Reactions of Amine Hydrochlorides with Phosphorus Trichloride Oxide; Preparation and *X*-Ray Crystal Structure of 2,4,6-Trichloro-1,3,5-triphenyl-1,3,5,2λ^5,4λ^5,6λ^5-triazatriphosphorinane 2,4,6-Trioxide $(PhNPOCl)_3$†

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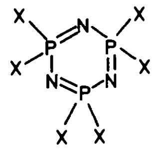
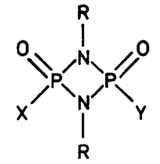
The reaction of aniline hydrochloride with $POCl_3$ has been shown to yield the trimeric cyclophosphazane $(PhNPOCl)_3$ in good yield and purity, in opposition to the earlier results of Michaelis which assigned a dimeric structure to the product. The trimeric nature has been confirmed by ^{31}P n.m.r. spectroscopy, mass spectroscopy, and an *X*-ray crystallographic structure determination. The analogous 4-methylphenyl and 4-methoxyphenyl compounds have been similarly prepared. The products are relatively inert to nucleophiles but reactions with ethoxide and hydroxide ions yield products which give evidence for a mechanism involving ring contraction by transannular attack of nitrogen on phosphorus.

Many phosphorus–nitrogen ring compounds are known, which may be conveniently subdivided into two categories, the cyclophosphazenes, *e.g.* (**1**), which contain alternating double and single bonds in the ring, and the cyclophosphazanes, *e.g.* (**2**)—(**10**), which only have single bonds in the ring. Both categories have been reviewed by Shaw.[1] Cyclophosphazenes are known in a wide range of ring sizes from six upwards, but cyclophosphazanes are, with very few exceptions, only known as four-membered rings, *e.g.* (**2**)—(**5**). While four-membered rings would be expected for both five- and three-co-ordinated phosphorus, since both of these have bond angles at phosphorus close to 90°, six-membered rings might be expected for four-co-ordinated phosphorus, which has bond angles close to 109°. Nevertheless, most cyclophosphazanes containing four-co-ordinated phosphorus also have a ring size of four. The few known exceptions are either prepared from cyclophosphazenes of the same ring size [*e.g.* (**6**), prepared by pyrolysis of (**1**)[2]] or contain other ring systems fused onto the phosphorus–nitrogen ring, *e.g.* (**10**).[3] Cyclophosphazanes which contain five-co-ordinate phosphorus display reactivity similar to the acyclic analogues, while those containing four-co-ordinate phosphorus and four-membered rings are normally quite reactive because of the ring strain, which is relieved by the formation of the five-co-ordinate intermediates normally involved in nucleophilic reactions at phosphorus. Thus compounds of the type $(RNPOCl)_2$ [*e.g.* (**2**)] are easily hydrolysed by water[4] whereas the acyclic analogues $(RNH)_2POCl$ are much more stable to water at ambient temperatures.

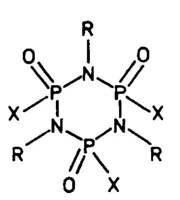
In reviewing the literature on compounds of the type $(RNPOCl)_2$ we were surprised to find two references to $(PhNPOCl)_2$ (**3**) which ascribed quite different properties to the compound. Thus Michaelis[5] had prepared the compound from aniline hydrochloride and phosphorus trichloride oxide, obtaining a crystalline material, m.p. 228 °C, which was water stable. Green *et al.*,[6] however, had prepared the compound along with a series of alkyl analogues by the reaction of the five-co-ordinated cyclophosphazanes $(RNPCl_3)_2$ with SO_2 and obtained a solid material with m.p. 144.5—145 °C, which was extremely water sensitive. They also showed, by ^{31}P n.m.r. spectroscopy,[7] the presence of the two isomers expected for a four-membered ring structure.



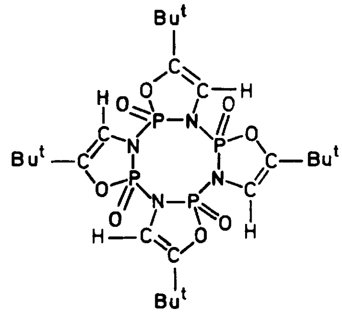
(**1**) X = OMe



	X	Y	R
(**2**)	Cl	Cl	Me
(**3**)	Cl	Cl	Ph
(**4**)	Cl	Cl	$C_6H_3Me_2$-2,6
(**5**)	Cl	HNC_6H_4Me-4	C_6H_4Me-4



	X	R
(**6**)	OMe	Me
(**7**)	Cl	Ph
(**8**)	Cl	C_6H_4OMe-4
(**9**)	Cl	C_6H_4Me-4



(**10**)

The disparity between the properties of the two reported products, and the unexpected stability to hydrolysis of Michaelis' product, led us to repeat Michaelis' work, since we believed that his product might in fact be the six-membered ring isomer $(PhNPOCl)_3$ (**7**).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

