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Synthesis and structural studies (^{1}H, ^{13}C, ^{31}P NMR and X-ray) of new C-bonded cyclotriphosphazenes with heterocyclic substituents from novel phosphinic acid derivatives

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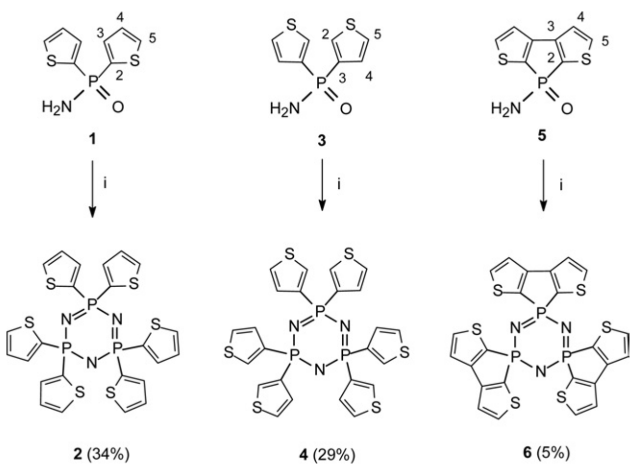
Three new C-bonded cyclotriphosphazenes, [N_3P_3(2-thienyl)$_6$], **2**, [N_3P_3(3-thienyl)$_6$], **4**, and [N_3P_3(3,3′-bithienyl-2,2′-ylene)$_3$], **6**, have been prepared by two new synthetic procedures and are the first examples of non-spiro and trispirocyclotriphosphazene derivatives composed of thiophene and 3,3′-dithiophene substituents, respectively. Their ^{1}H, ^{13}C and ^{31}P NMR parameters are given. The solid state structures of **2**, **4** and **6** have been determined by X-ray crystallography.

Introduction

As compared with cyclotriphosphazenes (CTP) having P–O or P–N side groups, cyclotriphosphazenes with substituents linked to the skeleton *via* P–C bonds have been much less described. However, both higher chemical and thermal stabilities could be expected for this type of CTP, as already known for polyphosphazenes.[1–3] We describe here a new class of stable hexasubstituted symmetric cyclotriphosphazenes having P–C side groups (**2**,**4** and **6**; Scheme 1), which could be considered as potential materials precursors. Indeed, in these cyclotriphosphazenes, the phosphorus substituents are either free-rotating thienyl groups around the P–C bonds or rigidified bithienyl groups. These compounds, thanks to their geometrical properties, could lead by coordination of the free heteroatoms with transition metals to stacked structures (Fig. 1) with potentially interesting electronic properties.

We have thus developed synthetic methods that allowed us to prepare the first examples of non-spiro and trispirocyclotriphosphazenes with heterocyclic substituents attached to the P_3N_3 ring by phosphorus–carbon bonds, respectively the hexa(2-thienyl)- and hexa(3-thienyl)cyclotriphosphazenes **2** and **4** and the tri(3,3′-bithienyl-2,2′-ylene)cyclotriphosphazene **6** (Scheme 1).



Scheme 1 Synthesis of cyclotriphosphazenes **2**, **4** and **6**: (*i*) 1.2 PPh_3/CCl_4/Et_3N in CH_2Cl_2, 5 h, 40 °C.

Results and discussion

The nucleophilic substitution of hexahalogenocyclotriphosphazene $N_3P_3X_6$ (X = F, Cl) constitutes the more usual route to prepare symmetric cyclotriphosphazenes substituted by aromatic side groups through P–O or P–N bonds.[4,5] This method failed to produce the hexaphenylcyclotriphosphazene $N_3P_3Ph_6$,[6] giving only partially substituted products when $N_3P_3Cl_6$ or $N_3P_3F_6$ are allowed to react with nucleophilic species like phenyl Grignard reagent[7] or phenyllithium.[8,9] For example, the reaction of phenyllithium with $N_3P_3F_6$ leads to the creation of no more than five P–C bonds to give $N_3P_3FPh_5$.[8]

Accordingly, we applied another pathway, previously used in our laboratory[10] to form the phosphazenic ring, to the syntheses of hexa(2-thienyl)cyclotriphosphazene (**2**),

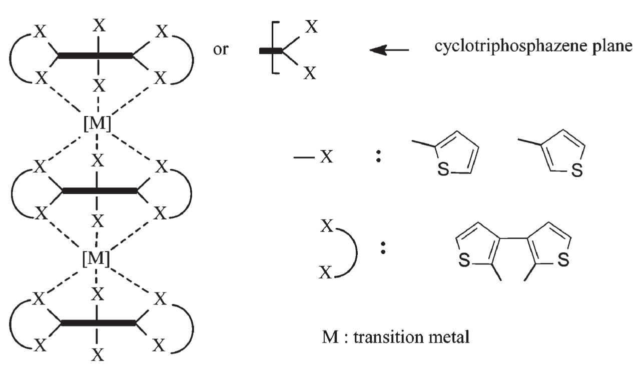


Fig. 1

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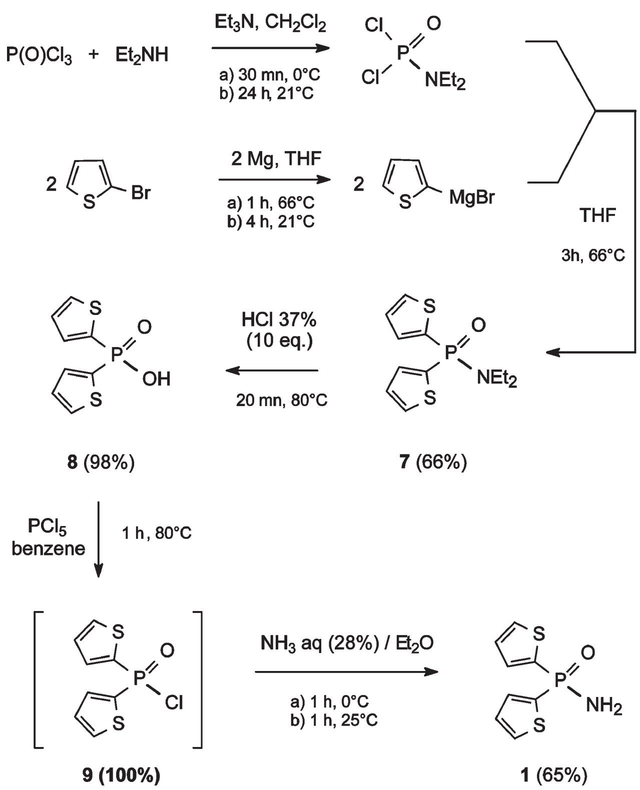
hexa(3-thienyl)cyclotriphosphazene (**4**) and tri(3,3′-bithienyl-2,2′-ylene)cyclotriphosphazene (**6**). This route (Scheme 1) involves reaction of the appropriate phosphinic amide with the Appel reagent[11] (a mixture of triphenylphosphine, carbon tetrachloride and triethylamine).

