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Phosphorus–Nitrogen Compounds. 14. Synthesis, Stereogenism, and Structural Investigations of Novel N/O Spirocyclic Phosphazene Derivatives

Elif Ece İlter, Nuran Asmafiliz, and Zeynel Kılıç*

Department of Chemistry, Ankara University, 06100 Tandoğan-Ankara, Turkey

Muhammet Işıklan

Department of Chemistry, Kırıkkale University, Kırıkkale, Turkey

Tuncer Hökelek

Department of Physics, Hacettepe University, 06800 Beytepe-Ankara, Turkey

Nagihan Çaylak

Department of Physics, Sakarya University, 54187 Esentepe-Adapazarı, Turkey

Ertan Şahin

Department of Chemistry, Atatürk University, 25240 Erzurum, Turkey

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The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with N/O donor-type N-alkyl-*o*-hydroxybenzyl- and *o*-hydroxynaphthylamines result in novel mono- (**3a**, **4a** and **4b**), di- (**5a** and **5b**), and tri- (**3b**, **6a**, and **6b**) spirocyclic phosphazene derivatives. The tetrakis-pyrrolidinophosphazene, **3b**, has been obtained from the reaction of partly substituted compound **3a** with the excess pyrrolidine in tetrahydrofuran. The relationship between the endocyclic NPN (α) and exocyclic NPO (α') bond angles of the analogous spirocyclic phosphazenes with the δP shifts of NPO phosphorus atoms have been presented. It was observed that there is a linearity between α angles and δP shifts, while no linear relationship has been observed for α' angles. In addition, we have found the correlation between Δ(P–N) and δ_{NPO} shifts, which implies a linear relationship. Δ(P–N) = (*a* – *b*), where *a* and *b* are the average lengths of two adjacent P–N bonds. The structural investigations of all of the compounds have been made by elemental analyses; mass spectrometry; Fourier transform infrared spectroscopy; one-dimensional ^{1}H, ^{13}C, and ^{31}P NMR; distortionless enhancement by polarization transfer; and two-dimensional correlation spectroscopy, heteronuclear shift correlation, and heteronuclear multiple-bond correlation homo- and heteronuclear correlation techniques. The solid-state structures of **3a**, **4a**, **4b**, and **5a** have been determined by X-ray crystallographic techniques. The asymmetric units of compounds **3a** and **4a** contain two independent molecules, and **3a** has strong intermolecular N–H···N hydrogen bonds linking three phosphazene rings. The molecular structure of **6a** looks like a propeller where the chemical environment of P1 is different from that of P2 and P3. On the other hand, compounds **5a** and **5b** are expected to exist as cis- or trans-geometric isomers and to be in cis (meso) or trans (racemic) configurations. The crystallographic and preliminary chiral solvating agents results show that both of them are trans (racemic). In addition, **6a** and **6b** are also expected to exist as cis–trans–trans- and cis–cis–cis-geometric isomers; both of them are found to be in cis–trans–trans geometries. According to the two-dimensional spectroscopic data, the possible conformations of **3a** and **4a** in $CDCl_3$ are the same with the solid-state structures.

Introduction

Cyclophosphazene derivatives and poly(organo)phosphazenes containing alternate phosphorus and nitrogen atoms in their cyclic skeletons are an important family of inorganic ring systems.[1,2] The use of cyclophosphazene derivatives as ligands is an area of interest for transition metal cations.[1b,1c,3] Ligation through a ring nitrogen atom or a substituted ligating group on the phosphazene ring can afford very interesting

* Author to whom correspondence should be addressed. Phone: +90-312-2126720. Fax: +90-312-2232395. E-mail: zkilic@science.ankara.edu.tr.

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mono- and multinuclear structures.[3,4] They have also drawn considerable attention for the further design of highly selective anticancer and antibacterial reagents, such as the aziridine-crown substituted phosphazene obtained by Brandt et al.[5] It cleaves the DNA and halts the growth of cancer cells. In addition, cyclophosphazenes have found industrial applications in the production of lubricants,[6] inflammable textile polyphosphazene fibers, advanced elastomers with different organic and inorganic side groups,[7] and rechargeable lithium batteries[8] and multidimensional use as biomedical materials including synthetic bones.[9]