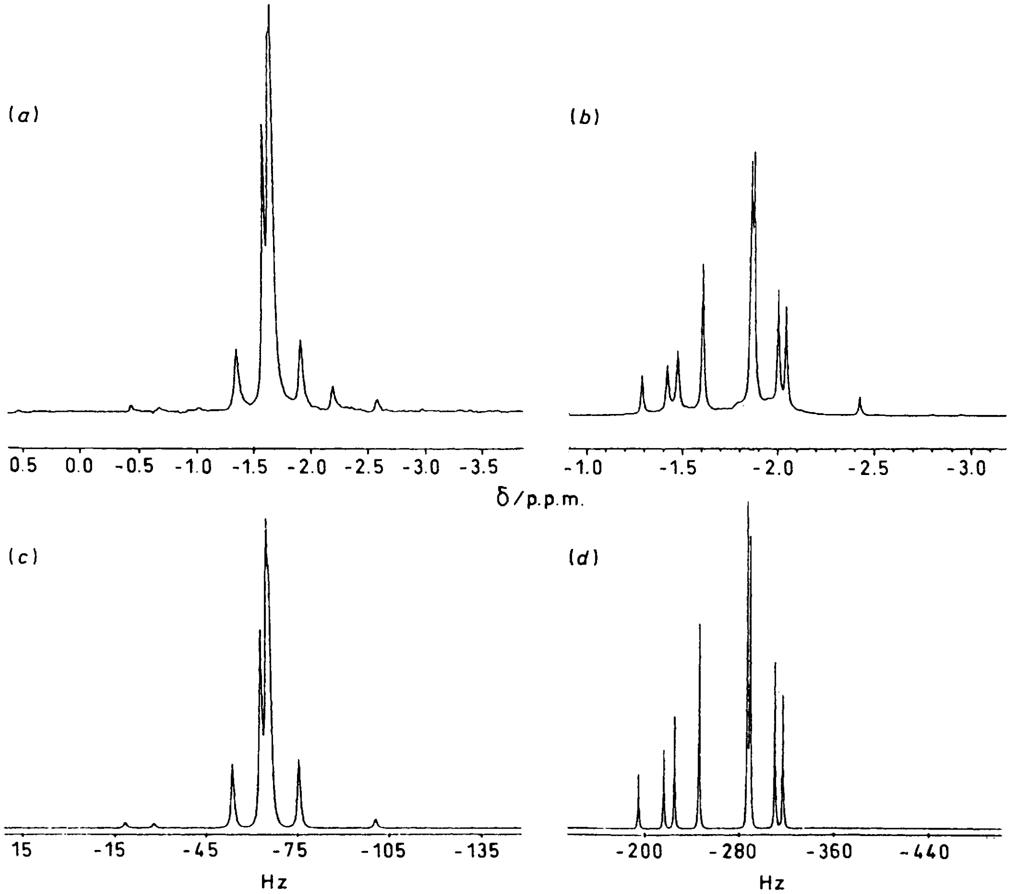


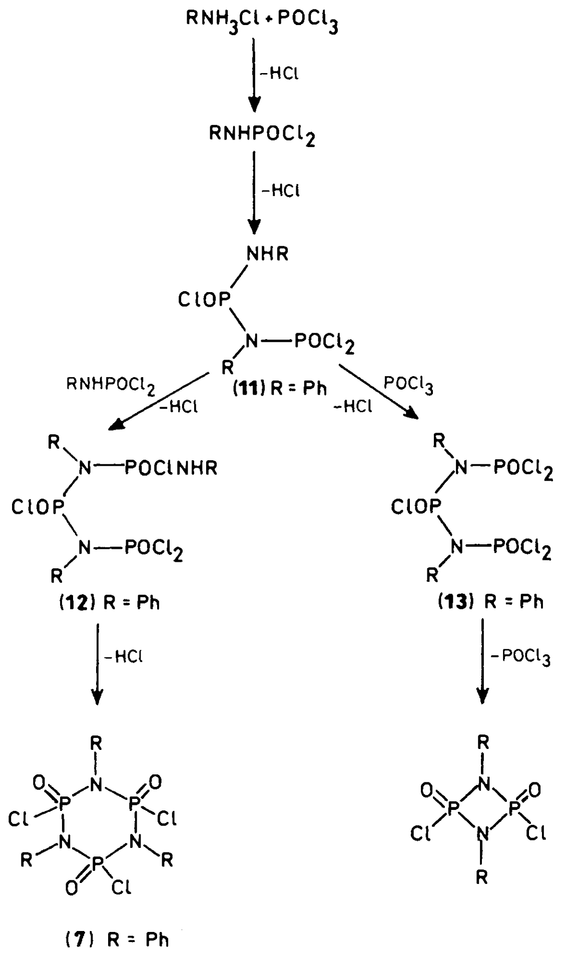
Figure 1. Phosphorus-31 n.m.r. spectra of compound (7) in $CDCl_3$, (*a*) measured at 36.4 MHz, (*b*) measured at 161.7 MHz, and (*c*) simulation of 36.4-MHz spectrum, (*d*) simulation of 161.7-MHz spectrum. Simulations were performed with the NUMARIT program using the values of the coupling constants and chemical shifts given in the text

Results

Michaelis described very precise details for the preparation of his 'oxyphosphazobenzolchlorid,' as he named his product in analogy with the monomeric aromatic diazo compounds.[5] We originally followed his method as closely as possible, and followed the course of the reaction by ^{31}P n.m.r. spectroscopy. Separations of reaction products were only undertaken when the n.m.r. spectra indicated that the reaction had given reasonable yields.

Heating aniline hydrochloride with $POCl_3$ with small amounts of xylene as solvent leads to the evolution of hydrogen chloride, and the first product which can be detected is *N*-phenylphosphoramidic dichloride, $PhNHPOCl_2$, which is easily recognised in the ^{31}P n.m.r. spectrum as a singlet at 8.8 p.p.m. If equimolar amounts of the reactants are used, $PhNHPOCl_2$ is essentially the only phosphorus compound observed in the reaction mixture after heating to 140 °C for 24 h. Further heating to 170 °C for 72 h leads to further evolution of hydrogen chloride, and a number of products can then be identified in the reaction mixture. Among these are the two isomers of $(PhNPOCl)_2$ as prepared by Green *et al.*,[6] with ^{31}P n.m.r. shifts of -13.3 and -9.9 p.p.m., though the amount of these species formed is very small unless an excess of $POCl_3$ is used. Present in all reactions is a diphosphorus species (δ_P 12.9 and 4.8 p.p.m., J_{PP} 31.7 Hz), which we assume to be $PhNHPOCl(PhN)POCl_2$ (**11**), previously reported by Kukhar.[8] Additional evidence for this assignment is the fact that the signal at 4.8 p.p.m., which we assign to the phosphorus carrying the NHPh group, is split into a doublet when the spectrum is measured without decoupling of the ^1H nuclei. Also observed is a singlet at -1.6 p.p.m., which becomes stronger on further heating, and which shows fine structure when examined under high resolution. Careful control of the temperature and time of heating can result in this species being the principal phosphorus-containing product of the reaction (yield estimated by n.m.r. $> 70\%$).

In his description of the preparation, Michaelis[5] boiled the reaction mixture with water to separate his product from the xylene and hydrolysable side products. We find that this treatment usually destroys the product with δ_P -1.6 p.p.m., but that this product can be obtained in good yield by dissolving the reaction mixture in chloroform and washing the chloroform solution with water. The water removes any unreacted starting materials, as well as any easily hydrolysable side products, such as the three other species observed in the ^{31}P n.m.r. spectra, and evaporation of the washed chloroform solution, followed by flash chromatography, yields a crystalline product, m.p. 223 °C, which is clearly identical with Michaelis' product.[5] The high-resolution ^{31}P n.m.r. spectrum at 36.24 MHz is very second-order, but can be analysed as an AB_2 spin system, giving values of $\delta_{PA} = -1.5$ p.p.m., $\delta_{PB} = -1.9$ p.p.m., $J_{PP} = 26.3$ Hz, which are confirmed by the 161.7-MHz spectrum and computer simulations of both spectra (Figure 1). The AB_2 spectrum observed confirms that the product is indeed the trimer $(PhNPOCl)_3$ (**7**), the non-equivalence of the three phosphorus atoms being due to two of the phosphoryl oxygen atoms being on one side of the ring, with the third on the other side. The composition is confirmed by microanalysis, and the molecular



Scheme 1.

weight by mass spectroscopy, which gives a molecular ion with the expected m/z of 519 with the predicted peak pattern due to the relative abundances of the carbon and chlorine isotopes.

