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Facile synthesis, spectroscopic characterization, and crystal structures of dioxybiphenyl bridged cyclotriphosphazenes

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1. Introduction

Cyclotriphosphazenes, which are an important family of inorganic heterocyclic ring systems [1,2], have been attracted a great attention in the past decades [3–5]. This is because that on one hand, they have a wide range of properties and applications such as liquid crystals [6], electrical conductivity [7], flame-retardant materials [8,9], as well as biomedical activity [10-13]; on the other hand, they have a rich synthetic chemistry. For instance, various substituted cyclotriphosphazenes are very stable and easily prepared by nucleophilic substitution reactions of hexachlorocyclotriphosphazene (1) with a variety of organic and organometallic reagents [14,15].

Notably, the difunctional reagents such as diols and diamines can react with (1) to give a great variety of different cyclotriphosphazene derivatives. If only one of two functional groups reacts with (1) an open-chain derivative is obtained; meanwhile, utilization of two functional groups may give rise to the spiro, ansa, and double-bridged derivatives [16]. Among these derivatives, the double-bridged cyclotriphosphazenes bearing the dialkyl groups have been widely studied [17-22]. However, few diaromatic-bridged cyclotriphosphazenes have been prepared [23-28], only three crystal structures of which are reported to date [26–28].

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ABSTRACT

Three dioxybiphenyl bridged cyclotriphosphazenes (2-4) containing the (1,1'-biphenyl)-4,4'-diol (BPD), 4,4'-sulfonyldiphenol (SDP), and 4,4'-(propane-2,2-diyl)diphenol (PDP) groups were prepared from the nucleophilic substitution reaction of hexachlorocyclotriphosphazene (1) with three different diphenols, respectively. All these compounds were structurally characterized using ESI-MS, FTIR, and NMR (¹H, 31 P) spectroscopies. Moreover, the molecular structures of **2–4** were unequivocally confirmed by X-ray crystallography, in which the two cyclotriphosphazene (N₃P₃) rings are linked via a dioxybiphenyl bridge. © 2017 Elsevier Ltd. All rights reserved.

> Based on the aforementioned information, we recently carried out the substitution reaction between hexachlorocyclotriphosphazene (1) and three kinds of dinucleophilic reagents such as (1,1'-biphenyl)-4,4'-diol (BPD), 4,4'-sulfonyldiphenol (SDP), and 4,4'-(propane-2,2-diyl)diphenol (**PDP**) to give the dioxybiphenyl bridged cyclotriphosphazenes (2-4) in 75-79% yields, respectively. In this work, we report on the synthesis, spectroscopic characterization, and X-ray analysis of the BPD-bridged (2), SDP-bridged (3), and PDP-bridged (4) cyclotriphosphazenes. While 4 was synthesized before [23,24], its crystal structure is obtained for the first time.

2. Experimental

2.1. Materials and methods

Hexachlorocyclotriphosphazene (1) was obtained from Zibo Lanyin Chemical Co., Ltd., and purified by recrystallization from *n*-heptane prior to use. (1,1'-biphenyl)-4,4'-diol (**BPD**), 4,4'-sulfonyldiphenol (SDP), and 4,4'-(propane-2,2-diyl)diphenol (PDP) were purchased from Aladdin Industrial Corporation, China. Sodium hydride (NaH), sodium sulfate (Na₂SO₄), tetrahydrofuran (THF), petroleum ether, dichloromethane (CH₂Cl₂), ethyl ether (Et₂O) and *n*-heptane were purchased from Tianjin Guangfu Fine Chemical Research Institute, China. THF was distilled from sodium benzophenone ketal prior to use, and the other chemicals and reagents were used as received.





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¹H and ³¹P{H} NMR spectra were recorded by a BrukerAvance-IIITM 400 MHz spectrometer using tetramethylsilane (TMS) and 85% H₃PO₄ as the internal standard, respectively. FTIR spectrum was measured by a Nicolet iS50 Fourier transform infrared spectrophotometer at room temperature using KBr disk method. Melting points were determined on a YRT-3 apparatus and are uncorrected. Mass spectrometric studies (ESI-MS) were carried out on Finnigan LCQ-Advantage spectrometer.