The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, with bifunctional reagents have been investigated, and the first examples of spiro, ansa, and spiro-ansa cyclophosphazenic derivatives have been obtained.[10] There are four possible routes known for the reactions of $N_3P_3Cl_6$ with bifunctional reagents: (i) the replacement of two geminal Cl atoms to give a spiro architecture, (ii) the replacement of two nongeminal Cl atoms to afford an ansa architecture, (iii) intermolecular reactions between Cl atoms of phosphazene rings to yield a bino architecture, or (iv) intermolecular condensation reactions to give cyclolinear or cyclomatrix polymers.[11] It has been observed that, when the reactions are carried out with aminoalcohols and $N_3P_3Cl_6$, the major product is a spiro derivative in tetrahydrofuran (THF). However, the first ansa product was separated by Harris and Williams in 1984 under different reaction conditions.[12] In recent years, our group has been investigating the chemistry of bulky bifunctional reagents such as podands,[13] diaza-crown ethers,[14] and N-arylaminophenols[15] with $N_3P_3Cl_6$. The reactions of diaminopodands with $N_3P_3Cl_6$ produce spiro, dispiro, spiro-ansa, and bino architectures,[16,17] while N-arylaminophenols lead to the formation of spiro architectures.[15] Additionally, the interesting reactions of bifunctional reagents with fluoro- and chlorophosphazenes give spiro, ansa, spiro-ansa and bis ansa skeletons in different solvents.[1b,1c,18] The ansa derivatives of fluorophosphazenes are readily transformed to the spirocycles in the presence of fluorinated or nonfluorinated bases, while the analogous tetrachloro ansa compounds are not.

In 2003, the stereogenic properties of cyclophosphazenes were discovered as a new subject of interest.[19] Generally, three kinds of stereogenism have been observed in trimeric phosphazene derivatives, given as follows: (i) phosphorus atoms having four different chemical environments give rise to stereogenism;[20] (ii) substituent groups, such as binaphthyls and biphenyls bonded to phosphorus atoms, produce stereogenic properties,[11a,21] and (iii) exocyclic nitrogen atoms in crypta-phosphazenes having pyramidal configurations may

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Table 1. The Selected Bond Lengths (Å) and Angles (deg) for **3a**, **4a**, **4b**, and **5a**

	3a	**3a′**	**4a**	**4a′**	**4b**	**5a**
P1−N1	1.624(4)	1.599(4)	1.589(7)	1.596(7)	1.603(3)	1.566(3)
P1−N3	1.594(4)	1.584(4)	1.598(7)	1.587(7)	1.589(3)	1.598(3)
P1−N4	1.601(4)	1.601(4)	1.630(8)	1.609(7)	1.608(3)	1.645(3)
P1−O1	1.588(3)	1.580(3)	1.575(6)	1.567(6)	1.570(3)	1.584(3)
P2−N1	1.535(4)	1.559(4)	1.555(7)	1.556(7)	1.549(3)	1.582(3)
P2−N2	1.589(4)	1.575(4)	1.557(7)	1.570(6)	1.581(3)	1.583(3)
P2−N5						1.635(3)
P2−O2						1.582(3)
P3−N3	1.553(4)	1.558(4)	1.5513(94)	1.5566(76)	1.603(3)	1.550(3)
P3−N2	1.553(5)	1.592(5)	1.5686(87)	1.5802(76)	1.589(3)	1.558(3)
P1−N1-P2	122.8(2)	122.5(3)	123.5(4)	123.9(4)	123.69(17)	125.17(18)
P1−N3-P3	122.6(2)	122.2(3)	124.3(4)	124.3(4)	124.08(18)	120.86(18)
N1−P2-N2	118.8(2)	119.1(2)	120.0(4)	119.7(4)	119.64(15)	114.99(15)
N3−P3-N2	119.8(2)	119.6(2)	118.9(4)	119.5(3)	119.34(15)	120.30(16)
P2−N2-P3	120.7(3)	119.5(3)	119.6(5)	118.8(4)	119.27(17)	121.32(19)