The fact that the trimer (PhNPOCl)$_3$ (**7**) rather than the dimer (PhNPOCl)$_2$ (**3**) is formed as the principal product of the reaction provides good evidence that the reaction does not proceed *via* dimerisation of a three-co-ordinated monomeric intermediate PhNPOCl, which might be assumed to be formed by thermal loss of HCl from PhNHPOCl$_2$. If this three-co-ordinated species is formed, it almost certainly reacts immediately with PhNHPOCl$_2$ to give Kukhar's linear diphosphorus species PhNHPOCl(PhN)POCl$_2$ (**11**). It is however equally feasible that this species is formed by direct nucleophilic attack of the NH group of PhNHPOCl$_2$ on the POCl$_2$ group of a second molecule of the same compound. The fact that the four-membered ring species (**2**) is formed only when an excess of POCl$_3$ is present in the reaction mixture suggests that the dimer is the result of attack of POCl$_3$ on one of the intermediates, the most likely being (**11**). Reaction of this with POCl$_3$ could yield a triphosphorus species [(**13**), Scheme 1], which could then lose POCl$_3$ to give the four-membered ring species (**2**). If no excess of POCl$_3$ is present, compound (**11**) can react only with PhNHPOCl$_2$, and the triphosphorus species so formed [(**12**), Scheme 1] can then lose HCl to form the trimeric product (PhNPOCl)$_3$ observed.

Further confirmation that we have prepared (PhNPOCl)$_3$ was obtained from an X-ray crystallographic study of a crystal obtained by slow evaporation of a chloroform–light petroleum solution of the product. The structure is shown in Figure 2; values of the atomic co-ordinates are presented in Table 1 and the principal bond lengths and angles in Table 2.

Table 1. Atomic co-ordinates ($\times 10^4$) for compound (7)

Atom	x	y	z
P(1)	3 217(1)	8 488(1)	1 957(1)
Cl(1)	3 505(1)	7 709(1)	3 183(1)
O(1)	3 522(3)	9 377(2)	2 204(3)
N(1)	1 817(3)	8 352(2)	1 564(3)
C(12)	401(3)	8 991(2)	2 765(2)
C(13)	−347	9 660	3 036
C(14)	−462	10 382	2 389
C(15)	171	10 436	1 470
C(16)	918	9 767	1 198
C(11)	1 033	9 045	1 846
P(2)	1 153(1)	7 473(1)	1 087(1)
Cl(2)	835(2)	6 695(1)	2 284(1)
O(2)	92(3)	7 664(3)	464(3)
N(2)	2 238(3)	6 980(2)	495(3)
C(22)	2 571(3)	5 422(2)	538(2)
C(23)	2 367	4 601	128
C(24)	1 592	4 488	−735
C(25)	1 020	5 198	−1 190
C(26)	1 224	6 019	−780
C(21)	2 000	6 131	83
P(3)	3 410(1)	7 456(1)	12(1)
Cl(3)	2 760(2)	8 308(1)	−1 061(1)
O(3)	4 238(4)	6 886(3)	−440(4)
N(3)	3 957(3)	8 051(2)	987(3)
C(32)	6 041(3)	7 791(2)	1 463(3)
C(33)	7 224	7 995	1 367
C(34)	7 546	8 679	726
C(35)	6 686	9 158	182
C(36)	5 503	8 953	278
C(31)	5 181	8 269	919

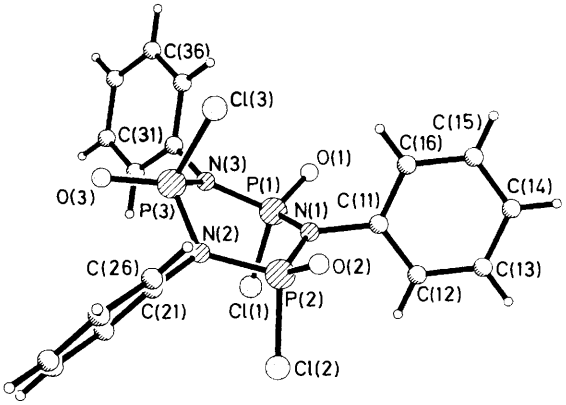


Figure 2. Perspective drawing of the molecular structure of compound (7). Atoms are drawn as spheres of arbitrary diameter

The structure confirms the presence of the unsymmetric six-membered ring (2α, 4α, 6β) suggested by the ^{31}P n.m.r. spectra. The ring has a distorted boat structure, with the unique phosphorus at the 'bow.' The six P–N bonds vary in length from 1.651 to 1.669 Å, somewhat shorter than the 'typical' value of 1.759 Å for the P–N single bond in $Na^+[H_3N{-}PO_3]^-$,[9] suggesting a degree of multiple bonding caused by overlap of the filled $2p$ orbitals on nitrogen with the $3d$ orbitals of the phosphorus; this is also indicated by the planarity of the three atoms around the nitrogens (sum of angles at nitrogen >357° for each of the three nitrogen atoms in the structure). Similar

Table 2. Bond lengths (Å) and angles (°) for compound (**7**)

P(1)–Cl(1)	1.990(2)	P(2)–Cl(2)	1.985(2)	P(3)–Cl(3)	2.022(2)
P(1)–O(1)	1.458(4)	P(2)–O(2)	1.453(4)	P(3)–O(3)	1.429(4)
P(1)–N(1)	1.669(4)	P(1)–N(3)	1.661(4)	P(2)–N(1)	1.666(4)
P(2)–N(2)	1.657(4)	P(3)–N(2)	1.663(4)	P(3)–N(3)	1.651(4)
N(1)–C(11)	1.452(4)	N(2)–C(21)	1.442(5)	N(3)–C(31)	1.442(5)

