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Five- and Six-Membered Spirocyclic Cyclotriphosphazene Derivatives with Methacryloyl Substituents on the Spirocyclic Ring

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ABSTRACT: *Synthetic procedures have been developed for the preparation of spiro(2,3-dioxypropylmethacryloyltetrachlorcyclotriphosphazene, $N_3P_3Cl_4[OCH_2CH(OC(O)=CH_2)O]$ (**2**) and spiro((2-methyl-3-oxy-2-(oxymethyl)propyl)methacryloyltetrachlorocyclotriphosphazene, $N_3P_3Cl_4[OCH_2CMe(CH_2OC(O)=CH_2)CH_2O]$ (**3**). The ^1H, ^{13}C and ^{31}P NMR spectra have been analyzed using two-dimensional (COSY and HETCOR) techniques and spectra simulation methods. The crystal and molecular structure of* **3** *has been investigated by single-crystal X-ray diffraction techniques. The crystals are monoclinic with the space group $P2_1/C$ with $a = 12.154(5)$, $b = 7.825(5)$, and $c = 20.208(10)$ Å and $\beta = 103.240°$ with $V = 1870.8(17)$ Å° and $Z = 4$.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 669–677, 1998

INTRODUCTION

The preparation of cyclophosphazenes with substituents capable of undergoing further synthetic elaboration allows a significant expansion of the number and types of derivatives of this widely studied class of materials [1]. In the case of exocyclic groups containing an olefinic moiety, addition polymerization reactions lead to organic backbone polymers with the inorganic ring system as a substituent [2,3]. We have recently focused on the synthesis and polymerization of cyclophosphazenes with methacrylates as the exocyclic group [4–6]. In the course of these investigations, it was discovered that the most convient of the methacrylate derivatives, the phosphazene derivative obtained from 2-hydroxyethyl methylmethacrylate, $N_3P_3Cl_5O(CH_2)_2OC(O)C(CH_3=CH_2$, undergoes a slow phosphazene–phosphazane rearrangement [5]. The preliminary report of the mechanism of this rearrangement indicated a first-order process involving dissociation of the carbon-oxygen bond linking the organic component to the phosphazene ring [5]. We are exploring routes to methacrylate monomers for which this process is obviated [6]. In this article, we report one such approach involving anchoring the exocyclic group to the phosphazene using two points of attachment, i.e., via spirocyclic derivatives.

EXPERIMENTAL

Materials

Organic compounds were purchased from Aldrich Chemical Company and used as delivered except as noted. Solvents were purchased from J. T. Baker Inc. Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (**1**), was received from Nippon Soda Co. and was sublimed prior to use. Deuterated solvents were purchased

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Dedicated to Prof. Robert Holmes on the occasion of his 70th birthday.
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from Cambridge Isotope Labs, Inc. All reactions were run under a nitrogen (N_2) atmosphere.

Methods

All NMR spectra were acquired on a Bruker ARX-500 spectrometer equipped with an Aspect Station computer. Data work-up was done using Bruker UXNMR software running under the UNIX/X11 operating system. Spectrometer operating frequencies were 500.13 MHz(^{1}H), 202.46 MHz(^{31}P), and 125.76 MHz(^{13}C). Tetramethylsilane was used as an internal reference for ^{1}H and ^{13}C spectra and 85% H_3PO_4 as an external reference for ^{31}P spectra. Broad band (Waltz16) ^{1}H decoupling was used for ^{13}C experiments unless otherwise noted. Gated decoupling experiments utilized standard Bruker parameter sets and pulse programs, as did two-dimensional experiments (COSY and HETCOR). Time domain data sizes for COSY experiments were adjusted as needed for adequate resolution, and zero filling in the f_1 domain was used to square the frequency domain data matrix when necessary. Infrared spectra were recorded on a Perkin Elmer System 2000 FT-IR. NMR simulations were done using a modified version [7] of the UEANMR spin simulation program compiled for use in an MSDOS(DOS/4G runtime) environment. Crystallographic details have been deposited with the Fachinformationszcntium Karlsruhe.

Preparation of spiro(2,3-dioxypropylmethacryloyltetrachloro-cyclotriphosphazene (**2**). Freshly distilled pyridine (7.0 mL, 0.086 mol) was added to a solution of **1** (12.53 g, 0.036 mol) and *p*-methoxyphenol (ca. 5 mg) in anhydrous diethyl ether (90 mL). A solution of 2,3-dihydroxypropyl methacrylate [8] (4.61 g, 0.028 mol) in anhydrous diethyl ether (40 mL) was then slowly added to the phosphazene-pyridine solution. Stirring was continued for 2 hours at room temperature, after which the reaction mixture was brought to a gentle reflux. After 96 hours, heating was stopped and the apparatus allowed to cool to room temperature. The reaction mixture was filtered to remove the pyridine hydrogen chloride and washed sequentially with 2M HCl, saturated $NaHCO_3$ solution, and water. The solution was dried over $MgSO_4$, filtered, and the ether removed by rotoevaporation to yield 15.12 g of a white, sticky paste. Flash chromatography (60% diethyl ether in low boiling petroleum ether) of 2.55 g of the crude solid yielded 1.14 g of a light yellow oil that could be induced to crystallize in low-boiling petroleum ether to yield 0.68 g of **2** (27%) as a fine white crystalline solid (melting point 73.5–75°C). Anal calcd for $C_7H_{10}O_4N_3P_3Cl_4$: C, 19.33; H, 2.32; N, 9.66; mol wt 434.91. Found: C, 19.59; H, 2.28; N, 9.58; mol wt 435 (mass spec).