2.2. Synthesis of BPD-bridged cyclotriphosphazene (2)

A THF (100 mL) solution of hexachlorocyclotriphosphazene (1) (34.8 g, 0.10 mol) was allowed to react with NaH (60% in mineral oil, 4.0 g) at -20 °C under nitrogen atmosphere. A THF (100 mL) solution of (1,1'-biphenyl)-4,4'-diol (BPD) (9.3 g, 0.05 mol) was added dropwise into the above suspension over 2 h with agitation, followed by stirring for 12 h at -20 °C. Then, the reaction solution was warmed to room temperature and stirred for 2 h. After the reaction was completed, the reaction mixture was filtered and separated. The resulting organic layer was washed repeatedly with deionized water, dried with anhydrous Na₂SO₄, and concentrated on a rotatory evaporator under reduced pressure. The collected residue was further purified by silica gel column chromatography eluting with CH_2Cl_2 /petroleum ether (1:1, v/v) to obtain the white solid as the target product (2). Yield 32.1 g (79%). M.p.: 160.8-162.2 °C. ESI-MS (CH₂Cl₂, positive mode): 808.6061 [M+H]⁺ for C₁₂- $H_8^{35}Cl_8^{37}Cl_2N_6O_2P_6$ (calcd. 808.6034). FTIR (KBr disk): v 1175 and 1150 (P=N), 968 (P-O-C), 574 and 498 (P-Cl) cm⁻¹. ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.59 (d, I_{HH} = 8.4 Hz, 4H, PhH-b), 7.35 (dd, J_{HH} = 8.4 Hz, J_{PH} = 2.0 Hz, 4H, PhH-a) ppm. ³¹P{H}-NMR (162 MHz, CDCl₃, 85% H₃PO₄): δ 22.46 (d, J_{PP} = 61.1 Hz, 2P, ClPCl), 12.23 (t, J_{PP} = 61.1 Hz, 1P, ClPO) ppm.

2.3. Synthesis of SDP-bridged cyclotriphosphazene (3)

Compound **3** was prepared by a similar procedure to that used for compound **2**, except that 4,4'-sulfonyldiphenol (**SDP**) (12.5 g, 0.05 mol) was used instead of (1,1'-biphenyl)-4,4'-diol (**BPD**) (9.3 g, 0.05 mol). Compound **3** was obtained as a white solid. Yield 33.1 g (76%). M.p.: 168.3–169.0 °C. ESI-MS (CH₂Cl₂, positive mode): 872.5667 [M+H]⁺ for C₁₂H₃⁸⁵Cl₃³⁷Cl₂N₆O₄P₆S (calcd. 872.5653). FTIR (KBr disk): *v* 1174 and 1150 (P=N), 1103 (S=O), 967 (P-O-C), 592 and 519 (P-Cl) cm⁻¹. ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.00 (d,

*J*_{*HH*} = 8.4 Hz, 4H, Ph*H*-b), 7.42 (dd, *J*_{*HH*} = 8.4 Hz, *J*_{*PH*} = 2.0 Hz, 4H, Ph*H*-a) ppm. ³¹P{H}-NMR (162 MHz, CDCl₃, 85% H₃PO₄): δ 22.55 (d, *J*_{*PP*} = 62.9 Hz, 2P, ClPCl), 11.74 (t, *J*_{*PP*} = 62.9 Hz, 1P, ClPO) ppm.

2.4. Synthesis of PDP-bridged cyclotriphosphazene (4)

Compound **4** was prepared by a similar procedure to that used for compound **2**, except that 4,4'-(propane-2,2-diyl)diphenol (**PDP**) (11.4 g, 0.05 mol) was used instead of (1,1'-biphenyl)-4,4'-diol (**BPD**) (9.3 g, 0.05 mol). Compound **4** was obtained as a white solid. Yield 31.9 g (75%). M.p.: 114.0–114.9 °C. ESI-MS (CH₂Cl₂, positive mode): 850.6641 [M+H]⁺ for C₁₅H₁₅³⁴Cl₈³⁷Cl₂N₆O₂P₆ (calcd. 850.6504). FTIR (KBr disk): *v* 1180 and 1150 (P=N), 967 (P–O–C), 591 and 515 (P–Cl) cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆, TMS): δ 7.15 (d, *J*_{HH} = 8.4 Hz, 4H, PhH-b), 7.05 (d, *J*_{HH} = 8.4 Hz, 4H, PhH-a), 1.59 (s, 6H, CH₃-c) ppm. ³¹P{H}-NMR (162 MHz, DMSO-*d*₆, 85% H₃PO₄): δ 22.34 (d, *J*_{PP} = 60.4 Hz, 2P, ClPCl), 12.35 (t, *J*_{PP} = 62.9 Hz, 1P, ClPO) ppm.