Cl(1)–P(1)–O(1)	112.2(2)	Cl(1)–P(1)–N(1)	106.7(1)
O(1)–P(1)–N(1)	113.8(2)	Cl(1)–P(1)–N(3)	104.9(2)
O(1)–P(1)–N(3)	115.0(2)	N(1)–P(1)–N(3)	103.4(2)
P(1)–N(1)–C(11)	115.0(3)	P(1)–N(1)–P(2)	129.0(2)
C(11)–N(1)–P(2)	115.0(2)	N(1)–C(11)–C(12)	120.1(2)
N(1)–C(11)–C(16)	119.9(2)	N(1)–P(2)–Cl(2)	108.3(1)
N(1)–P(2)–O(2)	112.8(2)	Cl(2)–P(2)–O(2)	111.8(2)
N(1)–P(2)–N(2)	102.0(2)	Cl(2)–P(2)–N(2)	103.0(2)
O(2)–P(2)–N(2)	117.9(2)	P(2)–N(2)–C(21)	116.9(3)
P(2)–N(2)–P(3)	125.7(2)	C(21)–N(2)–P(3)	114.6(3)
N(2)–C(21)–C(22)	119.6(2)	N(2)–C(21)–C(26)	120.4(2)
N(2)–P(3)–Cl(3)	105.1(2)	N(2)–P(3)–O(3)	115.0(2)
Cl(3)–P(3)–O(3)	111.6(2)	N(2)–P(3)–N(3)	105.1(2)
Cl(3)–P(3)–N(3)	104.9(2)	O(3)–P(3)–N(3)	114.3(2)
P(1)–N(3)–P(3)	126.6(2)	P(1)–N(3)–C(31)	117.8(3)
P(3)–N(3)–C(31)	115.3(3)	N(3)–C(31)–C(32)	120.7(2)
N(3)–C(31)–C(36)	119.3(2)		

bond lengths have been measured in other six- and eight-membered ring cyclophosphazanes.[10] The fact that the delocalisation of the nitrogen lone pairs involves the phosphorus atoms and not the phenyl rings is indicated by the fact that the planes of the phenyl rings are approximately perpendicular to the P–N–P planes. A result of this arrangement of the phenyl rings is that the rings are asymmetric, and six rather than four signals are expected for each ring in the ^{13}C n.m.r. spectrum. At ambient temperature only four signals are observed for each ring, indicating that rotation about the C–N bond is rapid on the n.m.r. time-scale, though the signal assigned to the *o*-carbons of the unique phenyl ring (δ 129.7) is significantly broadened. On lowering the temperature the spectrum changes considerably, and at −80 °C most of the expected twelve lines are observed, though there is considerable overlap, all the lines lying within a range of 2 p.p.m., which makes assignments difficult. Studies of this fluxional process are continuing and will be reported elsewhere.

In view of the limited amount of 1,3 steric interaction between the chlorine and oxygen atoms in the measured structure, it is perhaps surprising that evidence was not obtained for the symmetrical isomer ($2\alpha,4\alpha,6\alpha$) with all three oxygen atoms on the same side of the ring. Such a species would be expected to give a singlet in the ^{31}P n.m.r. spectrum (A_3 spin system) and although a weak singlet is observed at −2.4 p.p.m. in the ^{31}P n.m.r. spectrum of a recrystallised sample of (**7**), we have not been able to prove that this is in fact the symmetrical isomer. The *X*-ray crystal structure of compound (**6**)[10] shows that it also exists as the unsymmetrical isomer, and for the analogous six-membered phosphorus–oxygen ring system, $(Et_2NPO_2)_3$,[11,12] *X*-ray crystallographic evidence was found for the presence of the symmetrical isomer in small amounts, but the overwhelming majority of the compound was the unsymmetrical isomer. We have studied this and other phosphorus–oxygen six-membered ring systems by n.m.r. spectroscopy[13] and found that the predominant product formed in all cases is the unsymmetrical isomer.

Since the preparation of $(PhNPOCl)_3$ forms a simple and convenient route to the previously little known triazatriphosphorinane ring system, we were hopeful that we would be able to use similar methods to produce analogous compounds with different substituents. We attempted such syntheses by two routes, first using different primary amine hydrochlorides to produce analogues with different substituents at nitrogen, and secondly by attempts to substitute the chlorine atoms in $(PhNPOCl)_3$ by different groups to produce analogues with different substituents at phosphorus.

Table 3. Comparison of ^{31}P n.m.r. chemical shifts with pK_a of corresponding amines

Aliphatic or aromatic amines	pK_a* (aqueous at 25 °C)	^{31}P N.m.r. shift of $RNHPOCl_2$ ($CDCl_3$)
$4\text{-}O_2NC_6H_4NH_2$	1.0	4.18
$2,6\text{-}Me_2C_6H_3NH_2$	3.95	10.34
$PhNH_2$	4.63	8.55
$4\text{-}MeC_6H_4NH_2$	5.08	9.35
$4\text{-}MeOC_6H_4NH_2$	5.34	11.27
$Pr^iCH_2NH_2$	10.41	17.10
$MeNH_2$	10.62	18.40

Isolated trimeric cyclophosphazanes

		^{31}P N.m.r. shifts ($CDCl_3$) and coupling constants (Hz)		
Cyclophosphazane	Yield (%)	P_a	P_b	$J_{P_aP_b}$
$(PhNPOCl)_3$	25	−1.5	−1.9	26.3
$(4\text{-}MeC_6H_4NPOCl)_3$	1	−1.3	−1.7	29.0
$(4\text{-}MeOC_6H_4NPOCl)_3$	8	−1.1	−1.5	33.5

* 'CRC Handbook of Chemistry and Physics,' 53rd edn., Chemical Rubber Company, Cleveland, Ohio, 1972.

No aliphatic amine hydrochlorides that we used gave any evidence for either four- or six-membered ring products on reaction with $POCl_3$. The usual products of such reactions, after the initial formation of the phosphoramidic dichlorides $RNHPOCl_2$, were polymeric products, presumably consisting of –P–N–P–N chains, which could not be purified or further characterised. This behaviour is analogous to that observed by Keat[14] in the pyrolysis of $Me_3SiNMePOCl_2$, and by Holmes and Forstner[15] in the pyrolysis of $(MeNH)_3PO$. Both of these reactions could be expected to lead to cyclic products of formula $(MeNPOX)_n$ (X = Cl or NHMe). With aromatic amine hydrochlorides slightly better results were obtained; 4-methoxyaniline hydrochloride gave an 8% isolated yield of the trimer $(4\text{-}MeOC_6H_4NPOCl)_3$ (**8**), and *p*-toluidine hydrochloride gave a small yield of $(4\text{-}MeC_6H_4NPOCl)_3$ (**9**), though the product obtained, m.p. 125—126 °C, seems to be different from the product Michaelis obtained from this reaction[5] which had m.p. 336 °C and for which Michaelis proposed the structure (**5**).