^{1}H NMR($CDCl_3$): δ(vinyl H_{cis}) 6.26 (d of q, 1 H), $^2J(H_{cis}H_{trans})$ = 1.2, $^4J(H_{cis}H_{Me})$ = 0.9; δ(vinyl H_{trans}) 5.67 (d of q, 1 H), $^4J(H_{trans}H_{Me})$ = 1.6; δ(C<u>H</u>) 4.91 (m, 1 H); $\delta(-CH_2OP\equiv)$ 4.42 (m, 2 H); $\delta(-COC\underline{H}_2-)$ 4.39 (m, 2 H); δ(Me) 1.98 (d of d, 3 H). ^{13}C NMR($CDCl_3$); δ(C=O) 167.4; δ(=C<) 136.0; $\delta(H_2C=)$ 127.9; δ(CH) 76.8(d), ^2J(CP) = 1.9; $\delta(-CH_2OP\equiv)$ 68.2(d), ^2J(CP) = 1.3; $\delta(-COCH_2^-)$ 63.8(d), ^3J(CP) = 5.7; δ(Me) 18.9. ^{31}P NMR ($CDCl_3$); $\delta(PCl_2)$ 26.1 (m); $\delta(PO_2)$ 24.0 (m). IR(neat); 2970 (m, CH str); 1724 (s, C=O str); 1638 (m, C=C str); 1453 (m, CH_2 scsr); 1243 (vs, PN str); 1204, 1157 (vs, CO str); 1087, 1072, 1035 (s, PO str); 886, 848 (m, PCl asym); 743 (m, PCl sym).

Preparation of spiro((2-methyl-3-oxy-2-(oxymethyl)propyl)methacryloyltetrachlorocyclotriphosphazene (**3**). 2,2-dimethoxypropane (55.7 mL, 0.43 mol) was added to a solution of 37.50 g (0.31 mol) of tris(hydroxymethyl)ethane (THME) in dry acetonitrile (500 mL). A solution of 0.97 g (0.0051 mol) of dehydrated *p*-toluenesulfonic acid monohydrate in 20 mL of dry acetonitrile was added, whereupon the reaction mixture turned yellow. After approximately 19 hours of reaction, the solution had become dark red. The solvent was removed, leaving an orange residue that was then redissolved in 500 mL of anhydrous diethyl ether. The ethereal solution was washed with saturated $NaHCO_3$ solution and saturated NaCl solution, dried over $MgSO_4$, and filtered. The ether was removed by rotoevaporation to yield a yellow liquid that was distilled to give 37.53 g (bp 130.5–131.5°C, 75.2% yield) of 5-(hydroxymethyl)-2,2,5-trimethyl-1,3-dioxane (HMTD, confirmed by ^{1}H NMR).

Methacryloyl chloride was slowly added to a cold (0°C) solution of 5.0 g (0.031 mol) of HMTD and 4.54 g (0.037 mol) of 4-(*N,N*-dimethylamino)pyridine (DMAP) in anhydrous diethyl ether (20 mL). After addition was complete, the reaction mixture was allowed to warm to room temperature and stand for 2 hours. The chalky white mixture was then washed with 0.15 M HCl solution, saturated $NaHCO_3$ solution, and saturated NaCl solution; dried over $MgSO_4$; and filtered. Evaporation of the ether resulted in the isolation of 4.08 g (58% yield) of (5-(oxymethyl)-2,2,5-trimethyl-1,3-dioxane) methacrylate (OMTDM) as a clear liquid (confirmed by ^{1}H NMR). The entire sample was deprotected (using a previously described method [8]) to generate 2.73 g (82% yield) of (3-hydroxy-2-(hydroxymethyl)-2-methyl propyl)methacrylate (confirmed by ^{1}H NMR).

The diol (4.08 g 0.017 mol) was slowly added to a solution of 7.42 g (0.021 mol) of **1**, 5.13 g (0.042

mol) of DMAP, and a few milligrams of *p*-methoxyphenol in 100 mL of anhydrous diethyl ether. After 72 hours, the solids were filtered and the ether solution was washed with 2M HCl, saturated $NaHCO_3$ solution, and saturated NaCl solution. The organic phase was dried over $MgSO_4$, filtered, and solvent removed by evaporation to give 4.30 g of a white paste. A pure sample of spiro((2-methyl-3-oxy-2-(oxymethyl)propyl)methacryloyltetrachlorocyclotriphosphazene was isolated from 1.98 g of the crude material by flash chromatography (1.5% diethyl ether/methylene chloride). A total of 0.33 g (17% yield) of an off-white solid was collected. The material was further purified by recrystallization from petroleum ether to yield **3** as white/clear needles (melting point 94.5–95.5°C). Anal calcd for $C_8H_{14}O_4N_3P_3Cl_4$: C, 23.35; H, 3.05; N, 9.08; mol wt 462.96. Found: C, 23.62; H, 2.95; N, 8.96; mol wt 464 ([M + 1], mass spec).