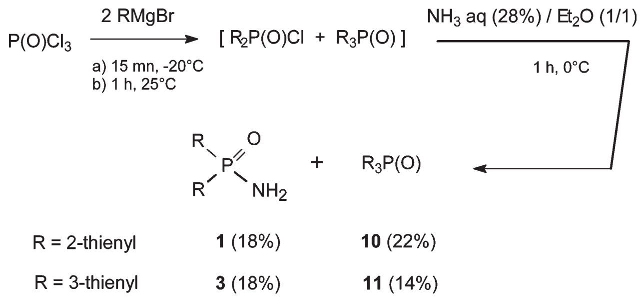
Synthesis of hexa(2-thienyl)cyclotriphosphazene (2)

Di(2-thienyl)phosphinic amide (**1**) has been prepared for the first time according to the multistep synthesis described in Scheme 2. Firstly, the *N*,*N*-diethylphosphinic amide **7** was obtained (66%) by reaction of dichloro-*N*,*N*-diethylphosphinic amide[12] with the Grignard reagent of 2-bromothiophene.[13] Then, in the presence of concentrated hydrochloric acid, it gave di(2-thienyl)phosphinic acid (**8**), which was easily recovered by filtration of the reaction mixture (98%). The phosphinic acid **8** itself led to di(2-thienyl)phosphinic amide (**1**) in two steps. The reaction of compound **8** with phosphorus pentachloride gave the di(2-thienyl)phosphinic chloride **9**, which has not been isolated but directly added to a biphasic 1:1 diethyl ether–aqueous ammonia mixture to yield di(2-thienyl)-phosphinic amide (**1**), recovered by column chromatography (65%). The reaction of **1** with the Appel reagent (Scheme 1) gave the expected cyclotriphosphazene **2** (34%), together with triphenylphosphine oxide.[11] *N*-Di(2-thienyl)phosphinyltriphenylphosphine imine [$Ph_3P{=}N{-}P(O)R_2$] and (chloromethyl)triphenylphosphonium chloride [$Ph_3PCH_2Cl^+$ Cl^-] were also obtained as by-products, as explained by the cyclisation reaction mechanism given by Appel *et al.*[11]

With the aim to reduce the number of steps needed to synthesise the di(2-thienyl)-phosphinic amide **1**, trichlorophosphine oxide was allowed to react with varying amounts of the Grignard reagent of 2-bromothiophene[13] in THF (Scheme 3). The reaction was followed by recording ^{31}P spectra of the reaction mixtures using conditions for quantitative measurements (see Experimental). At the same time, it was found that the ^{31}P signals of **1** and **10** were strongly dependent on solvent and that the best way to identify them without ambiguity is



Scheme 2 Multistep synthesis of the di(2-thienyl)phosphinic amide **1**.



Scheme 3 New pathway for the synthesis of phosphinic amides **1** and **3**.

to record the spectra in gated-decoupling mode or without ^{1}H irradiation (Fig. 2). Another difference that may be useful to identify the ^{31}P signals of **1** and **10** is the value of $^{1}J_{PC}$, which is 154.0 Hz in **1** and 127.9 Hz in **10**. This coupling constant is accessible from the ^{13}C satellites of the ^{31}P signals.

The best conditions were found to be a stoichiometry of 1 equiv. of $P(O)Cl_3$ for 2 equiv. of the Grignard reagent at −20 °C. The intermediate halogenated compounds were not isolated and the crude product was directly added to a biphasic 1:1 mixture of diethyl ether and 28% aqueous ammonia. The phosphinic amide **1** and the tri(2-thienyl)phosphine oxide **10**[14,15] were readily separated by column chromatography. Some traces of an unidentified monothiophenic compound, detected from its ^{31}P signal, were also observed.

This new pathway allowed us to obtain the phosphinic amide **1** in two steps (yield of the one-pot procedure is 18%) instead of five steps for the usual synthesis described in Scheme 2 (overall yield 37%).

Synthesis of hexa(3-thienyl)cyclotriphosphazene (4)

The new phosphinic amide **3**, required to synthesise the cyclotriphosphazene **4**, was obtained according to the method reported in Scheme 3. As previously, the ^{31}P spectra of the organic phase show the presence of nearly equal amounts of the di(3-thienyl)phosphinic amide **3** and its corresponding phosphine oxide **11**.[15] The pure compounds were isolated with 18% (**3**) and 14% (**11**) yields.

The presence of the two compounds **3** and **11** in the reaction medium was ascertained by recording the ^{1}H coupled ^{31}P spectrum followed by a simulation of the corresponding $[ABC]_2X$ and $[ABC]_3X$ spin systems as previously. Then a selective irradiation of the two ^{31}P signals allowed the assignment of the ^{1}H signals to each of the compounds **3** and **11**. As for the couple **1** and **10**, their ^{31}P signals may also be identified from their

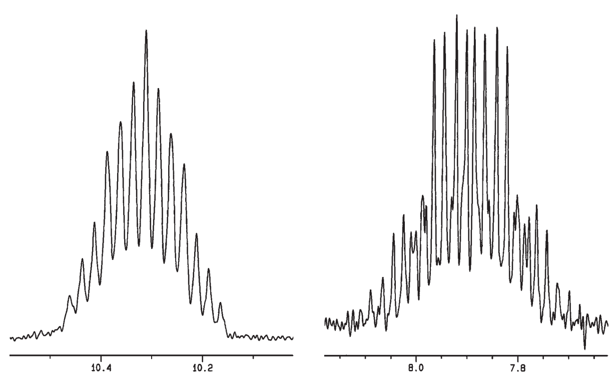


Fig. 2 ^{31}P NMR spectra of compounds **1** and **10** in $CDCl_3$, recorded without ^{1}H broad-band irradiation.

values of $^1J_{PC}$ (139.2 Hz for **3** and 113.9 Hz for **11**). No monothiophenic compounds were observed in this reaction. One may notice that the stoichiometry of **3** and **11** can be confirmed by the integral ratios of the two compounds in the mixture: if the concentration ratio [**11**]/[**3**] is found to be n in the ^{31}P spectrum, it has to be $3n/2$ in the ^{1}H spectrum of the same sample.