4-Nitroaniline hydrochloride failed to give any identifiable products on reaction with $POCl_3$ other than the initially formed phosphoramidic dichloride $4\text{-}O_2NC_6H_4NHPOCl_2$, while 2,6-dimethylaniline hydrochloride gave an apparently polymeric product from which two isomers of $(2,6\text{-}Me_2C_6H_3NPOCl)_2$ (**4**) could be sublimed. While in this case we assume that steric factors are important, for the other amines, both aromatic and aliphatic, there seems to be a correlation between the basicity of the amine employed and the possibility of formation of the trimeric products; a similar correlation exists with the ^{31}P chemical shifts of the phosphoramidic dichlorides $RNHPOCl_2$, except for the 2,6-dimethylaniline derivative, where we assume that steric factors become important. These correlations are apparent from the data presented in Table 3. The correlation between amine basicity and ^{31}P chemical shift for the phosphoramidic dichlorides is in contrast to the trimeric ring compounds, all three examples that we have prepared having closely similar chemical shifts (*ca.* −1.8 p.p.m. for both types of phosphorus). This is no doubt associated with the fact that in these compounds the planes of the aromatic groups attached to

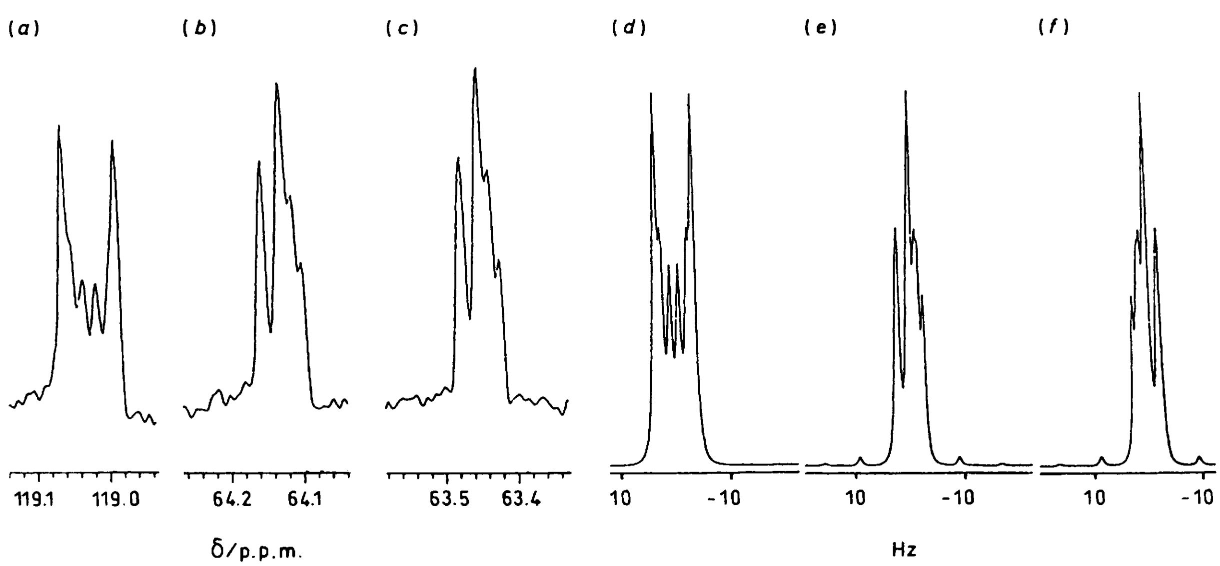


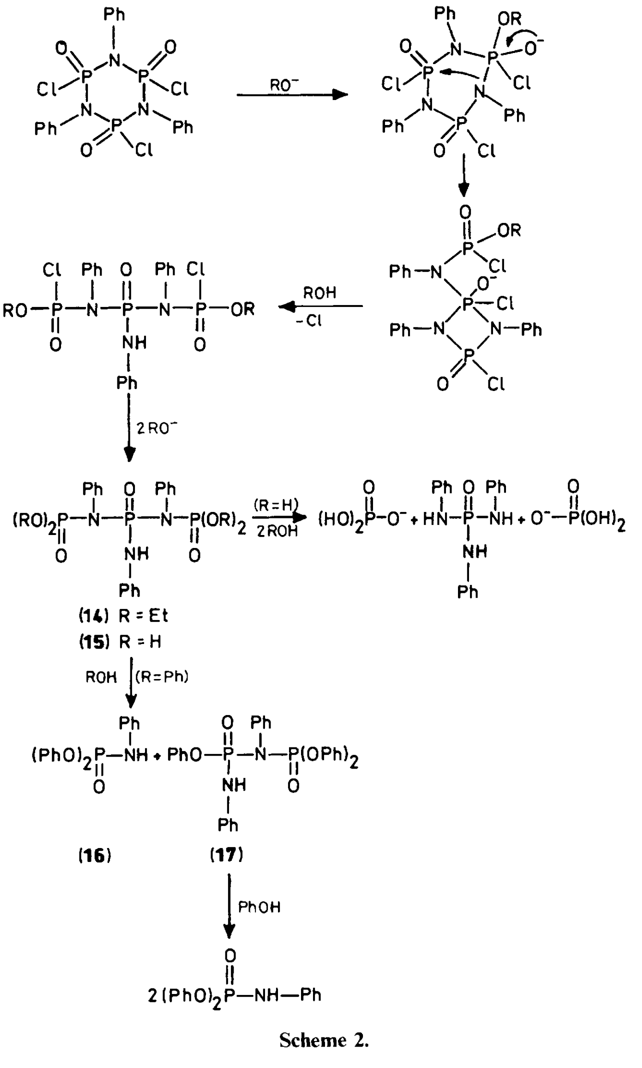
Figure 3. 100.1-MHz ^{13}C N.m.r. spectrum of the product of the reaction between compound (**7**) and 3 equivalents of sodium ethoxide in ethanol, (*a*) observed spectrum of the *o*-carbons of the PhNHP group, (*b*) and (*c*) observed spectra of the methylene carbons of the POEt groups, (*d*) simulation of (*a*), using the phosphorus shifts derived from the ^{31}P AB$_2$ spectrum (see text), $J_{PP} = +28.65$ Hz and $J_{CP_A} = +7.0$ Hz (an identical simulation was obtained with $J_{PP} = -28.65$ Hz), (*e*) simulation of (*b*) and (*c*) with $J_{PP} = -28.65$ Hz and $J_{CP_B} = +5$ Hz, and (*f*) simulation of (*b*) and (*c*) with $J_{PP} = +28.65$ Hz and $J_{CP_B} = +5$ Hz

the nitrogen atoms are at right angles to the plane of the sp^2-hybridised nitrogens, thus preventing the conjugative transmission of electronic effects from the rings to the phosphorus atoms.