^{1}H NMR($CDCl_3$): δ(vinyl H_{cis}) 6.12 (d of q, 1 H), $^2J(H_{cis}H_{trans})$ = 1.2, $^4J(H_{cis}H_{Me})$ = 0.9; δ(vinyl H_{trans}) 5.62(d of q, 1 H), $^4J(H_{trans}H_{Me})$ = 1.6; $\delta(\equiv POCH_2-)$ 4.3(d, 2H), ^3J(PH) = 11.3, 4.3(d, 2 H), ^3J(PH) = 15.4; $\delta(-OCH_2-)$ 4.26 (s, 2 H); $\delta(CH_2 = C(C\underline{H}_3)-)$ 1.97 (d of d, 3 H); $\delta(H_3\underline{C}C(CH_2O-)_3)$ 1.03 (s, 3 H). ^{13}C NMR ($CDCl_3$); $\delta(C=O)$ 167.3, $\delta(=C)$ 135.4; $\delta(H_2C=)$ 126.9; $\delta(\equiv POCH_2-)$ 73.6 (d), ^2J(CP) = 6.2; $\delta(-OCH_2-)$ 65.8; $\delta(H_3C\underline{C}(CH_2O-)_3)$ 36.6 (d), $^3J_{cp}$ = 5.3; $\delta(CH_2 = C(\underline{C}H_3)-)$ 18.9; $\delta(H_3\underline{C}C(CH_2O-)_2)$ 17.2.

^{31}P NMR($CDCl_3$); $\delta(PCl_2$ 25.2 (d of d), $^2J(PCl_2P_{spiro})$ = 76.3, $^2J(PCl_2 - PCl_2)$ = 61.0, $\delta(PCl_2)$ 23.3 (d of d), $^2J(PCl_2-P_{spiro})$ = 62.1; $\delta(P_{spiro})$ 3.5 (d of d). IR(film cast from CH_2Cl_2); 2977 (m, CH str); 1723 (s, C=O str); 1639 (m, C=C str); 1469, 1437, 1402, 1377 (m, CH_2 scsr); 1246 (vs, PN str); 1202, 1158 (vs, CO str); 1059, 1012 (vs, PO str); 849 (m, PCl sym).

RESULTS AND DISCUSSION

The synthesis of the spirocyclic phosphazene compounds **2** and **3** is more complicated than that previously reported for other spirocyclic phosphazenes. Currently, there are no dihydroxyalkyl methacrylates commercially available, so the parent diols used for the production of the spirocyclic monomers had to be synthesized. The linking groups are derived from triols that if simply reacted with $N_3P_3Cl_6$ would lead to a complex mixture of products. For example, in the case of the reaction of glycerol with $N_3P_3Cl_6$, four structural isomers of disubstituted phosphazenes are possible [9]. The reaction between two polyfunctional reagents also has the potential of leading to the formation of bridged species and ultimately matrix polymers. To circumvent these problems, two of the three hydroxyl functionalities of the triol can be protected by forming acetonides (Schemes 1 and 2). The remaining hydroxyl group can be used to form methacrylate esters. The acetonides can then be deprotected to generate the diols that are reacted with $N_3P_3Cl_6$ trimer [10].

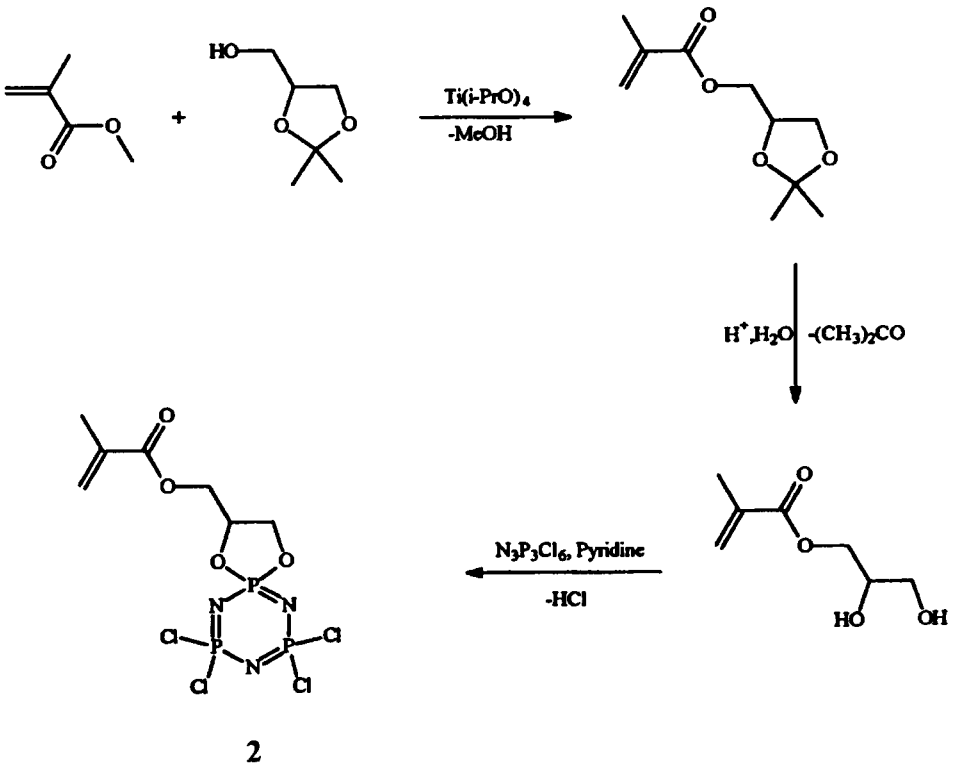
The method used to prepare **2** is shown in Scheme 1. Substitution at the phosphazene ring was monitored by ^{31}P NMR spectroscopy. At 70°C in chloroform, the concentration of the spiro product increased rapidly during the first 12 hours of reaction, and after approximately 24 hours, the reaction appeared to have reached equilibrium at 66% conversion. In the later stages of the reaction, small amounts of what is believed to be a dispiro product were detected, presumably owing to the buildup of the monospiro product, whereas the concentration of unreacted diol was still significant.