Finally, the new hexa(3-thienyl)cyclotriphosphazene **4** was obtained in 29% yield by the same procedure used for the hexa(2-thienyl)cyclotriphosphazene **2** (Scheme 1).

Synthesis of tri(3,3′-bithienyl-2,2′-ylene)cyclotriphosphazene (6)

Unfortunately, the preparation of the (3,3′-bithienyl-2,2′-ylene)phosphinic amide **5** with the new short procedure described in Scheme 3 was unsuccessful. Its synthesis required the previous multistep method represented in Scheme 4.

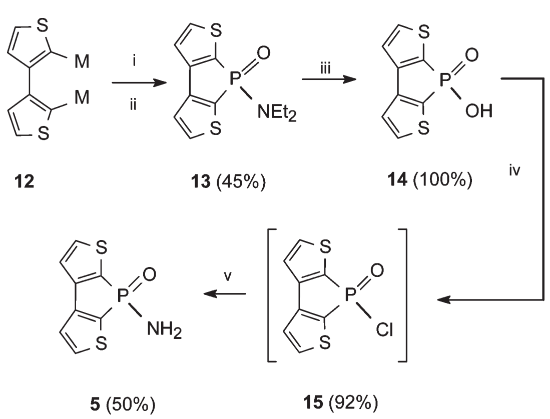
Step 1. Dichloro-*N*,*N*-diethylphosphinic amide[16] was allowed to react with the 3,3′-bithienyl-2,2′-dilithium salt.[17] The intermediate aminophosphine was not isolated but directly oxidised to give the *N*,*N*-diethylphosphinic amide **13** in 45% isolated yield.

Step 2. (3,3′-Bithienyl-2,2′-ylene)phosphinic acid **14** was synthesised by stirring a mixture of phosphinic amide **13** and 12 N hydrochloric acid at 0 °C during 15 min, then at 25 °C for 5 h.

Step 3. The phosphinic acid **14** has been readily converted into the phosphinic chloride **15** through reaction with phosphorus pentachloride (Scheme 4). The product **15** was not isolated but directly used for the next step.

Step 4. It seemed convenient to prepare **5** by the previous method (Scheme 2), which allowed us to synthesise the di(2-thienyl)phosphinic amide **1** from di(2-thienyl)phosphinic chloride in biphasic diethyl ether and aqueous ammonia medium. This method applied to the phosphinic chloride **15** did not lead to the precipitation of the phosphinic amide **5**. After evaporation of solvents under vacuum, only degradation products were recovered. Actually, the expected phosphinic amide **5** was isolated in a correct yield (50%) by addition of **15** to an anhydrous solution of gaseous ammonia in ether.

Finally, the tri(3,3′-bithienyl-2,2′-ylene)cyclotriphosphazene **6** has been obtained, as for cyclotriphosphazenes **2** and **4**, by cyclisation of the phosphinic amide **5** (Scheme 1).[10,11] This new cyclotriphosphazene **6** is the first to possess rigid heterocyclic substituents. The very low yield (5%) may be explained by the strain due to the presence of three phosphole rings in the same structure.



Scheme 4 Synthesis of the (3,3′-bithienyl-2,2′-ylene)phosphinic amide **5**: (*i*) Et_2NPCl_2, 0 °C (M = MgBr, Li); (*ii*) H_2O_2 (3%), 1 h, 10 °C; (*iii*) 12 N HCl (17 equiv.), 15 min, 0 °C; 5 h, 25 °C; (*iv*) PCl_5/benzene, 1 h, 80 °C; (*v*) $NH_3(g)/Et_2O$, 0 °C.

NMR spectroscopy

All compounds with only one phosphorus atom (*i.e.*, **1**, **3**, **5**, **7–11**, **13–15**) show simple ^{1}H spectra that gave chemical shifts and coupling constants using first-order analysis, except for compound **3**, which shows a ABMX system (see Table 2 below) because the signals of H-4 and H-5 are very close in $CDCl_3$ ($\Delta\nu$ = 5.5 Hz at 250.13 MHz).

Much more complex are the {^{1}H}^{13}C spectra of cyclotriphosphazenes when a symmetry exists in the three phosphorus spin system,[18–21] as in the case of compounds **2**, **4** and **6**. They show second-order spectra from which, however, ^{31}P–^{13}C coupling constants can be easily obtained.[21] These parameters are gathered in Table 1 with the ^{13}C chemical shifts.

From Table 1, one may observe that $^1J_{PC}$ is weakly affected by a bridge between two *gem* thiophenic substituents (157.3 Hz for freely rotating thiophenes in **2** *versus* 155.1 Hz for bridged thiophenes in **6**), whereas $^2J_{PC}$ shows at the same time the largest variation (12.5 Hz in **2** *versus* 24.1 Hz in **6**). For the corresponding phosphinic amides (**1** and **5**) we find that the remark involving $^2J_{PC}$ is valid whereas the variation of $^1J_{PC}$ is larger for the phosphinic amides **1** and **5** (154.0 and 142.8 Hz, respectively) than for the corresponding phosphazenes **2** and **6**. In general, the cyclisation of phosphinic amides into cyclotriphosphazenes induces, for the carbons not linked to the phosphorus, a decrease of the chemical shifts and an increase of the J_{PC} coupling constant (Table 1).

The ^{1}H spectra of the cyclotriphosphazenes **2**, **4** and **6** are theoretically much more complex than the ^{13}C spectra because ^{1}H is not a rare spin.[21] Nevertheless, with the help of homonuclear ^{1}H selective irradiations and {^{31}P}^{1}H spectra, all chemical shifts and coupling constants have been obtained and are collected in Table 2 with those of the corresponding phosphinic amides.

It can be seen that the formation of the phosphazenic ring from the phosphinic amide has a significative influence (+0.4 Hz) on the coupling constants between the phosphorus and the hydrogen atoms "ortho" to the phosphorus substituent only, this kind of hydrogen being absent in compound **6**. In the same way, the coupling constants J_{HP} of the cyclotriphosphazene **2** with free rotating groups are larger than those of the cyclotriphosphazene **6** with rigid substituents. A larger relative difference is observed for the coupling constant $^4J_{HP}$, which is reduced by 0.9 Hz (about 40%) from **2** to **6**.