Reactions of $(PhNPOCl)_3$ with nucleophiles in attempts to substitute the chlorine atoms were only moderately successful, and in general did not yield the expected results. Thus the product is stable at ambient temperatures to water, aliphatic and aromatic amines, and alcohols. Reaction with sodium ethoxide in ethanol yielded a precipitate of sodium chloride, and the product, a white gummy solid, did give an AB$_2$ ^{31}P n.m.r. spectrum as would be expected for a product $[PhNPO(OEt)]_3$ obtained by substituting the three chlorine atoms by Et groups. Carbon-13 and ^{1}H n.m.r. spectra were not in agreement with the above structure, however, showing instead the presence of four OEt groups (in two non-equivalent pairs) and a PhNHP group in addition to two equivalent PhNP$_2$ groups. [These two groups are distinguishable by the ^{13}C chemical shifts of the *o*-carbons of the phenyl groups, which occur at *ca.* 119 p.p.m. for PhNHP groups, *e.g.* $(PhNH)_3PO$, and at *ca.* 131 p.p.m. for PhNP$_2$ groups, *e.g.* $(PhNPOCl)_3$.] Simulation of the second-order ^{13}C n.m.r. spectra (see Figure 3) allowed the relative signs of the C–P and P–P coupling constants to be determined, and demonstrated that the PhNH group was attached to the central (A) phosphorus atom of the AB$_2$ spin system and that the OEt groups were attached to the similar (B) phosphorus atoms. This evidence demonstrates that the ring has been opened, giving a structure (**14**) (Scheme 2).

The mass spectrum is in agreement with this structure, which we can only assume has arisen by a transannular attack of nitrogen at phosphorus (Scheme 2). A four-membered ring intermediate as suggested would be favoured by the five-co-ordinated phosphorus formed as a result of nucleophilic attack by an OEt group. Subsequent ring opening by ethanol and substitution of chlorine by OEt would then yield the observed product. The product appears to be extremely susceptible to hydrolysis, for example on dissolving it in diethyl ether a cloudy solution is always obtained, and we were unable to obtain an entirely satisfactory microanalysis.

Attack of hydroxide anion (in dilute sodium hydroxide



Scheme 2.

solution) on $(PhNPOCl)_3$ also yields an unexpected product in the form of $(PhNH)_3PO$, easily identified by its ^{31}P chemical shift of −4.0 p.p.m.[16] and m.p. of 213—215 °C.[17] This presumably arises by a similar mechanism to the product from reaction with sodium ethoxide (Scheme 2, R = H), the anion of the acid (**15**) being cleaved to give the phosphoramide and phosphate. A similar mechanism can be invoked to explain Michaelis' results of the reaction of his product with sodium phenoxide (Scheme 2, R = Ph), where he observed both the monophosphorus (**16**) and diphosphorus species (**17**) shown in Scheme 2.

From these reactions of the six-membered ring, it can be concluded that the stability of the ring, relative to that of the four-membered ring analogues,[6,7] is not maintained when it is subjected to nucleophilic attack. This appears to be due to the strain introduced by the five-co-ordinated phosphorus species arising from the nucleophilic attack, and it therefore has not been possible to carry out any reactions which give products retaining the six-membered ring. This behaviour is paralleled by the lack of success of our attempts to prepare analogues of the ring by aminolysis reactions of phosphorus chlorides containing appropriate -P–N- open chains.

Experimental

Reactions were carried out under dried oxygen-free nitrogen. Phosphorus trichloride oxide was distilled before use and its purity checked by ^{31}P n.m.r. spectroscopy. Amine hydrochlorides were recrystallised from ethanol–diethyl ether. Chromatography was carried out using Merck Kieselgel 60 (200—600 mesh ASTM) as support. N.m.r. spectra were obtained on JEOL FX90Q and GX400 spectrometers; chemical shifts are in p.p.m. (δ), referenced to internal tetramethylsilane (^1H and ^{13}C) or external H_3PO_4 (^{31}P). In the assignments of the ^{13}C n.m.r. spectra, C^1 *etc.* refers to the two equivalent phenyl rings, while $C^{1'}$ *etc.* refers to the unique phenyl ring. Carbon nuclei which have unequal couplings to the two chemically equivalent phosphorus atoms of the AB_2 spin systems show deceptively simple triplets for the BB′X spin system. The separation of the outer lines of these triplets is N_{CP}, which is equal to $J_{CP} + J_{C'P}$. Melting points are uncorrected.

Synthesis of 2,4,6-*Trichloro*-1,3,5-*triphenyl*-1,3,5,2λ^5,4λ^5,6λ^5-*triazatriphosphorinane* 2,4,6-*Trioxide* $(PhNPOCl)_3$ (**7**).—Aniline hydrochloride (20 g, 0.15 mol), $POCl_3$ (14.2 cm^3, 0.15 mol), and xylene (6.2 cm^3) were mixed and heated slowly to obtain a melt which was maintained at 130—140 °C for 24 h. The temperature was then raised to 170 °C and maintained for a further 72 h. After cooling the reaction mixture was dissolved in chloroform (*ca.* 250 cm^3) and washed with water. This solution was dried and treated with activated charcoal. Enough diethyl ether (*ca.* 150 cm^3) was added to precipitate polymeric impurities. Filtration and evaporation, followed by flash chromatography using acetone–light petroleum (b.p. 60—80 °C) yielded 6.5 g (25%) of $(PhNPOCl)_3$ (**7**) as white needles, m.p. 222—224 °C [lit.,[5] for $(PhNPOCl)_2$ 228 °C]. An analytical sample was recrystallised from absolute ethanol (Found: C, 41.2; H, 3.05; Cl, 20.6; N, 8.15. $C_{18}H_{15}Cl_3N_3O_3P_3$ requires C, 41.5; H, 2.90; Cl, 20.5; N, 8.05%). Mass spectrum: *m/z* 519 (M^+, 17), 229 (11), 201 (6), 173 (14), 155 (9), 121 (4), 106 (10), 93 (100), and 66 (42%). M^+ isotopic distribution was consistent with $C_{18}H_{15}Cl_3N_3O_3P_3$. N.m.r.: ^{31}P ($CDCl_3$), AB_2 spin system, −1.5(P_a), −1.9(P_b), J_{ab} 26.3 Hz; −2.4 (proposed *sym* isomer); ^{13}C ($CDCl_3$), 131.9 (m, C^1), 131.1 (t, $C^{1'}$), 130.6 (m, C^2), 130.5 (m, C^4), 130.3 (m, $C^{3'}$), 130.2 (m, C^3), and 129.7 p.p.m. (br, $C^{2'}$).