Table 2. Crystallographic Details

compound	**3a**	**4a**	**4b**	**5a**
empirical formula	$C_{11}H_9Cl_4N_4OP_3$	$C_{10}H_{13}Cl_4N_4OP_3$	$C_9H_{11}Cl_4N_4OP_3$	$C_{20}H_{26}Cl_2N_5O_2P_3$
fw	447.93	439.95	425.93	532.27
crystal system	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/a$
a (Å)	8.2643 (9)	9.5684(11)	8.947(5)	9.311(5)
b (Å)	12.545(2)	11.5791(19)	11.090(5)	22.628(5)
c (Å)	18.595(3)	17.129(2)	17.058(5)	12.208(5)
α (deg)	107.546(13)	93.663(13)	90	90
β (deg)	98.551(12)	92.424(10)	97.040(5)	99.111(5)
γ (deg)	97.400(11)	107.067(13)	90	90
V (Å^3)	1786.6(5)	1806.8(4)	1679.8(13)	2539.6(18)
Z	4	4	4	4
μ (cm^{-1})	86.4 (CuK_α)	85.24 (CuK_α)	9.91 (MoK_α)	4.72 (MoK_α)
ρ (calcd) (g cm^{-1})	1.665	1.617	1.684	1.392
number of reflections total	7005	7226	47215	70088
number of reflections unique	7332	7119	5132	7766
R_{int}	0.0229	0.0525	0.0580	0.0707
$2\theta_{max}$ (deg)	148.50	148.42	61.12	61.16
T_{min}/T_{max}	0.109/0.264	0.158/0.278	0.7229/0.8655	
number of parameters	423	398	215	291
R [$F^2 > 2\sigma(F^2)$]	0.0685	0.0808	0.0595	0.0773
wR	0.1848	0.2670	0.1763	0.2330

also have stereogenism.[14] The structures of some of the stereogenic phosphazene derivatives have been determined by ^{31}P NMR spectroscopy upon the addition of chiral solvating agents [CSA; (*S*)-(+)-2,2,2-trifluoro-1-(9′-anthryl)-ethanol] and X-ray crystallographic analyses.[14,19−21]

We report here (i) the synthesis of novel mono- (**3a**, **4a**, and **4b**), di- (**5a** and **5b**), and tri- (**3b**, **6a** and **6b**) spirocyclicphosphazene derivatives; (ii) the preparation of tetrakis-pyrrolidinophosphazene (**3b**) by the addition of an excess of pyrrolidine to **3a**; (iii) the structures of the compounds determined by elemental analyses, mass spectrometry (MS); Fourier transform infrared spectroscopy (FTIR); CSA (for **5a** only); one-dimensional ^{1}H, ^{13}C, and ^{31}P NMR; distortionless enhancement by polarization transfer (DEPT); and two-dimensional correlation spectroscopy (COSY), heteronuclear shift correlation (HETCOR), and heteronuclear multiple-bond correlation (HMBC) homo- and heteronuclear correlation techniques; (iv) the solid-state structures of mono- (**3a**, **4a**, and **4b**) and di- (**5a**) spirocyclic architectures established by X-ray diffraction techniques; (v) the relationships between α and α′ angles versus δP-shift values, as well as Δ(P−N) values versus δ_{NPO} shifts.