Due to the poor solubility of these products, all spectra were not recorded in the same solvent, preventing any comparison of their chemical shifts.

Table 1 ^{13}C NMR chemical shifts and J_{PC} coupling constants (in parentheses) of phosphinic amides **1**, **3**, **5** and cyclotriphosphazenes **2**, **4**, **6**; 2-th = 2-thienyl, 3-th = 3-thienyl, bith = 3,3′-bithienyl-2,2′-ylene (numbering system in Scheme 1)

Compound (solvent)	δ(C-2)	δ(C-3)	δ(C-4)	δ(C-5)
$(2\text{-th})_2P(O)NH_2$	134.20	136.57	128.36	133.80
1 ($CDCl_3$)	(154.0)	(11.5)	(16.0)	(6.0)
$N_3P_3(2\text{-th})_6$	140.03	134.44	127.61	132.12
2 (d_6-DMSO)	(157.3, 3.1, 3.1)	(12.5, 0.7, 0.7)	(16.6)	(6.5)
$(3\text{-th})_2P(O)NH_2$	134.86	135.20	129.30	127.35
3 ($CDCl_3$)	(16.0)	(139.2)	(16.0)	(16.8)
$N_3P_3(3\text{-th})_6$	132.47	140.31	128.72	126.72
4 ($CDCl_3$)	(18.6, 2.0, 2.0)	(141.6, 2.5, 2.5)	(17.9)	(17.1)
$bithP(O)NH_2$	132.08	147.53	120.55	136.84
5 ($CDCl_3$)	(142.8)	(23.4)	(13.9)	(5.9)
$N_3P_3bith_3$	134.56	146.81	121.09	137.56
6 (d_6-DMSO)	(155.1)	(24.1)	(14.1)	(6.6)

Table 2 ^{1}H NMR chemical shifts and J_{HH} and J_{HP} coupling constants of phosphinic amides **1**, **3**, **5** and cyclotriphosphazenes **2**, **4**, **6** (numbering system in Scheme 1)

Compound Solvent	**1** CD_3OD	**2** d_6-DMSO	**3** $CDCl_3$	**4** $CDCl_3$	**5** CD_3OD	**6** d_6-DMSO
δ(H-2)	–	–	8.003	7.670	–	–
δ(H-3)	7.698	7.481	–	–	–	–
δ(H-4)	7.214	7.149	7.374	7.325	7.204	7.358
δ(H-5)	7.864	7.895	7.396	7.339	7.676	8.050
$^4J_{24}$	–	–	1.2	1.1	–	–
$^4J_{25}$	–	–	2.9	2.9	–	–
$^3J_{34}$	3.6	3.5	–	–	–	–
$^4J_{35}$	1.1	1.2	–	–	–	–
$^3J_{45}$	4.8	4.8	5.0	4.9	4.6	4.6
$^3J_{2P}$	–	–	7.8	8.2	–	–
$^3J_{3P}$	7.7	8.1	–	–	–	–
$^3J_{4P}$	–	–	3.8	4.3	–	–
$^4J_{4P}$	2.4	2.4	–	–	1.6	1.5
$^4J_{5P}$	4.7	4.9	2.5	2.1	4.6	4.6

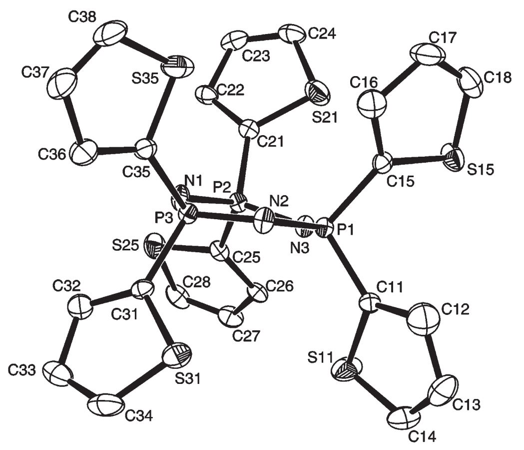
Crystal structures of compounds 2, 4 and 6

The molecular structures of compounds **2**, **4** and **6** consist of a central six-membered ring of alternating nitrogen and phosphorus atoms with each phosphorus atom bonded to two thiophenic substituents for **2** and **4** and to a bithiophene unit for **6**, which has adopted the "paddlewheel" conformation common to trispirocyclotriphosphazene compounds, with the cyclotriphosphazene and bithienyl heterocycles in nearly orthogonal planes.[10,22] The molecular structure of **2**, **4** and **6** are depicted in Fig. 3.

The nitrogen–phosphorus bond lengths in **2**, **4** and **6** are approximately equivalent with a mean value of 1.597 Å. The N–P–N bond angles within the N_3P_3 ring are approximately equal with a mean value of 117.4° for **2** and **4** and 116.1° for **6**. The P–N–P bond angles have a mean value of 121.5°, 121.7° and 122.0°, respectively. The phosphorus–carbon bond lengths are all very similar with a mean value of 1.785 Å for **2**, 1.791 Å for **4** and 1.798 Å for **6**. The largest difference existing between these two kinds of compounds (**2** and **4** *versus* **6**) lies in the C–P–C mean angle values, which are equal to 107.9° for **2**, 103.8° for **4**, and 89.2° for **6**.

The influence of spiro substituents on the C–P–C angles was also reported in an earlier work for hexaphenylcyclotriphosphazene (**16**) and trispiro(biphenyl)cyclotriphosphazene (**17**).[10] It was shown that the size of the C–P–C angles is smaller in compound **17** (91.7°) than in **16** (103.8°), as is observed for products **6** and **2**. It can be seen also that the C–P–C angles in the spiro compound **6** are smaller than in **17** with biphenyl substituents. These values of the C–P–C angles reflect the strong steric constraint existing in the spiro cyclotriphosphazenes **6** and **17**. This observation may explain the reported difficulties in synthesising these two compounds.