Attempts were made to derivatize **2** by substituting trifluoroethoxide groups for the chlorine atoms on the phosphazene ring. The use of sodium trifluoroethoxide caused the formation of an insoluble gel presumably involving the anionic polymerization of the methacrylate groups. No further attempts at functionalization of either spirocyclic derivatives were made.

Because 5-(hydroxymethyl)-2,2,5-trimethyl-1,3-dioxane is not commercially available, the synthesis of **3** required the protection of the parent triol 1,1,1-(hydroxymethyl)ethane as the acetonide, adding a step to the overall synthetic procedure (Scheme 2). The methacrylate ester of this triol acetonide was much more sensitive to acidic conditions than the solketal methacrylate used in the synthesis of **2**, making deprotection much easier. This spirocyclic compound, **3**, was more stable than **2** to decomposition in air around its melting point, even after several heating and cooling cycles.

^{1}H NMR Studies

The ^{1}H NMR data for **2** and **3** are tabulated along with other related compounds in Table 1. The chemical shifts associated with the methacrylate unit of **2** and **3** (vinyl and α-methyl protons) were found to be very similar to those of (2-oxyethyl methacryloyl)pentachlorocyclotriphosphazene, $N_3P_3Cl_5$ ($OCH_2CH_2OC(O)C(CH_3) = CH_2$ (**4**) and methyl methacrylate (MMA). The chemical shifts of the protons of the spacer group, part of which makes up the phosphate ring of the spirocycle, were found to be at higher frequency relative to the protons of the nonspirocyclic spacer of **4**. Restricted rotation around the PO–CC bond in **2** and **3** causes the $^3J_{PH}$ values to deviate substantially from those of conformationally



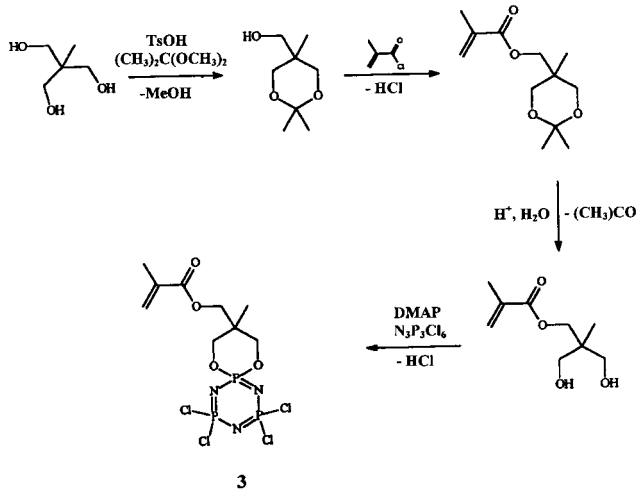
2

SCHEME 1

unconstrained spacer groups in **4**. A Karplus relationship is known for P–H couplings that allows the prediction of which proton is in an equatorial position (larger coupling constant) and which is in an axial position (smaller coupling constant) [11]. When applied to **2**, it can be deduced that the exocyclic substituent on the tertiary carbon of the five-membered ring is in the expected equatorial position. The axial and equatorial protons of the methylene groups in the phosphate ring of **3** can be identified by the coupling constants ($^3J_{PH}$) of 8.0 Hz and 20.2 Hz, respectively, but absolute identification cannot be made. The analysis of the proton NMR spectrum of **3** is complicated by the additional symmetry present in the structure and the rapid ring inversion.

The proton NMR spectra for both monomers were observed to contain second-order spin systems in the protons of the alkyl chain due to the presence of enantiotopic methylene sites that give rise to AB-type subspectra. Observation of these spin systems was complicated owing to splittings caused by neighboring protons and by the phosphorus center. Broadband phosphorus decoupling of the proton spectrum was often used to simplify the splitting patterns. In addition, ^{1}H COSY experiments were done to aid in the assignment of chemical shifts. The proton spectrum of **2** was found to be an AMNOP spin system with additional splitting observed for the A,M,O, and P resonances due to ^{31}P coupling.

A comparison of the observed and simulated spectrum for **2** (phosphate ring portion) is shown in Figure 1. The spacer group/phosphate ring is composed of an endocyclic methine group (spin A) and endocyclic methylene unit (spins M and P) and an exocyclic methylene unit (spins N and O). Only the methine proton is coupled to all of the other spins (including the ^{31}P spirocyclic center). In the case of **3**, an AB spectrum, close to the A_2 limit, is observed for the methylene protons of the phosphate ring. The rapid exchange of the protons between axial and equatorial positions in the six-membered ring creates two average environments and results in two chemical shifts that are only slightly different from each other and are not resolved in the ^{31}P decoupled spectrum. If coupling to ^{31}P is maintained, the high-frequency lines of each resonance overlap whereas the low-frequency lines are resolved. When observed in conjunction with the lower-frequency resonance of the exocyclic methylene protons, the spectrum appears as a deceptively symmetric pattern (Figure 2).