2.5. X-ray structure determination

Single crystals of **2–4** suitable for X-ray diffraction analysis were grown by slow evaporation of the CH₂Cl₂/hexane solution at 5 °C. Single crystals of **2–4** were mounted on a Rigaku MM-007 CCD diffractometer. Data were collected at 278 K for **2**, 113 K for **3**, and 272 K for **4** by using a graphite monochromator with Mo-K α radiation ($\lambda = 0.71073$ Å) in the ω - φ scanning mode. Data collection, reduction and absorption correction were performed by CRYSTALCLEAR program [29]. The structure was solved by direct methods using the SHELXS-97 program [30] and refined by full-matrix least-squares techniques (SHELXL-97) on F^2 [30]. Hydrogen atoms were located using the geometric method.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

As displayed in Scheme 1, the nucleophilic substitution reactions of starting hexachlorocyclotriphosphazene (1) with 0.5 equivalent diphenols such as (1,1'-biphenyl)-4,4'-diol (**BPD**), 4,4'sulfonyldiphenol (**SDP**), and 4,4'-(propane-2,2-diyl)diphenol (**PDP**), resulted in the formation of three dioxybiphenyl bridged cyclotriphosphazenes (2–4) in 75–79% yield, respectively.



Scheme 1. Preparation of the target compounds 2-4.

All three compounds **2–4** are air-stable white solids and soluble in the polar organic solvents such as THF, CH_2Cl_2 , $CHCl_3$, and acetone etc. Their molecular structures have been characterized by means of ESI-MS, FTIR, and NMR (¹H, ³¹P) techniques.

As shown in Fig. 1, the positive mode ESI-MS spectra of **2–4** give the apparent quasimolecular ion peak $[M+H]^+$ at m/z 808.6061 (cacld. 808.6034), 872.5667 (calcd. 872.5653), and 850.6641 (cacld. 850.6504), respectively, which are well in accord with the corresponding molecular formula of $C_{12}H_8^{35}Cl_8^{37}Cl_2N_6O_2P_6$ (**2**), $C_{12}H_8^{35}-Cl_8^{37}Cl_2N_6O_4P_6S$ (**3**), and $C_{15}H_{14}^{35}Cl_8^{37}Cl_2N_6O_2P_6$ (**4**).

The FTIR spectra of all these compounds feature some absorption bands at 1175/1150 (P=N) and 574/498 (P-Cl) cm⁻¹ for **2**, 1174/1150 (P=N) and 592/519 (P-Cl) cm⁻¹ for **3**, as well as 1180/1150 (P=N) and 591/515 (P-Cl) cm⁻¹ for **4**, attributed to

the typical cyclotriphosphazene ring [31]. Meanwhile, there is an additional absorption band at 1103 cm^{-1} for the S=O group in the IR spectrum of compound (3). The appearance of a new band at 968 (2), 967 (3), and 967 (4) cm⁻¹, which is assigned to the P–O–C groups, indicates that precursor (1) successfully reacted with different diols, BPD, SDP, and PDP.

As displayed in Fig. 2, the ¹H NMR spectra of **2**–**4** in the region of 8.0–7.0 ppm display two groups of the similar proton signals at 7.59/7.35 (**2**), 8.00/7.42 (**3**), and 7.15/7.05 (**4**) ppm, which can be attributed to two *ortho*-position protons (marked as H-b and H-a) of their disubstituted phenyl rings. Additionally, the ¹H NMR spectrum of **4** show a sharp singlet at 1.59 ppm for its methyl group.



Fig. 1. ESI-MS spectra of (A) BPD-bridged (2) and (B) SDP-bridged (3) cyclotriphosphazenes in CDCl₃ solution, and PDP-bridged (4) cyclotriphosphazene in DMSO-d₆ solution.



Fig. 2. ¹H NMR spectra of (A) BPD-bridged (2) and (B) SDP-bridged (3) cyclotriphosphazenes in CDCl₃ solution, and PDP-bridged (4) cyclotriphosphazene in DMSO-d₆ solution.