As for compound **17**, the crystal arrangement of **6** shows the presence of tunnels (Fig. 4) resulting from the stacking of individual molecules along their C_3 symmetry axis. This phenomenon, which allows clathrate formation,[23] is commonly observed in spirocyclotriphosphazenes[24,25] and has permitted the use of these compounds to trap selectively some molecules.[22,25,26]



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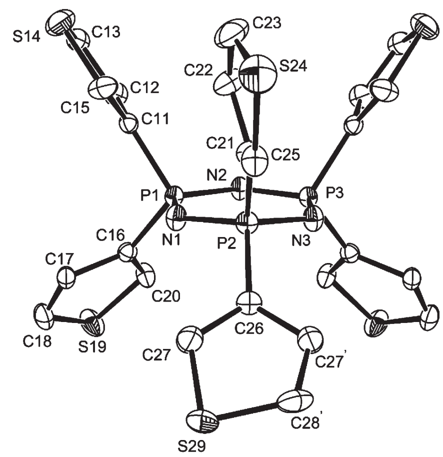

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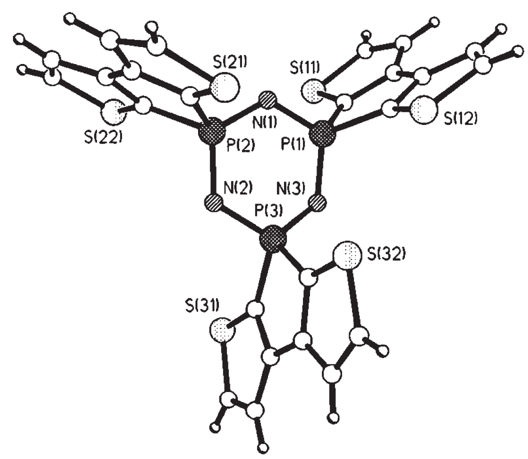

6

Fig. 3 Molecular structure of compounds **2**, **4** and **6**.

Conclusions

In this work we have synthesised three new cyclotriphosphazenes bearing free rotating or bridged thiophenic substituents. Their ^{1}H and ^{13}C NMR spectra have been analysed and compared to those of the corresponding phosphinic amides. The recorded X-ray crystal structures reveal a steric constraint in the bridged molecules. These compounds, which are the first cyclotriphosphazenes with heteroaryl substituents linked to the P_3N_3 skeleton by P–C bonds, are stable and will be soon tested in coordination chemistry with the aim to obtain stacked structures such as these sketched in Fig. 1. It is worthy of note that among the cyclotriphosphazenes obtained, compound **6** is particularly promising thanks to the arrangement of the six potentially coordinating sulfur atoms around its C_3 symmetry axis.

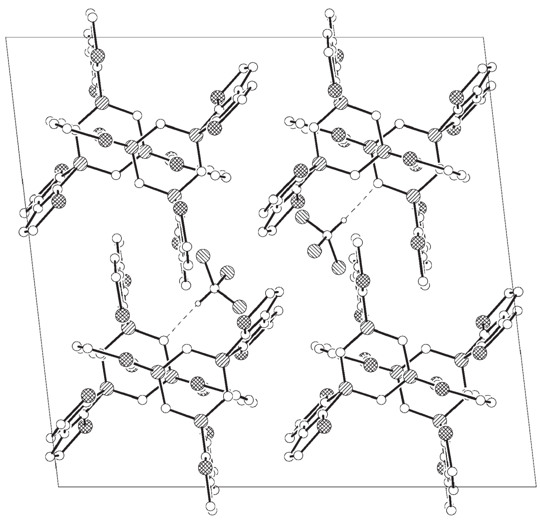

Fig. 4 The crystal packing of $6{\cdot}CHCl_3$ viewed down the *b* axis of the unit cell. The cavity defined by layers of the 4-molecule motif of **6**, shown here as an upper layer and a lower layer, encloses two chloroform solvate molecules.

Experimental

General remarks

All reactions were carried out with careful exclusion of moisture and air. The THF and diethylether used were dried with sodium/benzophenone and freshly distilled prior to use.

The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AC-200, Avance-250 and Avance-400 spectrometers working at 200.130, 250.130 and 400.130 MHz, respectively. The chemical shifts (in ppm) were referenced to internal TMS for ^{1}H and ^{13}C, using the substitution method,[27] or to external 85% H_3PO_4 for ^{31}P, and the coupling constants are expressed in Hz. For coupling constant measurements, zero-filling was applied to FID recorded with TD and SW chosen to give digital resolutions below 0.1 Hz per point. Quantitative ^{31}P spectra have been recorded using the following conditions: no ^{1}H broad-band irradiation to suppress the nuclear Overhauser effect and 30° pulse angles with which it has been verified that relaxation delays D1 longer than 5 s are not needed, owing to the relaxation times below 10 s[28] for the studied compounds in undegassed solutions.

Mass spectra were recorded using a JEOL JMS-DX 300 spectrometer at the Laboratoire de Mesures Physiques (Université Montpellier 2). The elemental analyses were carried out by the Laboratoire Central de Microanalyse du CNRS (Lyon) and the X-ray analyses of compounds **2** and **4** at the Laboratoire de Chimie de Coordination (LCC) (Toulouse).

Synthesis of phosphinic amide 1 (procedure 1)

***N*,*N*-Diethyl-di(2-thienyl)phosphinic amide (7).** A solution of dichloro-*N*,*N*-diethylphosphinic amide (59.4 mmol)[12] in dry THF (10 mL) was added slowly at 21 °C to a solution of 2-thienyl magnesium bromide (136.0 mmol)[13] in THF (160 mL). The reaction mixture was heated at 66 °C for 3 h before cooling to 0 °C and hydrolysis (55 mL of water). The two phases were separated and the aqueous phase was extracted with chloroform (3 × 55 mL). The organic phases were dried ($MgSO_4$), concentrated and the solid recrystallised from acetone. Yield 66%. M.p. (acetone) 122 °C (lit.[29] 122–124 °C). MS: m/z = 285 $[M]^+$. ^{1}H NMR ($CDCl_3$): δ = 1.12 (t, $^{3}J_{HH}$ = 7.1, CH_3), 3.14 (qd, $^{3}J_{HH}$ = 7.1, $^{3}J_{HP}$ = 11.5, CH_2), 7.15 (ddd, $^{3}J_{HH}$ = 4.7, $^{3}J_{HH}$ = 3.6, $^{4}J_{HP}$ = 2.2, H-4), 7.63 (ddd, $^{3}J_{HH}$ = 3.6, $^{4}J_{HH}$ = 1.1, $^{3}J_{HP}$ = 7.6, H-3), 7.68 (ddd, $^{4}J_{HH}$ = 1.1, $^{3}J_{HH}$ = 4.7, $^{4}J_{HP}$ = 4.7, H-5). ^{13}C NMR ($CDCl_3$): δ = 14.11 (d, $^{3}J_{PC}$ = 3.9, CH_3), 39.27 (d, $^{2}J_{PC}$ = 4.3, CH_2), 128.07 (d, $^{3}J_{PC}$ = 15.3, C-4), 133.46 (d, $^{3}J_{PC}$ = 5.7, C-5), 134.27 (d, $^{1}J_{PC}$ = 149.1, C-2), 136.52 (d, $^{2}J_{PC}$ = 11.0, C-3). ^{31}P NMR ($CDCl_3$): δ = 16.8.