SCHEME 2

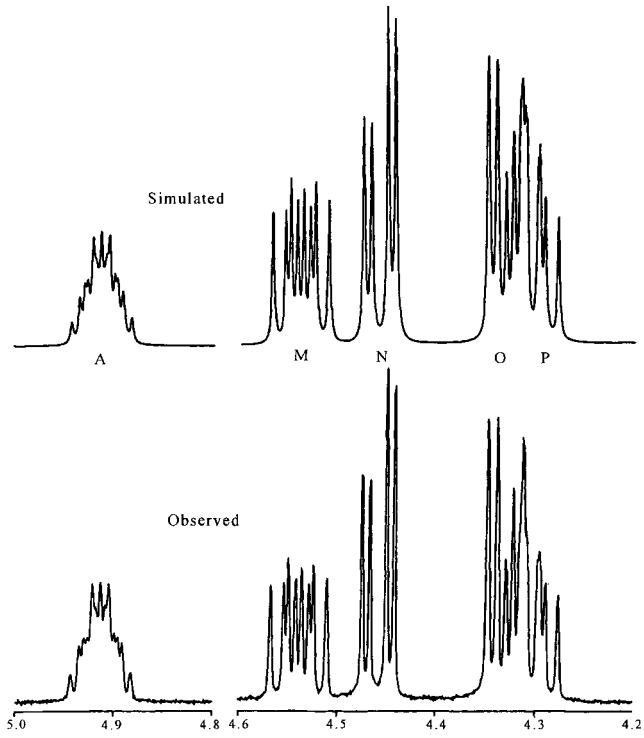


FIGURE 1 Methine and methylene region of the proton NMR spectrum of spiro(2,3-dioxypropylmethacryl)tetrachlorocyclotriphosphazene (**2**).

^{13}C NMR Studies

The ^{13}C NMR data for **2** and **3** are tabulated along with other selected compounds in Table 2. The chemical shifts associated with the methacrylate unit of **2** and **3** (vinyl and α-methyl carbons) were found to be very similar to those of **4** and MMA. Because β-carbon vinyl chemical shifts can be correlated to the electron withdrawing power of the α-substituent [12,13], the higher frequency of the β-carbon chemical shifts of **2** and **4** relative to the parent alcohols, 2,3-dihydroxypropyl methacrylate (DHPMA) and 2-hydroxyethyl methacrylate (HEMA), suggests that additional deshielding is due to the presence of the phosphazene ring. Hyperconjugation through the spacer group may play an additional role in the unusually long range of the electron withdrawing effect. The observation that the β-carbon of the vinyl group of **2** experiences a greater deshielding effect from the phosphazene than in **4** reflects the two points of attachment of the organic group to the phosphazene in **2**, thus providing two paths for electronic induction compared with the single path available in **4**. Restriction of the possible conformations along the spacer chain may also increase the effect of hyperconjugative interactions. The shortest path for electron induction in **3** is through a propyl chain, but multiple connectivity and possible restricted conformations result in a greater overall electron withdrawing effect of the phosphazene phosphorus center.

Phosphorus coupling constants were also measured. In **2**, the $^{2}J_{CP}$ value was less than the $^{3}J_{CP}$ value. Although it seems counterintuitive that the long range coupling is stronger, it has been observed previously in phosphazene compounds ([13] and in **4**) and is consistent with the general observation that the magnitude of the coupling constants for phosphorus-carbon couplings is $^{1}J \gg {}^{3}J > {}^{2}J > {}^{4}J$. Because this anomaly can cause confusion when assigning chemical shifts based on the magnitude of carbon-phosphorus coupling, chemical shift assignments for **2** and **3** were based on ^{1}H-^{13}C HETCOR experiments. Significant deviations from the average coupling constant values for the spiro compounds may be explained by considering that the net value of the coupling constant is the sum along all paths between coupled nuclei ($J_{obs.} = J_{path1} + J_{path2}$) [11]. The nuclei along the various coupling paths have been labeled in Figure 3. It is known that coupling constants vary in sign based on whether an odd or even number of bonds connect the nuclei. On taking these two considerations into account and using estimations for coupling along various paths, estimations for the coupling constants in **2** can be made.

The estimations of the endocyclic two-and three-bond coupling constants are based on the averages observed for other methacryloylphosphazene monomers. The exocyclic three-bond coupling constant was estimated to be less than the endocyclic one. Based on Karplus relationships, endocyclic POCC

TABLE 1 ^{1}H NMR Data for Spirocyclic Phosphazene Compounds and Related Compounds

Compound	$\underline{H}_2C=$[b]	$POC\underline{H}_2$	$C(O)OC\underline{H}_2$	$=C(C\underline{H}_3)COO-$	$^{3}J_{PH}$	$^{4}J_{PH}$
2[a]	6.26, 5.67	4.91,[c] 4.42	4.39	1.98	8.2,[c] 12.7, 10.3	0.6
3[c]	6.12, 5.62	4.31	4.30	1.97	8.0, 20.2	—
4 [14]	6.28, 5.40	4.00	4.00	1.98	9.7	—
MMA [15]	6.10, 5.57	—	3.76	1.94	—	—
$N_3P_3Cl_4(OCH_2CH_2O)$ [16]	—	4.48	—	—	11.2	—
$N_3P_3Cl_4(OCH_2CH_2CH_2O)$ [16]	—	4.53	—	—	12.9	1.6

[a]Coupling constants for 1 and 2 are taken from results of spin simulations.
[b]Vinyl proton shifts are listed as *cis* and *trans* (respectively) to the α-methyl.
[c]Methine proton.
MMA = methyl methacrylate.

dihedral angles would be close to 0° (a maximum for J) and the exocyclic dihedral one would be 120° (an intermediate value for J). The four-bond coupling value was estimated to be no larger than the average line width of the ^{13}C resonance (ca. 1 Hz), as these constants were not observed in the ^{13}C NMR spectra of any monomer. The signs are arbitrary, with even bond couplings assumed to be positive and odd bond couplings negative. The absolute values of the estimates are in qualitative agreement with the observed values, of **2**, and help to rationalize the observed couplings in this compound. Application of this estimation technique to rationalize the coupling constants of **3** is not as straightforward. The unique torsional environment of the six-membered ring makes it difficult to estimate coupling constants along the various paths, and therefore no reasonable predictions can be made.