Fig. 3. ³¹P{¹H} NMR spectra of (A) BPD-bridged (2) and (B) SDP-bridged (3) cyclotriphosphazenes in CDCl₃ solution, and PDP-bridged (4) cyclotriphosphazene in DMSO-d₆ solution.

 Table 1

 ³¹P{¹H} NMR parameters for compounds 2-4.

Compounds	Chemical shifts (ppm)		$^{2}J_{PP}$ (Hz)
	PCl ₂	P(OCl)	
2	22.46	12.23	61.1
3	22.55	11.74	62.9
4	22.34	12.35	60.4

Notably, the proton-decoupled ³¹P NMR spectra of **2–4** are depicted in Fig. 3. The corresponding chemical shifts and the phosphorus-phosphorus coupling constants (${}^{2}J_{PP}$) are summarized in Table 1. The proton-decoupled ³¹P NMR spectra of **2–4** are observed as the expected A₂X spin system, the assignment of which is as follows: one doublet (2P) at *ca.* 22 ppm for the ClPCl group and one triplet (1P) at *ca.* 12 ppm for the OPCl moiety. This observation is due to the different environments for the two different phosphorus nuclei on the cyclotriphosphazenes.

3.2. Crystal structures

The molecular structures of compounds **2–4** have been further confirmed by X-ray crystallography, as depicted in Figs. **4–6**. The crystallographic parameters, data collection and structure refinement of are summarized in Table 2. The selected bond lengths and angles are listed in Table 3.

It can be seen from Figs. 4–6 that the solid-state molecules of **2**– **4** contain two cyclotriphosphazene (N_3P_3) rings joined together through a dioxybiphenyl moiety, which are very similar with those of the previously reported double-bridged analogues [26–28].

As depicted in Fig. 4, compound **2** is centrosymmetric with the midpoint of the C(4)-C(4A) bond distance as an inversion center. The central (1,1'-biphenyl)-4,4'-diol (**BPD**) group is almost perpen-

dicular to the cyclotriphosphazene (N_3P_3) unit, in which the two N_3P_3 rings are parallel and are in *trans*-position relative to the coplanar phenyl rings. This is reflected by the following facts: (i) the dihedral angle between the two N_3P_3 rings [P(1)-N(3)/P(1A)-N(3A) planes] is 0°; (ii) the angle between the two phenyl rings [C(1)-C(6)/C(1A)-C(6A) planes] is 0°; (iii) the angle between the phenyl ring and the N_3P_3 ring is 77.2°.

As shown in Figs. 5 and 6, compounds 3 and 4 are the asymmetric molecules, possibly because of the asymmetric property of the central 4,4'-sulfonyldiphenol (SDP) and 4,4'-(propane-2,2-diyl) diphenol (**PDP**) units. This can be verified from the dihedral angles between two phenyl rings [C(1)-C(6)/C(7)-C(12)] planes for **3** and C (1)-C(6)/C(10)-C(15) planes for **4**] are 77.1° and 100.6°, respectively. In the case of **3**, both of the N₃P₃ rings are almost perpendicular to only one phenyl ring of the central SDP unit; meanwhile, the former are closely parallel to each other and are in *trans*-position relative to the latter. These observations may be explained from the corresponding dihedral angles between the planes P(1)-N(3)/C(1)-C(6) (109.0°), the ones P(4)-N(6)/C(1)-C(6) (86.3°), and the ones P(1)-N(3)/P(4)-N(6) (24.4°). But for 4, only one N₃P₃ ring is closely perpendicular to the phenyl ring linked to it through the O(1) atom, together with the dihedral angles between the planes P(1)-N(3)/C(1)-C(6) (73.1°). Furthermore, two N₃P₃ rings are almost perpendicular to each other with the angle between the planes P(1)-N(3)/P(4)-N(6) (82.3°) in 4.