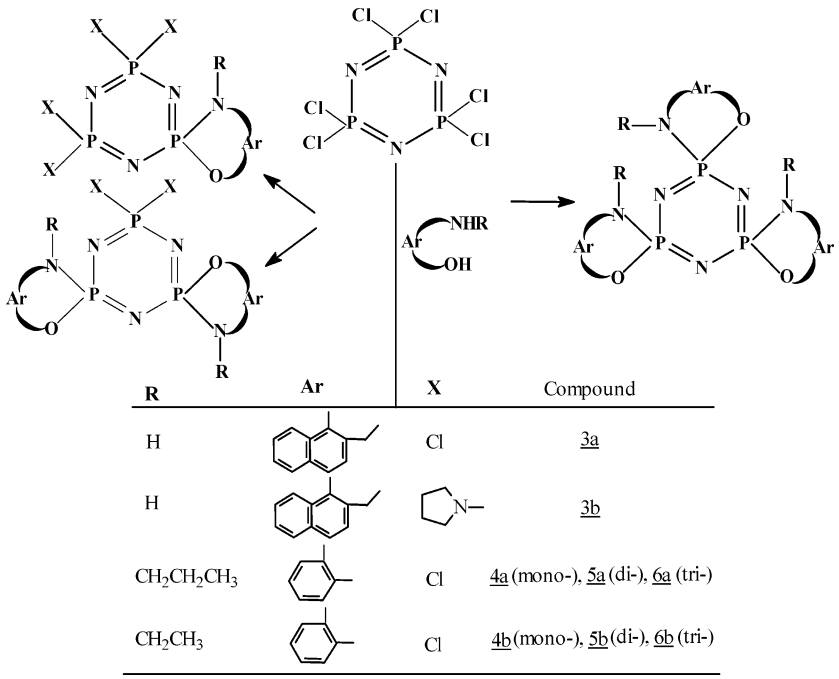
Experimental Section

General Methods. The reagents were of commercial grade and used without further purification. Hexachlorocyclotriphosphazatriene was purchased from Aldrich. THF was dried over 3 Å molecular sieves. The other solvents were purified and dried according to standard methods.[22] Melting points were measured on a Gallenkamp apparatus using a capillary tube. All experiments were carried out under an argon atmosphere. ^{1}H, ^{13}C, and ^{31}P NMR; HETCOR; and HMBC spectra were recorded on a Bruker DPX FT-NMR (500 MHz) spectrometer ($SiMe_4$ as an internal standard and 85% H_3PO_4 as an external standard). The spectrometer was equipped with a 5 mm PABBO BB inverse gradient probe. Standard Bruker pulse programs[23] were used throughout the entire experiment. IR spectra were recorded on a Mattson 1000 FTIR spectrometer in KBr discs and were reported in cm^{-1} units. Microanalyses were carried out by the microanalytical service of TUBITAK-Turkey. Electrospray ionization (ESI) mass spectrometric analyses were performed on the AGILEND 1100 MSD spectrometer.

Preparation of Compounds. N-propyl-*o*-hydroxybenzylamine

(22) Perrin, D. D.; Armarego, W. L.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, 1980.
(23) *1D WIN-NMR*, release 6.0; *2D WIN-NMR*, release 6.1; Bruker: Madison, WI.

Scheme 1. The Reaction Pathway of $N_3P_3Cl_6$ with N-alkyl-*o*-hydroxybenzylamines (**1** and **2**) and *o*-hydroxynaphthylamine (**3**)



(**1**),[24] N-ethyl-*o*-hydroxybenzylamine (**2**),[24] and *o*-hydroxynaphthylamine hydrochloride (**3**)[25] have been prepared according to the methods reported in the literature.

4,4,6,6-Tetrachloro-3,4-dihydro-spiro[1,3,2-naphthoxazaphosphorine-[2λ^5,4λ^5,6λ^5][1,3,5,2,4,6]-triazatriphosphorine (3a). A solution of **3** (0.53 g, 2.50 mmol) in THF (100 mL) and triethylamine (2.00 mL) were slowly added to a stirred solution of $N_3P_3Cl_6$ (0.87 g, 2.50 mmol) in THF (50 mL) at room temperature. The mixture was stirred for 3 h, and the precipitated aminehydrochloride salt was filtered off. The solvent was evaporated completely and the oily residue purified by column chromatography with benzene. White powder was crystallized from acetonitrile ($CHCl_3$, R_f = 0.87). Yield: 0.90 g (59%). mp: 170 °C. Anal. Calcd for $C_{11}H_9N_4OP_3Cl_4$: C, 29.46; H, 2.00; N, 12.50. Found: C, 30.01; H, 1.92; N, 12.48. ESI-MS (fragments are based on ^{35}Cl, I_r %): *m*/*z* 448 ([(M+H)]$^+$, 52.0). FTIR (KBr, cm^{-1}): ν 3088;3065 (C−H arom.), 2874;2826 (C−H aliph.), 1214;1190 (P═N), 590;517 (P−Cl). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.49 (bp, 1H, N*H*), 4.80 (dd, 1H, $^1J_{HH}$ = 4.60 Hz, $^3J_{PH}$ = 11.90 Hz, Ar−C*H*$_2$), 4.84 (dd, 1H, $^1J_{HH}$ = 4.60 Hz, $^3J_{PH}$ = 11.90 Hz, Ar−C*H*$_2$), 7.23−7.85 (6H, Ar-*H*). ^{13}C NMR (400 MHz, $CDCl_3$, ppm, numberings of aromatic carbons are given in Table 5 of the Supporting Information): δ 40.5 (d, $^2J_{PC}$ = 2.7 Hz, Ar-*C*H$_2$), 116.60 (d, $^3J_{PC}$ = 9.5 Hz, C_2), 120.10 (d, $^3J_{PC}$ = 9.5 Hz, C_4), 122.40 (C_5), 125.90 (C_8), 128.00 (C_{11}), 129.60 (C_9), 130.50 (C_{10}), 130.70 (C_6), 131.20 (C_7), 149.40 (d, $^2J_{PC}$ = 8.1 Hz, C_3).