Di(2-thienyl)phosphinic acid (8). Phosphinic amide (**7**; 35.0 mmol) was added to hydrochloric acid (12 N, 0.34 mol, 28 mL) and heated at 80° for 20 min. After cooling the crude product was filtered off and the solid washed with water and dried under vacuum with P_2O_5. Yield 98%. M.p. 190 °C (lit.[29] 192 °C). MS (EI): m/z = 230 $[M]^+$. ^{1}H NMR (CD_3OD): δ = 7.20 (ddd, $^{3}J_{HH}$ = 4.8, $^{3}J_{HH}$ = 3.6, $^{4}J_{HP}$ = 2.5, H-4), 7.61 (ddd, $^{3}J_{HH}$ = 3.6, $^{4}J_{HH}$ = 1.1, $^{3}J_{HP}$ = 7.9, H-3), 7.84 (ddd, $^{4}J_{HH}$ = 1.1, $^{3}J_{HH}$ = 4.8, $^{4}J_{HP}$ = 5.0, H-5). ^{13}C NMR (CD_3OD): δ = 128.92 (d, $^{3}J_{PC}$ = 16.3, C-4), 134.41 (d, $^{3}J_{PC}$ = 6.5, C-5), 135.08 (d, $^{1}J_{PC}$ = 163.9, C-2), 136.39 (d, $^{2}J_{PC}$ = 12.2, C-3). ^{31}P NMR (CD_3OD): δ = 14.3.

Di(2-thienyl)phosphinic amide (1). An equimolar solution of di(2-thienyl)phosphinic acid (**8**; 20.6 mmol) and phosphorus pentachloride in benzene (30 mL) was heated to 80 °C during 1 h before removal of the solvent and trichlorophosphine oxide by distillation. The di(2-thienyl)phosphinic chloride **9** is normally not isolated but is used directly in the next step without further purification. However, the first time the reaction was made, this chloride was isolated and characterised. Yield 100%. ^{1}H NMR ($CDCl_3$): δ = 7.22 (ddd, $^{3}J_{HH}$ = 4.8, $^{3}J_{HH}$ = 3.7, $^{4}J_{HP}$ = 2.9, H-4), 7.59 (ddd, $^{3}J_{HH}$ = 3.7, $^{4}J_{HH}$ = 1.2, $^{3}J_{HP}$ = 7.6, H-3), 7.68 (ddd, $^{4}J_{HH}$ = 1.2, $^{3}J_{HH}$ = 4.8, $^{4}J_{HP}$ = 4.7, H-5). ^{13}C NMR ($CDCl_3$): δ = 128.48 (d, $^{3}J_{PC}$ = 18.2, C-4), 134.29 (d, $^{1}J_{PC}$ = 151.2, C-2), 135.33 (d, $^{3}J_{PC}$ = 7.4, C-5), 137.12 (d, $^{2}J_{PC}$ = 13.4, C-3). ^{31}P NMR ($CDCl_3$): δ = 23.8.

9 was dissolved in chloroform (23 mL) and added under nitrogen to a mixture of diethyl ether (150 mL) and aqueous ammonia (28%, 150 mL) cooled to 0 °C, then the mixture was stirred at 25 °C during 1 h. The resulting precipitate was filtered off (solid A). The two phases of the filtrate were separated; the aqueous phase was saturated with NaCl and extracted with chloroform (3 × 100 mL). The organic phases were dried (Na_2CO_3) and the solvent removed under reduced pressure (solid B). The solids A and B were collected and extracted with a Soxhlet apparatus using chloroform as solvent to give **1**. Yield 65%. M.p. ($CHCl_3$) 163 °C. MS (EI): m/z = 229 $[M]^+$. ^{1}H NMR: see Table 2. ^{13}C NMR: see Table 1. ^{31}P NMR ($CDCl_3$): δ = 10.39. $C_8H_8NOPS_2$ (229.3) calcd C 41.91, H 3.51, N 6.11; found C 41.90, H 3.70, N 6.10.

Synthesis of phosphinic amides 1 and 3 (procedure 2)

This procedure was used to synthesise the phosphinic amides **1** and **3**. A solution of 2- or 3-thienyl magnesium bromide[13] (26.0 mmol) in dry THF (40 mL) was added slowly to a solution, cooled to −20 °C, containing trichlorophosphine oxide (13.0 mmol) in THF (40 mL). At the end of the addition, the temperature of the mixture was allowed to return to 25 °C. The solution was stirred during 1 h then added, under nitrogen, to a mixture of diethyl ether (200 mL) and aqueous ammonia (28%, 200 mL), cooled to 0 °C, and left 1 h at this temperature before rewarming to room temperature. The two phases were separated and the aqueous phase was extracted with chloroform (3 × 100 mL). The organic phases were dried ($MgSO_4$) and the solvent evaporated off. The solid was purified by chromatography to give the phosphinic amide **1** or **3** (yield 18% for both) and the corresponding phosphine oxide **10** or **11** (yields of 22 and 14%, respectively).[14,15]

Di(3-thienyl)phosphinic amide (3). R_f (alumina, CH_2Cl_2–AcOEt 8:2) = 0.06. M.p. 174 °C. MS (FAB^+): m/z = 230 $[M+H]^+$. ^{1}H NMR: see Table 2. ^{13}C NMR: see Table 1.

^{31}P NMR ($CDCl_3$): $\delta = 12.39$. $C_8H_8NOPS_2$ (229.25) calcd C 41.91, H 3.52, N 6.11; found C 41.74, H 3.51, N 6.14.