As can be obtained from Table 3, the mean P-N bond distances in **2** (1.576 Å), **3** (1.584 Å), and **4** (1.573 Å) are very close to those reported in the similar double-bridged species with the formula of $[N_3P_3Cl_5-(1,4-OC_6H_4O)-N_3P_3Cl_5]$ (1.580 Å) [26], $[N_3P_3Cl_5-(2,4-OC_4H_2N_2O)-N_3P_3Cl_5]$ (1.579 Å) [27], and $[N_3P_3Cl_5-(1,4-NHC_4H_8-NH)-N_3P_3Cl_5]$ (1.573 Å) [28]. Such an observation for the small change of the P-N bonds may be reasonably explained from the small difference in the electronegativity of the P(OCI) and PCl₂ centers [32]. It is noted that the P–CI bond distances pointing to the



Fig. 4. Molecular structure of 2 with thermal ellipsoid at 30% probability.

35



Fig. 5. Molecular structure of 3 with thermal ellipsoid at 30% probability.

phenyl moiety are slightly longer than the corresponding bond lengths away from the phenyl rings. For example, it can be apparently seen from Table 3 and Fig. 4 that the P(2)-Cl(2) [1.9874(12) Å] and P(3)-Cl(5) [1.9887(12) Å] bond distances are a bit longer than the respective P(2)-Cl(3) [1.9866(12) Å] and P(3)-Cl(4) [1.9814 (11) Å] bond lengths in the crystal structure of **2**. A straightforward explanation is that the lattice effects should be responsible for the small difference of the P–Cl bonds around the PCl₂ centers [26].

Meanwhile, the conformations of the cyclotriphosphazene (N_3P_3) rings in **2–4** are different, probably owing to the distinction in the planarity of their N_3P_3 rings [26]. As displayed in Fig. 4, the observed conformation of the N_3P_3 rings in **2** is the same envelope for the [P(1)-N(3)] and [P(1A)-N(3A)] rings with torsion angles ranging from $-6.2(3)^\circ$ to $7.6(3)^\circ$. As depicted in Figs. 5 and 6, the configurations of the cyclotriphosphazene rings in **3** and **4** approach an envelope for the [P(1)-N(3)] ring with the respective torsion angles $[-9.2(4)^\circ$ to $12.7(4)^\circ$ for **3**; $-11.9(3)^\circ$ to $7.3(3)^\circ$ for **4**] and a chair for the [P(4)-N(6)] ring with the corresponding torsion angles $[-19.9(4)^\circ$ to $27.6(4)^\circ$ for **3**; $-15.7(3)^\circ$ to $15.9(3)^\circ$ for **4**].

In addition, the solid-state structures of **2–4** were mainly stabilized by means of van der Waals' interactions among the molecules and the π - π stacking interactions among the adjacent phenyl rings and the surrounding cyclotriphosphazene rings in their crystal packing diagrams (as shown in Figs. 1S–3S for Supporting Information).

4. Conclusions

In this paper, we have described three dioxybiphenyl cyclotriphosphazenes (**2–4**) that are easily prepared from the facile substitution reaction of hexacyclotriphosphazene (**1**). All the compounds are fully characterized by MS, IR and NMR spectroscopies, and especially by X-ray crystallography. Notably, it should be pointed out that three single crystals of **2–4** were obtained for the first time, allowing for the crystal structures to be reported which is of interest since few structures of this class of bridged phosphazenes have appeared. Currently, our ongoing efforts are focused on the further functionality of **2–4** as a kind of precursors to afford some functional cyclotriphosphazene derivatives with highly flame retardancy [**33**].



Fig. 6. Molecular structure of 4 with thermal ellipsoid at 30% probability.

 Table 2

 Crystal data and structural refinements details for 2–4.