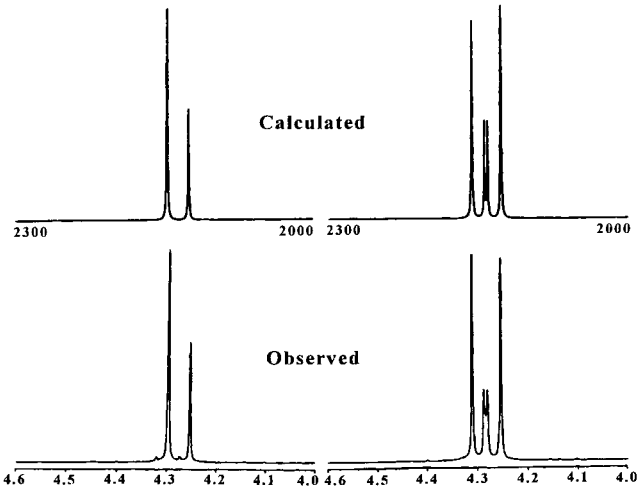


FIGURE 2 Proton NMR of methylene units in **3** with the ^{31}P nuclei decoupled (*left*) and ^{31}P nuclei coupled (*right*).

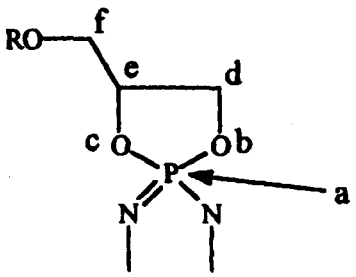
^{31}P NMR Studies

The ^{31}P NMR data for **2** and **3** area tabulated along with related compounds in Table 3. The monomers reported in this work contain disubstituted phosphazenes as part of a spirocyclic ring system. By definition, these spirocyclic ring systems have a geminal substitution pattern at the substituted phosphorus center. For nonspirocyclic alkoxy disubstitutions of phosphazenes, geminal substitution is not the preferred pathway and accordingly few gem-dialkoxytetrachlorocycloriphosphazenes have been reported. Of the few reported, it is seen that, as with the nonalkoxy phosphazenes, the effect of this substitution is to shift (relative to $N_3P_3Cl_5$) the resonance of the $\equiv PCl_2$ centers to higher frequency, and the resonance of the $\equiv P(OR)_2$ to lower frequency. The effect of the spirocyclic substitution on the $\equiv PCl_2$ center is to shift it to higher frequency; however, the effect of substitution on the shift of the $\equiv P_{(spiro)}$ center appears depend on the size of the phosphate ring. A correlation between OPO bond angles (from X-ray diffraction data) and ^{31}P NMR chemical shifts has been suggested for previously observed spirocyclic phosphazenes [17]. However, there is a considerable scatter of the phosphazene data around the suggested curve, as there is no assessment of the correlation of the data to the curve, and it does not include unconstrained geminal substitutions (nonspiro compounds). A simpler approach can be applied to the data by plotting δ versus $|\theta - 104.5°|$ (θ = OPO bond angle) to develop a linear correlation. When the data in Table 4 are plotted, they can be fitted to a straight line with a correlation coefficient (R^2) of 0.98, and the chemical shift at the "optimum" angle of 104.5 is predicted to be 1.7 ppm. According to this relationship, movement of the OPO angle away from the optimum causes the spiro phosphorus atom to be deshielded. Attempts to make correlations between X-ray diffraction data and the NMR data are difficult, as the former rep-

TABLE 2 ^{13}C NMR Data for Spirocyclic Phosphazene Compounds and Related Compounds

Compound	*C=O*	*=C<*	*=CH₂*	*POC*	*CCC*	*C(O)OC*	*=C(CH₃)–*	*²J_CP*	*³J_CP*
2	167.4	136.0	127.9	76.8,[a] 68.2	—	63.8	18.9	1.9,[a] 1.3	5.7
3	167.3	136.4	126.9	73.6	36.4	65.8	18.9	6.2	5.3
4 [14]	167.5	136.2	127.2	67.5	—	62.9	18.8	6.5	9.3
MMA [15]	167.9	136.3	125.3	—	—	51.8	18.3	—	—
HEMA [15]	167.8	136.4	126.0	61.1[b]	—	66.3	18.3	—	—
DHPMA [8]	167.1	136.0	125.9	70.3,[b] 65.4[b]	—	63.5	18.1	—	—

[a]Methine carbon.
[b]COH carbon.
MMA = methyl methacrylate; HEMA = 2-hydroxyethyl methacrylate; DHPMA = 2,3-dihydroxypropyl methacrylate.



J_{ace} and $J_{abd} = +7$ $\quad {}^2J_{ae} = (+7) + (-9) = -2$

J_{abde} and $J_{aced} = -9$ $\quad {}^2J_{ad} = (+7) + (-9) = -2$

$J_{acef} = -6$ $\quad {}^3J_{af} = (-6) + (+1) = -5$

$J_{abdef} = +1$

FIGURE 3 Phosphorus-proton coupling constrants for the alkyl spacer of **2**.

resents a static structure and the latter, the average of dynamic structures.