Tri(2-thienyl)phosphine oxide (10)[14,15]**.** R_f (alumina, CH_2Cl_2–hexane 8:2) = 0.2. MS (FAB^+): $m/z = 297$ $[M+1]^+$. ^1H NMR ($CDCl_3$): $\delta = 7.23$ (ddd, $^3J_{HH} = 3.6$, $^3J_{HH} = 4.6$, $^4J_{HP} = 2.0$, H-4), 7.62 (ddd, $^3J_{HH} = 3.6$, $^4J_{HH} = 1.2$, $^3J_{HP} = 8.0$, H-3), 7.79 (td, $^4J_{HH} = 1.2$, $^3J_{HH} = 4.6$, $^4J_{HP} = 4.6$, H-5). ^{13}C NMR ($CDCl_3$): $\delta = 128.27$ (d, $^3J_{PC} = 15.2$, C-4), 134.26 (d, $^3J_{PC} = 5.9$, C-5), 134.54 (d, $^1J_{PC} = 127.9$, C-2), 136.81 (d, $^2J_{PC} = 11.4$, C-3). ^{31}P NMR ($CDCl_3$): $\delta = 7.83$.

Tri(3-thienyl)phosphine oxide (11)[14,15]**.** R_f (alumina, CH_2Cl_2–AcOEt 8:2) = 0.41, MS (FAB^+): $m/z = 297$ $[M+1]^+$. ^1H NMR ($CDCl_3$): $\delta = 7.27$ (ddd, $^3J_{HH} = 5.0$, $^4J_{HH} = 1.2$, $^3J_{HP} = 4.0$, H-4), 7.475 (ddd, $^3J_{HH} = 5.0$, $^4J_{HH} = 2.8$, $^4J_{HP} = 2.2$, H-5), 7.81 (ddd, $^4J_{HH} = 1.2$, $^4J_{HH} = 2.8$, $^3J_{HP} = 7.9$, H-2), ^{13}C NMR ($CDCl_3$): $\delta = 128.27$ (d, $^2J_{PC} = 16.1$, C-4), 134.26 (d, $^3J_{PC} = 15.7$, C-5), 134.54 (d, $^2J_{PC} = 15.4$, C-2), 136.81 (d, $^1J_{PC} = 113.9$, C-3). ^{31}P NMR ($CDCl_3$): $\delta = 9.96$.

Synthesis of phosphinic amide 5

***N,N*-Diethyl(3,3′-bithienyl-2,2′-ylene)phosphinic amide (13).** Dichloro-*N,N*-diethylphosphinic amide (3.1 mmol)[16] dissolved in diethyl ether (5 mL) was added over 40 min to a solution of 2,2′-dilithio-3,3′-bithienyl (3.1 mmol)[17] cooled to 10 °C. The mixture was stirred 1 h, then treated with 3% hydrogen peroxide (7 mL) and stirred again for 1 h at 10 °C. The organic layer was washed with an aqueous saturated solution of NaCl, dried ($MgSO_4$) and filtered. The solvent was removed under reduced pressure and purified by chromatography to give **13**. Yield 45%. $R_f = 0.3$ (silica gel, 1:1 CH_2Cl_2–Et_2O). M.p. 138 °C. MS (EI): $m/z = 283$ $[M]^+$. ^1H NMR ($CDCl_3$): $\delta = 1.09$ (q, $^3J_{HH} = 7.1$, $^4J_{HP} = 7.1$, CH_3), 3.09 (td, $^3J_{HH} = 7.1$, $^3J_{HP} = 12.5$, CH_2), 7.09 (dd, $^3J_{HH} = 4.6$, $^4J_{HP} = 1.7$, H-4), 7.65 (dd, $^3J_{HH} = 4.6$, $^4J_{HP} = 4.9$, H-5). ^{13}C NMR ($CDCl_3$): $\delta = 13.89$ (d, $^3J_{PC} = 2.9$, CH_3), 38.36 (d, $^2J_{PC} = 5.4$, CH_2), 120.59 (d, $^3J_{PC} = 13.6$, C-4), 131.23 (d, $^1J_{PC} = 139.2$, C-2), 136.70 (d, $^3J_{PC} = 5.6$, C-5), 148.09 (d, $^2J_{PC} = 22.0$, C-3). ^{31}P NMR ($CDCl_3$): $\delta = 22.8$. $C_{12}H_{14}NOPS_2$ (283.35) calcd C 50.82; H 4.94; N 4.94; S 22.5; found C 50.80, H 5.10, N 4.9, S 22.60.

(3,3′-Bithienyl-2,2′-ylene)phosphinic acid (14). Hydrochloric acid (12 N; 12 mmol, 1 mL) was added to **13** (0.7 mmol) cooled to 0 °C. The viscous mixture obtained was allowed to reach 25 °C. After 5 h, crystalline solid **14** was filtered off and washed with water before drying under vacuum. Yield 100%. M.p. 152 °C. MS (EI): $m/z = 228$ $[M]^+$. ^1H NMR (CD_3OD): $\delta = 7.29$ (dd, $^3J_{HH} = 4.6$, $^4J_{HP} = 1.9$, H-4), 7.88 (dd, $^3J_{HH} = 4.6$, $^4J_{HP} = 5.2$, H-5). ^{13}C NMR (CD_3OD): $\delta = 121.95$ (d, $^3J_{PC} = 14.6$, C-4), 131.25 (d, $^1J_{PC} = 154.8$, C-2), 138.14 (d, $^3J_{PC} = 6.1$, C-5), 148.79 (d, $^2J_{PC} = 24.8$, C-3). ^{31}P NMR (CD_3OD): $\delta = 21.8$. $C_8H_5O_2PS_2$ (228.23) calcd C 42.10, H 2.19; found C 42.30, H 2.90.

(3,3′-Bithienyl-2,2′-ylene)phosphinic chloride (15). 14 (0.45 mmol) and phosphorus pentachloride (0.45 mmol) dissolved in benzene (3 mL) were heated to reflux for 1 h. The solvent and phosphorus oxychloride were removed by distillation to give yellow solid **15**. Yield 92%. MS (EI): $m/z = 246$ (61%) $[M]^+$, 248 (27%) $[M+2]^+$. ^1H NMR ($CDCl_3$): $\delta = 7.16$ (dd, $^3J_{HH} = 4.5$, $^4J_{HP} = 2.5$, H-4), 7.79 (dd, $^3J_{HH} = 4.5$, $^4J_{HP} = 6.1$, H-5). ^{13}C NMR ($CDCl_3$): $\delta = 120.66$ (d, $^3J_{PC} = 16.0$, C-4), 130.79 (d, $^1J_{PC} = 148.5$, C-2), 138.95 (d, $^3J_{PC} = 7.3$, C-5), 147.26 (d, $^2J_{PC} = 27.3$, C-3). ^{31}P NMR ($CDCl_3$): $\delta = 22.6$.