Compound	1	2	3
Empirical formula	$C_{12}H_8Cl_{10}N_6O_2P_6$	$C_{12}H_8Cl_{10}N_6O_4P_6$	C ₁₅ H ₁₄ Cl ₁₀ N ₆ O ₂ P ₆
Formula weight	808.56	872.62	850.64
T (K)	278	113(2)	272
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n	P2(1)/c
a (Å)	9.1750(4)	23.661(5)	22.6418(9)
b (Å)	14.5705(6)	7.9578(16)	8.5160(3)
<i>c</i> (Å)	11.7829(5)	33.582(7)	18.5529(7)
α (°)	90	90	90
β (°)	108.0850(10)	91.46(3)	113.1590(10)
γ (°)	90	90	90
V (Å ³)	1497.37(11)	6321(2)	3289.1(2)
Ζ	4	8	4
D_{calc} (g cm ⁻³)	1.793	1.834	1.718
μ (mm ⁻¹)	1.278	1.286	1.168
F (000)	796	3440	1688
Crystal size (mm)	0.34x0.26x0.24	0.20x0.18x0.12	0.46x0.38x0.28
$\theta_{\min}, \theta_{\max}$ (°)	2.84, 27.52	1.72, 25.02	2.92, 28.35
Reflections collected/unique	13408/3420	42325/10953	31354/8205
R _{int}	0.0286	0.0773	0.0348
hkl range	$-11 \le h \le 11$	$-28 \le h \le 27$	$-30 \le h \le 30$
-	$-18 \le k \le 18$	$-8 \le k \le 9$	$-11 \le k \le 9$
	$-15 \le l \le 14$	$-39 \le l \le 39$	$-24 \le l \le 24$
Completeness to θ_{max} (%)	99.4	98.1	99.6
Data/restraints/parameters	3420/0/163	10953/0/703	8205/0/354
Goodness-of-fit (GOF) on F^2	1.030	1.063	1.029
$R_1/wR_2 \left[I > 2\sigma(I) \right]$	0.0453/0.1176	0.0584/0.1217	0.0495/0.1124
R_1/wR_2 (all data)	0.0552/0.1277	0.0825/0.1348	0.0763/0.1272
Largest difference peak/hole (e A^{-3})	0.35/-0.59	0.50/-0.59	0.59/-0.62