The spectrum of **2** is observed as an A_2B spin system and was successfully simulated (Figure 4). The chemical shifts and coupling constants were found to be in agreement with those previously reported for $N_3P_3Cl_4(OCH_2CH_2O)$. The outer lines of the B spin resonances are sharp, whereas the inner lines are broad (all of the A spin resonances are also broad). This is observed in both the ^1H coupled and decoupled spectrum. Given that it is known that quadrupolar relaxation (due to the chlorine nuclei) broadens ^{31}P resonances, it is suggested that the spin states responsible for the outer lines are not influenced by this process as are the other transitions' spin states [18].

Unlike the previously reported compounds, $N_3P_3Cl_4(OCH_2CR_2CH_2O)$ (R = H, CH_3) [16,20] **3** exhibits an ABX spin system in its ^{31}P NMR spectrum (Figure 5). The deviation from A_2X is due to the presence of two different substituents ($-CH_3$ and $-CH_2OC(O)C(CH_3) = CH_2$) at the 5− position of the phosphate ring. Because the planes of the rings are

TABLE 4 OPO Bond Angles (θ) and ^{31}P Chemical Shifts (δ) of the ≡P(spiro) Center

Compound	θ	δ
$N_3P_3Cl_4(OCH_2CH_2O)$	98.3	24.5
$N_3P_3Cl_4(OCH_2CH_2CH_2O)$	105.4	3.4
$N_3P_3Cl_4(OCH_2CH_2CH_2CH_2O)$	106.1	9.2
3	104.0	3.5

TABLE 3 ^{31}P NMR Data for Sirocyclic Phosphazene Compounds and Related Compounds

Compound	*PCl₂*	*PClOR*	*(P(OR)₂*	*²J_PP*
2	26.1	—	24.0	68.5
3	25.2, 23.3	—	3.5	76.1,[a] 61.8,[a] 60.6[b]
gem-$N_3P_3Cl_4(OMe)_2$ [19]	25.1	—	9.2	65.0
$N_3P_3Cl_4(OCH_2CH_2O)$ [16]	26.5	—	24.5	68.0
$N_3P_3Cl_4(OCH_2CH_2CH_2O)$ [16]	24.1	—	3.4	69.2
$N_3P_3Cl_4(OCH_2C(Me)_2CH_2O)$ [20]	23.3	—	2.2	69.3

[a]PCl_2-P(spiro) coupling.
[b]PCl_2–PCl_2 coupling.

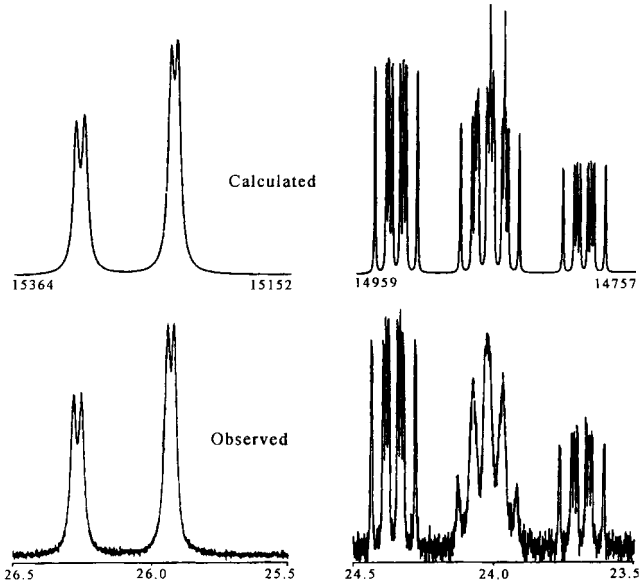


FIGURE 4 ^{31}P NMR spectrum of **2**, PCl_2 (A spins) on *left* and P(spiro) (B spin) on *right.*

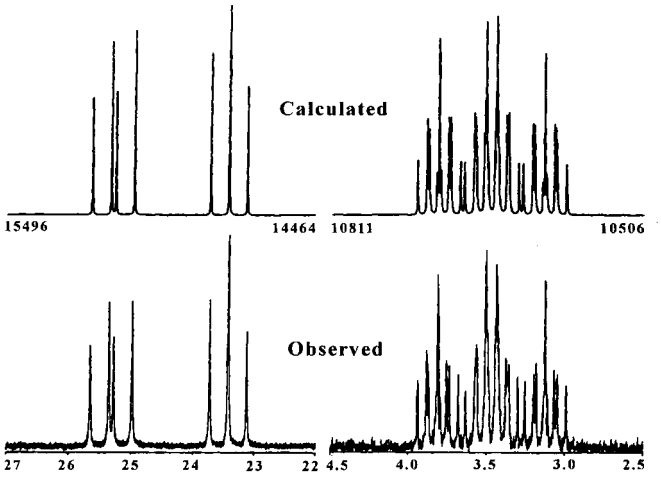


FIGURE 5 ^{31}P NMR spectrum of **3**, PCl_2 (AB spins) on *left* and P(spiro) (X spin) on *right.*

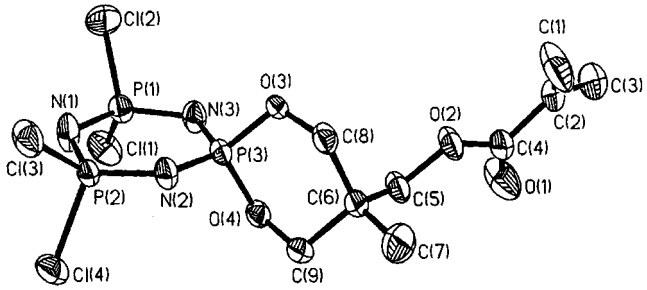


FIGURE 6 ORTEP view of **3**.

