cavities between the side groups can accommodate included guest compounds, but in crystals of (II) these spaces are essentially filled by the biphenyl groups themselves and the molecular packing arrangement further precludes the formation of channel clathrates. Thermal polymerization of (II) appears to be inhibited because the side-group orientation would cause serious steric repulsions in an open chain or macrocyclic polymer.

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