4,4,6,6-Tetrapyrrolidino-3,4-dihydro-spiro[1,3,2-naphthoxazaphosphorine-[2λ^5,4λ^5,6λ^5][1,3,5,2,4,6]-triazatriphosphorine (3b). To a THF (50 mL) solution of $N_3P_3Cl_6$ (1.74 g, 5.00 mmol) were added 1.05 g of **3** (5.00 mmol) in THF (75 mL) and triethylamine (5.00 mL) slowly at room temperature. The mixture was stirred for 2 h, and 2.56 g of pyrrolidine (3.00 mL, 40.0 mmol) was added slowly. The mixture was refluxed for 6 h, and the precipitated amine hydrochloride was filtered off. The solvent was evaporated at reduced pressure, and the oily residue was purified by column chromatography with chloroform. The product was crystallized from acetonitrile ($CHCl_3$, R_f = 0.69). Yield: 1.06 g (61%). mp: 148

Chart 1

Compound	R	Ar	X
1	$CH_2CH_2CH_3$	-	-
2	CH_2CH_3	-	-
3	H	-	-
3a	H		Cl
3b	H		
4a	$CH_2CH_2CH_3$		Cl
4b	CH_2CH_3		Cl
5a	$CH_2CH_2CH_3$		Cl
5b	CH_2CH_3		Cl
6a	$CH_2CH_2CH_3$		-
6b	CH_2CH_3		-

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°C. Anal. Calcd for $C_{27}H_{41}N_8OP_3$: C, 55.29; H, 6.99; N, 19.11. Found: C, 54.74; H, 7.18; N, 23.39. ESI-MS (I_r %): *m*/*z* 587 ($[(M+H)]^+$, 100.0), ($[(M-C_4H_8N)+H]^+$, 11.1), ($[(M-C_8H_{16}N_2)+H]^+$, 39.5). FTIR (KBr, cm^{-1}): ν 3059;3026 (C−H arom.), 2961;2861 (C−H aliph.), 1214;1190 (P═N). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.73 (m, 16H, pyrrolidine NCH_2CH_2), 2.69 (bp, 1H, N*H*), 3.10 (m, 16H, pyrrolidine NCH_2), 4.64 (dd, 1H, $^1J_{HH}$ = 7.05 Hz, $^3J_{PH}$ = 14.2 Hz, Ar−CH_2), 4.68 (dd, 1H, $^1J_{HH}$ = 7.06 Hz, $^3J_{PH}$ = 14.2 Hz, Ar−CH_2), 7.10−7.76 (6H, Ar-*H*). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 26.50 (d, $^3J_{PC}$ = 4.6 Hz, pyrrolidine NCH_2CH_2), 41.20 (d, $^2J_{PC}$ = 3.7 Hz, Ar-CH_2), 46.30 (d, $^2J_{PC}$ = 2.2 Hz, pyrrolidine NCH_2), 116.90 (d, $^3J_{PC}$ = 11.5 Hz, C_2), 117.00 (d, $^3J_{PC}$ = 11.5 Hz, C_4), 122.40 (C_5), 124.60 (C_8), 127.10 (C_{11}), 129.10 (C_9), 129.30 (C_{10}), 130.40 (C_6), 131.50 (C_7), 151.70 (d, $^2J_{PC}$ = 7.1 Hz, C_3).