Table 3	
Selected bond lengths (Å) and angles (°) for $\textbf{2-4}.$	

Compound 2			
P(1) - O(1)	1.571(2)	P(1) - N(1)	1.584(3)
P(1) - CI(1)	1.9872(12)	P(1) - N(3)	1.576(2)
P(2) - CI(2)	1.9874(12)	P(2) = N(1)	1.571(3)
P(2) - CI(3)	1.9866(12)	P(2) - N(2)	1.577(3)
P(3) - CI(4)	1.9814(11)	P(3) - N(2)	1.575(2)
P(3) - CI(5)	1.9887(12)	P(3) - N(3)	1.570(2)
O(1) - C(1)	1.419(4)	C(4)-C(4A)	1.493(6)
N(3) - P(1) - N(1)	117.09(13	P(2) - N(1) - P(1)	121.61(15)
N(1)-P(2)-N(2)	119.31(13)	P(3) - N(2) - P(2)	120.25(17)
N(3) - P(3) - N(2)	118.94(13)	P(3) - N(3) - P(1)	122.36(14)
O(1) - P(1) - CI(1)	98.27(9)	C(1) - O(1) - P(1)	118.35(17)
CI(3) - P(2) - CI(2)	100.89(5)	C(3) - C(4) - C(4A)	122.3(3)
CI(4) - P(3) - CI(5)	101.16(5)	C(3) - C(4) - C(5)	116.3(3)
C(2) - C(1) - C(6)	121.1(3)	C(5) - C(4) - C(4A)	121.3(3)
Compound 3			
P(1) - Cl(1)	1.9932(18)	P(4)-Cl(6)	2.0181(19)
P(1)-Cl(2)	2.0045(19)	P(5)-Cl(8)	1.9989(19)
P(2)-Cl(4)	1.9918(18)	P(5)-Cl(7)	2.0000(18)
P(2)-Cl(3)	2.0049(18)	P(6)-Cl(10)	1.9922(19)
P(3)-Cl(5)	1.9941(17)	P(6)-Cl(9)	2.0134(19)
P(3)-O(1)	1.591(3)	P(4)-O(4)	1.577(3)
P(1)-N(3)	1.587(4)	P(4)-N(4)	1.581(4)
P(1) - N(1)	1.591(4)	P(4)-N(6)	1.587(4)
P(2)-N(1)	1.571(4)	P(5)–N(5)	1.579(4)
P(2)-N(2)	1.581(4)	P(5)-N(4)	1.596(4)
P(3)-N(2)	1.580(4)	P(6)-N(5)	1.586(4)
P(3)-N(3)	1.596(4)	P(6)-N(6)	1.592(4)
O(1) - C(1)	1.426(5)	O(4) - C(10)	1.415(5)
S(1)-O(3)	1.448(4)	S(1)-C(7)	1.777(5)
S(1) - O(2)	1.451(3)	S(1)-C(4)	1.784(5)
N(3)-P(1)-N(1)	118.1(2)	N(4)-P(4)-N(6)	117.7(2)
N(1)-P(2)-N(2)	118.7(2)	N(5)-P(5)-N(4)	117.9(2)
N(2)-P(3)-N(3)	116.93(19)	N(5)-P(6)-N(6)	118.5(2)
P(2)-N(1)-P(1)	120.9(2)	P(4)-N(4)-P(5)	120.8(3)
P(3)-N(2)-P(2)	122.4(3)	P(5)-N(5)-P(6)	121.5(2)
P(1)-N(3)-P(3)	121.6(2)	P(4) - N(6) - P(6)	118.6(2)
Cl(1)-P(1)-Cl(2)	101.89(8)	CI(8) - P(5) - CI(7)	101.83(8)
Cl(4) - P(2) - Cl(3)	102.45(8)	CI(10) - P(6) - CI(9)	101.07(9)
O(1) - P(3) - CI(5)	98.05(13)	O(4) - P(4) - CI(6)	103.20(13)
C(1) - O(1) - P(3)	118.8(3)	C(10) - O(4) - P(4)	124.6(3)
O(3) - S(1) - O(2)	119.3(2)	C(7) - S(1) - C(4)	104.5(2)
Compound 4			
P(1)-Cl(1)	1.9915(13)	P(4)-Cl(6)	1.9957(14)
P(2)-Cl(4)	1.9917(13)	P(5)-Cl(9)	1.9870(13)
P(2)-Cl(5)	1.9868(14)	P(5)-Cl(10)	1.9846(16)
P(3)-Cl(2)	1.9877(16)	P(6)-Cl(7)	1.9925(12)
P(3)-Cl(3)	1.9780(14)	P(6)-Cl(8)	1.9914(13)
P(1) - O(1)	1.573(2)	P(4) - O(2)	1.558(2)
P(1) - N(1)	1.584(3)	P(4) - N(4)	1.580(3)
P(1) - N(3)	1.577(3)	P(4) - N(6)	1.578(3)
P(2) - N(1)	1.570(3)	P(5) - N(5)	1.575(3)
P(2) - N(2)	1.571(3)	P(5) - N(6)	1.559(3)
P(3) - N(2)	1.569(3)	P(6) - N(4)	1.561(3)
P(3) - N(3)	1.569(3)	P(6) - N(5)	1.576(3)
O(1) - C(1)	1.430(4)	O(2) - C(13)	1.420(3)
C(4) - C(7)	1.540(4)	C(7) = C(9)	1.533(5)
U(7) = U(8) V(2) = D(1) = V(1)	1.538(4)	U(7) = U(10) V(6) = D(4) = V(4)	1.531(4) 11756(15)
N(3) = F(1) = N(1) N(1) = P(2) = N(2)	11/.04(14) 110 20(1E)	N(0) = P(4) = N(4) N(6) = P(5) = N(5)	117.30(13)
N(1) = F(2) = N(2) N(3) = D(3) = N(3)	119.32(13)	N(0) = F(3) = N(3) N(4) = D(6) = N(5)	110.31(10)
D(2) - F(3) - IN(2) D(2) - N(1) - D(1)	10.70(10)	D(G) = D(A) = D(A)	115.14(15)
P(3) = N(2) = F(1)	121.33(17)	P(5) = N(5) = P(6)	120.71(10)
P(3) = N(2) = F(2) P(3) = N(3) = P(1)	120.33(10)	P(5) = N(6) = P(4)	120.40(18)
O(1) - P(1) - O(1)	97 84(10)	O(2) - P(4) - Cl(6)	102.95(10)
C (5)-P(2)-C (4)	101 98(6)	Cl(10) = P(5) = Cl(9)	101.07(6)
C[(3)-P(3)-C[(2)]	101.46(7)	Cl(8) - P(6) - Cl(7)	100.50(5)
C(1) = O(1) = P(1)	118.75(19)	C(13) - O(2) - P(4)	121.15(18)
C(9) - C(7) - C(8)	107.9(3)	C(10)-C(7)-C(4)	109.4(2)
	×- /		× /

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Appendix A. Supplementary data

CCDC 1482724, 1482729 and 1482728 contains the supplementary crystallographic data for **2**, **3** and **4**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac. uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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