Synthesis of 2,4,6-*Trichloro*-1,3,5-*tri*(p-*tolyl*)-1,3,5,2λ^5,4λ^5,6λ^5-*triazatriphosphorinane* 2,4,6-*Trioxide* $(4\text{-}MeC_6H_4NPOCl)_3$ (**9**).—A mixture of *p*-toluidine hydrochloride (20 g, 0.14 mol), $POCl_3$ (13 cm^3, 0.14 mol), and xylene (5 cm^3) was heated at 170—220 °C for 72 h. The ^{31}P n.m.r. spectrum at this stage indicated that > 50% of the mixture consisted of polymers. The reaction mixture was dissolved in chloroform (*ca.* 250 cm^3) and washed with aqueous sodium hydrogencarbonate solution until the aqueous extracts were no longer acidic. The chloroform solution was evaporated and the resulting solid purified by flash column chromatography. The reaction mixture was loaded in chloroform and $(4\text{-}MeC_6H_4NPOCl)_3$ (**9**) was eluted in 40—50% ethyl acetate-light petroleum. This yielded 221 mg (1%) of (**9**), m.p. 124—126 °C (lit.,[5] 336 °C) (Found: C, 44.7; H, 3.95; N, 7.90. $C_{21}H_{21}Cl_3N_3O_3P_3$ requires C, 44.8; H, 3.75; N, 7.45%). Mass spectrum: *m/z* 561 (M^+, 100), 440 (15), 334 (11), 241 (11), 136 (11), and 106 (30%); M^+ isotopic distribution was consistent with $C_{21}H_{21}Cl_3N_3O_3P_3$. N.m.r. ($CDCl_3$): ^{31}P, AB_2 spin system, −1.3(P_a), −1.7(P_b), J_{ab} 29 Hz; ^{13}C, 140.9 (d of t, J_{CP} 2.5, N_{CP} 2.5, C^4), 140.6 (t, J_{CP} 2.0, $C^{4'}$), 131.0 (t, J_{CP} 1.7, $C^{3'}$), 130.9 (m, C^3), 130.4 (d of t, J_{CP} 1.6, N_{CP} 1.6, C^2), 129.3 (br, $C^{2'}$), 129.2 (t, J_{CP} 1.8, $C^{1'}$), and 128.2 p.p.m. (d of t, J_{CP} 1.8 Hz, N_{CP} 1.8 Hz, C′).

Reaction of 2,6-*Dimethylaniline Hydrochloride with* 1 *equivalent of* $POCl_3$.—A mixture of 2,6-dimethylaniline hydrochloride (6.2 g, 0.04 mol), $POCl_3$ (3.7 cm^3, 0.04 mol), and xylene (15 cm^3) was heated slowly to 155 °C. This temperature was maintained for 24 h. A solid material slowly precipitated. It was washed with xylene (yield 6.02 g), was insoluble in all organic solvents, and decomposed after prolonged exposure to air. This material was presumably polymeric in nature. High vacuum sublimation (220 °C at 0.7 mmHg, *ca.* 93 Pa) yielded a white crystalline solid (**4**) which decomposed rapidly in air, m.p. 183—186 °C (Found: C, 47.8; H, 4.80; N, 6.95. $C_{16}H_{18}Cl_2N_2O_2P_2$ requires C, 47.6; H, 4.45; N, 6.95%). Mass spectrum: *m/z* 402 (M^+, 39), 367 (18), 268 (11), 201 (66), 184 (11), 165 (40), 120 (100), 106 (56), 91 (69), and 77 (28%); M^+ isotopic distribution was consistent with $C_{16}H_{18}Cl_2N_2O_2P_2$. ^{31}P N.m.r. ($CDCl_3$): −5.9 (s) and −8.5 p.p.m. (s) (proposed *cis* and *trans* isomers). Compound decomposes rapidly in solution.

Reactions of p-*Nitroaniline, Methylamine, and Isobutylamine Hydrochlorides with* $POCl_3$.—These were performed in an identical manner to that previously described for aniline hydrochloride. No products were isolated; the initially formed *N*-aryl- or *N*-alkyl-phosphoramidic dichlorides were identified by ^{31}P and ^1H n.m.r. spectroscopy.

Synthesis of 2,4,6-*Trichloro*-1,3,5-*tri*(p-*methoxyphenyl*)-1,3,5,2λ^5,4λ^5,6λ^5-*triazatriphosphorinane* 2,4,6-*Trioxide* $(4\text{-}MeOC_6H_4NPOCl)_3$ (**8**).—A mixture of *p*-methoxyaniline hydrochloride (5.66 g, 0.035 mol), $POCl_3$ (3.3 cm^3, 0.035 mol), and xylene (5 cm^3) was heated at 165 °C for 24 h. The reaction mixture was then cooled, dissolved in chloroform (*ca.* 250 cm^3), and the resulting solution washed with water until the aqueous extracts were no longer acidic. The chloroform layer was then evaporated and the crude product purified by flash column chromatography. The crude product was loaded in chloroform and $(4\text{-}MeOC_6H_4NPOCl)_3$ was eluted with acetone-light petroleum (40%). The product was re-columned using ethyl acetate-light petroleum (50—60%) yielding 622 mg (8.6%) of $(4\text{-}MeOC_6H_4NPOCl)_3$ (**8**), m.p. 110—112 °C (Found: C, 41.5; H, 6.75; Cl, 17.5; N, 3.65. $C_{21}H_{21}Cl_3N_3O_6P_3$ requires C, 41.3; H, 6.90; Cl, 17.4; N, 3.45%). Mass spectrum: *m/z* 609 (M^+, 100), 594 (5), 305 (5), 273 (7), 228 (5), 203 (9), 187 (9), 152 (14), 121 (27), 106 (10), and 91 (5%); M^+ isotopic distribution was consistent with $C_{21}H_{21}Cl_3N_3O_6P_3$. N.m.r. ($CDCl_3$): ^{31}P, AB_2 spin system, −1.1(P_a), −1.5(P_b), J_{ab} 33.5 Hz; −2.42 (proposed *sym* isomer); ^{13}C, 161.0 (m, C^4), 160.8 (t, J_{CP} 1.8 Hz, $C^{4'}$), 131.8

(s, C^3), 130.6 (br, $C^{3'}$), 123.9 (s, $C^{2'}$), 122.8 (s, C^2), 115.5 (s, $C^{1'}$) and 115.4 p.p.m. (s, C^1).