3-Propyl-4,4,6,6-tetrachloro-3,4-dihydro-spiro[1,3,2-benzoxazaphosphorine-[2λ^5,4λ^5,6λ^5][1,3,5,2,4,6]triazatriphosphorine (4a). A solution of 0.40 g of **1** (2.42 mmol) in THF (50 mL) and triethylamine (5.00 mL) were slowly added to a stirred solution of 0.85 g of $N_3P_3Cl_6$ (2.42 mmol) in THF (75 mL) at ambient temperature. The mixture was stirred for 4 h and the precipitated amine hydrochloride filtered off. The solvent was evaporated in vacuo, and the oily product was crystallized from *n*-hexane ($CHCl_3$, R_f = 0.74). Yield: 0.35 g (86%). mp: 84 °C. Anal. Calcd for $C_{10}H_{13}N_4OP_3Cl_4$: C, 28.27; H, 2.95; N, 12.72. Found: C, 28.34; H, 3.10; N, 13.03. ESI-MS (fragments are based on ^{35}Cl, I_r %): *m*/*z* 440 ($[(M+H)]^+$, 100.0); ($[(M-C_3H_7)+H]^+$, 16.7). FTIR (KBr, cm^{-1}): ν 3061;3026 (C−H arom.), 2932;2872 (C−H aliph.), 1222;1190 (P═N), 577;519 (P−Cl). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.99 (t, 3H, $^3J_{HH}$ = 7.38 Hz, $NCH_2CH_2CH_3$), 1.70 (m, 2H, $^3J_{HH}$ = 7.34 Hz, NCH_2CH_2), 3.10 (m, 2H, $^3J_{HH}$ = 7.38 Hz, $^3J_{PH}$ = 12.6 Hz, NCH_2), 4.30 (d, 2H, $^3J_{PH}$ = 15.5 Hz, $ArCH_2$), 7.05−7.30 (4H, Ar-*H*). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 11.30 ($NCH_2CH_2CH_3$), 21.10 (d, $^3J_{PC}$ = 2.04 Hz, NCH_2CH_2), 48.20 (d, $^2J_{PC}$ = 1.26 Hz, $ArCH_2$), 49.70 (d, $^2J_{PC}$ = 2.28 Hz, NCH_2), 118.70 (d, $^3J_{PC}$ = 4.62 Hz, C_4), 123.90 (d, $^3J_{PC}$ = 13.38 Hz, C_2), 124.20 (C_6), 126.40 (C_5), 128.90 (C_7), 149.90 (d, $^2J_{PC}$ = 4.68 Hz, C_3).

3-Ethyl-4,4,6,6-tetrachloro-3,4-dihydro-spiro[1,3,2-benzoxazaphosphorine-[2λ^5,4λ^5,6λ^5][1,3,5,2,4,6]triazatriphosphorine (4b). A total of 4.61 g of $N_3P_3Cl_6$ (13.2 mmol) in THF (75 mL) was added to a solution of **2** (2.00 g, 13.2 mmol) in THF (25 mL) and triethylamine (5.00 mL) at room temperature. The mixture was stirred for 2 h, and the precipitated amine hydrochloride was filtered off. The solvent was evaporated completely, and the oily residue was crystallized from *n*-heptane ($CHCl_3$, R_f = 0.72). Yield: 3.51 g (87%). mp: 78 °C. Anal. Calcd for $C_9H_{11}N_4OP_3Cl_4$: C, 25.35; H, 2.58; N, 13.14. Found: C, 25.62; H, 2.51; N, 13.17. ESI-MS (fragments are based on ^{35}Cl, I_r %): *m*/*z* 426 ($[(M+H)]^+$, 21.7); ($[(M-3Cl)+H]^+$, 13.7). FTIR (KBr, cm^{-1}): ν 3071;3034 (C−H arom.), 2926;2872 (C−H aliph.), 1200;1180 (P═N), 573;517 (P−Cl). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.30 (t, 3H, $^3J_{HH}$ = 7.16 Hz, NCH_2CH_3), 3.20 (m, 2H, $^3J_{HH}$ = 6.95 Hz, $^3J_{PH}$ = 13.4 Hz, NCH_2), 4.30 (d, 2H, $^3J_{PH}$ = 15.65 Hz, $ArCH_2$), 7.05−7.35 (4H, Ar-*H*). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 13.10 (NCH_2CH_3), 42.80 (d, $^2J_{PC}$ = 4.50 Hz, $ArCH_2$), 47.90 (d, $^2J_{PC}$ = 2.00 Hz, NCH_2), 119.40 (d, $^3J_{PC}$ = 8.20 Hz, C_4), 124.60 (d, $^3J_{PC}$ = 7.20 Hz, C_2), 125.0 (C_6), 127.30 (C_5), 129.70 (C_7), 150.80 (d, $^2J_{PC}$ = 8.2 Hz, C_3).