(3,3′-Bithienyl-2,2′-ylene)phosphinic amide (5). 15 (2.2 mmol) was dissolved in chloroform (15 mL) and added over 5 min to a saturated solution of ammonia in diethyl ether (100 mL) cooled to 0 °C. The solvent was removed under reduced pressure at 25 °C to give a white solid, which was washed with hot chloroform and filtered. The filtrate was concentrated, then recrystallised from chloroform–hexane (5–95%). Yield 50%. M.p. 180 °C. MS (EI): $m/z = 227$ $[M]^+$. ^1H NMR: see Table 2. ^{13}C NMR: see Table 1. ^{31}P NMR ($CDCl_3$): $\delta = 19.0$. $C_8H_6NOPS_2$ (227.24) calcd C 42.24, H 2.63, N 6.14, S 28.10; found C 42.1, H 2.6, N 6.0, S 28.0.

Formation of the phosphazenic ring

This general procedure was used to synthesise hexa(2-thienyl)-cyclotriphosphazene (**2**), hexa(3-thienyl)cyclotriphosphazene (**4**) and tri(3,3′-bithienyl-2,2′-ylene)cyclotriphosphazene (**6**). Triphenylphosphine (10 mmol), phosphinic amide (8.3 mmol), triethylamine (8.3 mmol) and carbon tetrachloride (8.3 mmol) were heated at reflux from methylene chloride (40 mL) for 5 h (higher yields were not obtained by increasing the reaction time). The solvent was removed under vacuum to give a powder, which was purified by chromatography to give the cyclotriphosphazene.

Hexa(2-thienyl)cyclotriphosphazene (2). Yield 34%. M.p. 269 °C. $R_f = 0.5$ (silica gel, CH_2Cl_2). MS (EI): $m/z = 633$ $[M]^+$. ^1H NMR: see Table 2. ^{13}C NMR: see Table 1. ^{31}P NMR ($CDCl_3$): $\delta = 3.21$. $C_{24}H_{18}N_3P_3S_6$ (633.74) calcd C 45.44, H 2.84, N 6.63; found C 45.80, H 3.40, N 6.70.

Hexa(3-thienyl)cyclotriphosphazene (4). Yield 29%. M.p. 250 °C. $R_f = 0.38$ (silica gel, CH_2Cl_2). MS (FAB^+): $m/z = 634$ $[M+1]^+$. ^1H NMR: see Table 2. ^{13}C NMR: see Table 1. ^{31}P NMR ($CDCl_3$): $\delta = 4.59$. $C_{24}H_{18}N_3P_3S_6$ (633.74) calcd C 45.44, H 2.84, N 6.63; found C 45.33, H 2.85, N 6.70.

Tri(3,3′-bithienyl-2,2′-ylene)cyclotriphosphazene (6). Yield 5%. M.p. 278 °C. $R_f = 0.4$ (silica gel, CH_2Cl_2). MS (EI): $m/z = 627$ $[M]^+$. ^1H NMR: see Table 2. ^{13}C NMR: see Table 1. ^{31}P NMR ($CDCl_3$): $\delta = 13.6$. $C_{24}H_{12}N_3P_3S_6 \cdot CHCl_3$ (753.14) calcd C 40.18, H 1.74, N 5.62; S 25.72; found C 40.5, H 1.5, N 5.5, S 25.3.

X-Ray crystallographic study† of cyclotriphosphazenes 2, 4 and 6

For **2** and **4**, data were collected on a Stoe IPDS diffractometer. The final unit cell parameters were obtained by the least-squares refinement of 5000 or 8000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections. The structures were solved by direct methods (SIR97)[30] and refined by least-squares procedures on F^2. All H atoms attached were introduced in the calculations in idealised positions [d(CH) = 0.96 Å] and treated as riding models with isotropic thermal parameters 20% higher than those of the carbon to which they are attached. In both compounds, some of the thiophene rings present a disordered arrangement with the positions on the ring occupied partially by S and C atoms. These disordered molecules were treated using the available restraints (SAME, SADI and FLAT) in SHELXL-97.[31] Least-squares refinements were carried out by minimising the function $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Models reached convergence with

† CCDC reference numbers 184619 (**2**), 184574 (**4**) and 204454 (**6**). See http://www.rsc.org/suppdata/nj/b3/b311046j/ for crystallographic data in .cif or other electronic format.

Table 3 Crystal data and structure refinement details for **2**, **4** and **6**

	2	**4**·$CHCl_3$	**6**·$CHCl_3$
Empirical formula	$C_{24}H_{18}N_3P_3S_6$	$C_{25}H_{19}Cl_3N_3P_3S_6$	$C_{25}H_{13}Cl_3N_3P_3S_6$
Formula weight	633.74	753.14	747.09
T/K	160(2)	180(2)	293(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1$	$Pnma$	$I2/a$
a/Å	11.2770(16)	9.828(2)	19.420(2)
b/Å	9.1335(10)	15.632(3)	15.7094(16)
c/Å	13.561(2)	20.084(4)	20.428(4)
β/°	101.04	90	96.673(7)
U/Å^3	1370.9(3)	3085.5(11)	6190.0(14)
Z	2	4	8
μ/mm^{-1}	0.696	0.883	0.88
Reflections collected	13 519	14 257	6293
Independent reflections	5198	2472	5446
R_{int}	0.0250	0.0512	0.0346
R_1 [$I > 2\sigma(I)$]	0.0268	0.0407	0.0593
wR_2 [$I > 2\sigma(I)$]	0.0712	0.1031	0.1099
R_1 (all data)	0.0284	0.0479	0.1220
wR_2 (all data)	0.0721	0.1078	0.1338

$R_1 = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$ having the values listed in Table 3. The calculations were carried out with the SHELXL-97 program using the integrated system WINGX(1.63).[32] Molecular views were realised with the help of ORTEP-3 for Windows (Version 1.076).[33]

For **6** data were collected on a colourless crystal of **6**·$CHCl_3$ on a Siemens P4 four-circle diffractometer using Mo-K_α radiation. The structure was solved by direct methods (SHELXTL) and from this and subsequent difference Fourier maps the positions of all the non-hydrogen atoms were located. Extended areas of electron density associated with the chloroform solvate molecules arising from rotational disorder of the chlorine atoms around the C–H axis of the molecule were modelled as two components in a population ratio of 60:40. Hydrogen atoms were placed in idealised positions with $U_H = 1.2\ U_{eq}$ of the parent carbon. In the final cycles of full-matrix least-squares refinement on F^2, anisotropic thermal parameters were assigned to non-hydrogen atoms of the asymmetric unit.

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