perpendicular to each other, the $\equiv PCl_2$ units are in different chemical environments and lead to different chemical shifts. A tentative assignment of the highfield $\equiv PCl_2$ resonance to the $\equiv PCl_2$ on the same side of the phosphate ring plane as the methyl group is proposed. This is based on comparison to the chemical shifts observed in $N_3P_3Cl_4(OCH_2C(CH_3)_2CH_2O)$. Although the individual $^2J(PCl_2 - P_{spiro})$ values in **3** are significantly different, the average value (69.0 Hz) is similar to that observed in other spirocyclic phosphazenes. The chemical nonequivalence of the $\equiv PCl_2$ units also makes it possible to observe PCl_2–PCl_2 coupling directly. Observation of the proton coupled ^{31}P NMR spectra clearly reveals that the X spin (3.5 ppm) is the $\equiv$P(spiro) center.

The crystal and molecular structure of **3** has been determined. The observed structure (Figure 6) confirms the interpretations of the NMR data presented here. The spirocyclic arrary that is the organofunctional phosphazene substituent exhibits expected geometric parameters (Tables 5 and 6), and the different environments of the $\equiv PCl_2$ centers due to the disposition of the methacryloyl substituent are clearly demonstrated. The range of endocyclic phosphorus–nitrogen bond lengths is 155.6 to 159.8 A, with an average of 157.7A (Table 5). The randomness of the variation is in contrast to several other disubstituted cyclophosphazenes where a definite pattern is observed in the endocyclic bond lengths [1]. The endocyclic bond angles at the phosphorus centers are all similar (Table 6). These observations suggest that any electronic effects operative on the phosophazene ring due to the substituents are similar for the chloro and spirocyclo entities.

TABLE 5 Bond Lengths (A) for **3**

P(3)-O(4)	1.574(4)	P(3)-O(3)	1.577(4)
P(3)-N(3)	1.556(5)	P(3)-N(2)	1.598(5)
P(2)-Cl(4)	1.998(2)	P(2)-Cl(3)	1.983(3)
P(2)-N(2)	1.565(5)	P(2)-N(1)	1.559(6)
P(1)-Cl(2)	1.990(3)	P(1)-Cl(1)	2.002(3)
P(1)-N(3)	1.584(6)	P(1)-N(1)	1.576(6)
O(4)-C(9)	1.472(8)	O(3)-C(8)	1.475(7)
C(2)-C(4)	1.511(8)	C(2)-C(3)	1.356(11)
C(2)-C(1)	1.479(12)	C(4)-O(2)	1.354(8)
C(4)-O(1)	1.180(9)	O(2)-C(5)	1.453(6)
C(6)-C(9)	1.536(7)	C(6)-C(8)	1.534(8)
C(6)-C(5)	1.528(9)	C(6)-C(7)	1.504(10)

In summary, the strategy for obtaining stable cyclotriphosphazenes with methacylates as substituents by the use of spirocyclic attachment has proved successful as demonstrated in the synthesis of **2** and **3**. The complex NMR (^1H, ^{13}C, ^{31}P) spectra noted for

TABLE 6 Bond Angles (°) for **3**

O(4)-P(3)-O(3)	104.0(2)	O(4)-P(3)-N(3)	107.8(3)
O(3)-P(3)-N(3)	108.0(2)	O(4)-P(3)-N(2)	110.2(2)
O(3)-P(3)-N(2)	108.9(2)	N(3)-P(3)-N(2)	117.2(3)
Cl(4)-P(2)-Cl(3)	100.9(1)	Cl(4)-P(2)-N(2)	110.7(2)
Cl(3)-P(2)-N(2)	109.0(2)	Cl(4)-P(2)-N(1)	108.9(2)
Cl(3)-P(2)-N(1)	108.0(3)	N(2)-P(2)-N(1)	117.9(3)
Cl(2)-P(1)-Cl(1)	101.3(1)	Cl(2)-P(1)-N(3)	109.5(2)
Cl(1)-P(1)-N(3)	108.6(2)	Cl(2)-P(1)-N(1)	108.5(3)
Cl(1)-P(1)-N(1)	108.9(2)	N(3)-P(1)-N(1)	118.7(3)
P(3)-O(4)-C(9)	115.0(3)	P(3)-O(3)-C(8)	117.1(3)
P(3)-N(3)-P(1)	121.5(3)	P(3)-N(2)-P(2)	121.3(3)
O(4)-C(9)-C(6)	111.2(4)	C(4)-C(2)-C(3)	113.9(6)
C(4)-C(2)-C(1)	119.2(6)	C(3)-C(2)-C(1)	126.9(6)
C(2)-C(4)-O(2)	109.3(6)	C(2)-C(4)-O(1)	127.4(6)
O(2)-C(4)-O(1)	123.3(5)	C(4)-O(2)-C(5)	114.9(5)
C(9)-C(6)-C(8)	109.7(5)	C(10)-C(6)-C(5)	106.3(5)
C(8)-C(6)-C(5)	112.9(5)	C(10)-C(6)-C(7)	108.1(5)
C(8)-C(6)-C(7)	108.5(5)	C(5)-C(6)-C(7)	111.0(6)
O(3)-C(8)-C(6)	112.1(5)	P(2)-N(1)-P(1)	121.0(4)
O(2)-C(5)-C(6)	107.1(5)		

these derivatives have been elucidated and rationalized. The molecular structure of **3** is in accord with the spectroscopic observations. Attempts at the homopolymerization and copolymerization of the methacrylate center in these compounds will be discussed in a future communication.

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