Hydrolysis of Compound (**7**) *with Sodium Hydroxide*.—The compound $(PhNPOCl)_3$ (280 mg) was dissolved in a solution of 2 mol dm^{-3} sodium hydroxide (1.5 cm^3), water (10 cm^3), and acetone (10 cm^3). The solution was stirred at room temperature for 12 h and then adjusted to pH 7 by dropwise addition of 2 mol dm^{-3} sodium hydroxide. Slow evaporation of this solution followed by recrystallisation of the resulting precipitate from acetone-light petroleum yielded 25 mg of a white crystalline solid, m.p. 211—213 °C. ^{31}P N.m.r. $[(CD_3)_2CO]$: −4.9 p.p.m. (s). Mass spectrum: *m/z* 323 (M^+, 100), 230 (36), 213 (15), 182 (11), 138 (9), 93 (99.5), and 65 (31%). Lit. for $(PhNH)_3PO$: m.p. 213—215 °C;[16] ^{31}P n.m.r. −4.8 p.p.m.[17]

Reaction of Compound (**7**) *with Sodium Ethoxide in Ethanol*.—Sodium (840 mg) was dissolved in absolute ethanol and the resulting sodium ethoxide solution was made up to 100 cm^3 with absolute ethanol. A 7.8 cm^3 volume of this solution was added to $(PhNPOCl)_3$ (494 mg) and stirred under nitrogen for 2 h. The solution was then filtered to remove the precipitate of sodium chloride. Evaporation of the filtrate yielded 455 mg of a white solid. This was washed with diethyl ether and the resulting solution evaporated to yield 210 mg (22%) of $[(EtO)_2PONPh]_2$-PONHPh as a white hygroscopic solid (Found: C, 50.4; H, 5.7; N, 7.2. $C_{26}H_{36}N_3O_7P_3$ requires C, 52.4; H, 6.05; N, 7.1%). Mass spectrum: *m/z* 595 (M^+, 22), 503 (4), 427 (28), 399 (3), 366 (6), 320 (8), 236 (11), 229 (17), 173 (23), 155 (28), 106 (16), 93 (100), 77 (12), and 65 (31%). N.m.r. ($CDCl_3$): ^{31}P, AB_2 spin system, −1.09(P_a) and −1.24(P_b), J_{PP} 28.6 Hz; ^1H, 7.95 (d, 1 H, J_{HP} 7.1, NH), 7.27 (m, 10 H, C_6H_5), 7.09 (m, 4 H, C_6H_5), 6.98 (m, 1 H, C_6H_5), 4.1—3.9 (m, 8 H, OCH_2), 1.18 (t, 6 H, J_{HH} 7.1, CH_3), and 1.15 (t, 6 H, J_{HH} 7.1 Hz, CH_3); on irradiation at 1.17 p.p.m. the multiplet at *ca.* 4 p.p.m. showed three signals at 4.15 (2 H), 4.06 (4 H), and 3.96 (2 H), each with J_{HH} 10, J_{HP} 5 Hz; ^{13}C, 139.9 (s, $C^{1'}$), 136.7 (s, C^1), 130.9 (m, C^2), 129.1 (m, C^2), 128.7 (m, $C^{2'}$), 127.9 (s, C^4), 121.9 (s, $C^{4'}$), 119.0 (m, C^2), 64.1, 63.4 (m, m, CH_2), and 15.9 p.p.m. (m, CH_3) (see text and Figure 3 for further details of this spectrum).

Crystal-structure Determination of Compound (**7**).—Crystals of compound (**7**) grow as large transparent cuboids from chloroform–light petroleum; the one chosen for diffraction study (*ca.* 0.2 × 0.3 × 0.4 mm) was sealed in a Lindemann glass capillary under dry nitrogen. Diffracted intensities were collected (ω—2θ scans) in the range $4.0 \leqslant 2\theta < 50.0°$ at 298 K on a Nicolet *P3m* four-circle diffractometer. Of 3 773 unique reflections, 2 456 had $I \geqslant 3\sigma(I)$, where $\sigma(I)$ is the standard deviation in I based on counting statistics. Only these data were used in final refinement of the structure, after all the data had been corrected for Lorentz and polarisation effects, and an analytical correction applied for *X*-ray absorption.[18]

Crystal data. $C_{18}H_{15}Cl_3N_3O_3P_3$, $M = 520.8$, monoclinic, $a = 11.401(2)$, $b = 15.545(3)$, $c = 12.695(3)$ Å, $\beta = 92.01(1)°$, $U = 2\,248.5(7)$ Å^3, $D_c = 1.54$ g cm^{-3}, $Z = 4$, $F(000) = 1\,056$, space group $P2_1/n$ (non-standard setting of no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 6.44 cm^{-1}.

Structure solution and refinement. The structure was solved by direct methods and all refinements, by blocked-cascade least-squares techniques, were performed on a Data General S230 'Eclipse' computer with the SHELXTL suite of programs.[18] All non-hydrogen atoms were refined with anisotropic thermal parameters and the phenyl-ring carbon atoms were fitted to regular hexagons (C–C 1.395 Å). The majority of the hydrogen-atom positions were located from a Fourier difference calculation but all were included in the refinements by the 'riding' method [C–H 0.96 Å, isotropic thermal parameter 1.2 times the equivalent ($U_{eq.}$) of the supporting carbon atom].

The weighting scheme applied during the refinement was of the form $w^{-1} = [\sigma^2(F_o) + 0.0003|F_o|^2]$. The atomic scattering factors are included in the program of ref. 18. 235 Least-squares variables were refined to an R value of 0.051 ($R' = 0.055$) at convergence; residual peaks and troughs in the final difference Fourier synthesis were between +0.5 and −0.5 e Å^{-3} respectively. Atomic co-ordinates are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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