6,6-Dichloro-bis{3-propyl-3,4-dihydro-spiro[1,3,2-benzoxazaphosphorine}[2λ^5,4λ^5,6λ^5][1,3,5,2,4,6]-triazatriphosphorine (5a). A solution of 3.83 g of **1** (23.21 mmol) in THF (75 mL) and triethylamine (5.00 mL) were slowly added to a stirred solution of 4.03 g of $N_3P_3Cl_6$ (11.6 mmol) in THF (75 mL) at room temperature. The mixture was stirred for 8 h, and the precipitated amine hydrochloride was filtered off. The solvent was evaporated completely in vacuo, and the oily residue was crystallized from *n*-hexane ($CHCl_3$, R_f = 0.51). Yield: 2.30 g (40%). mp: 101 °C. Anal. Calcd for $C_{20}H_{26}N_5O_2P_3Cl_2$: C, 45.11; H, 4.88; N, 13.15. Found: C, 45.74; H, 4.83; N, 13.43. ESI-MS (fragments are based on ^{35}Cl, I_r %): *m*/*z* 532 ($[(M+H)]^+$, 100.0). FTIR (KBr, cm^{-1}): ν 3080;3046 (C−H arom.), 2870;2853 (C−H aliph.), 1215;1178 (P═N), 555;506 (P−Cl). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.00 (t, 6H, $^3J_{HH}$ = 7.38 Hz, $NCH_2CH_2CH_3$), 1.75 (m, 4H, $^3J_{HH}$ = 7.40 Hz, NCH_2CH_2), 3.10 (m, 4H, $^3J_{HH}$ = 6.50 Hz,

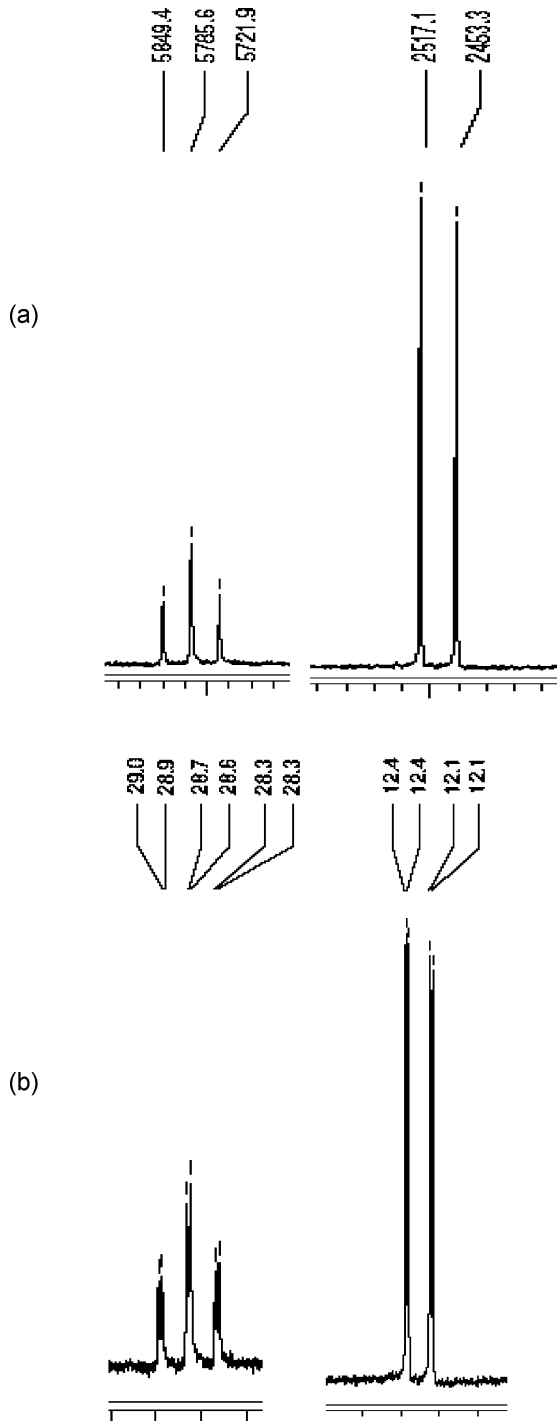


Figure 1. (a) ^{31}P NMR spectrum of compound **5b** before the addition of CSA. (b) ^{31}P NMR spectrum of compound **5b** after the addition of 10 drops of CSA.

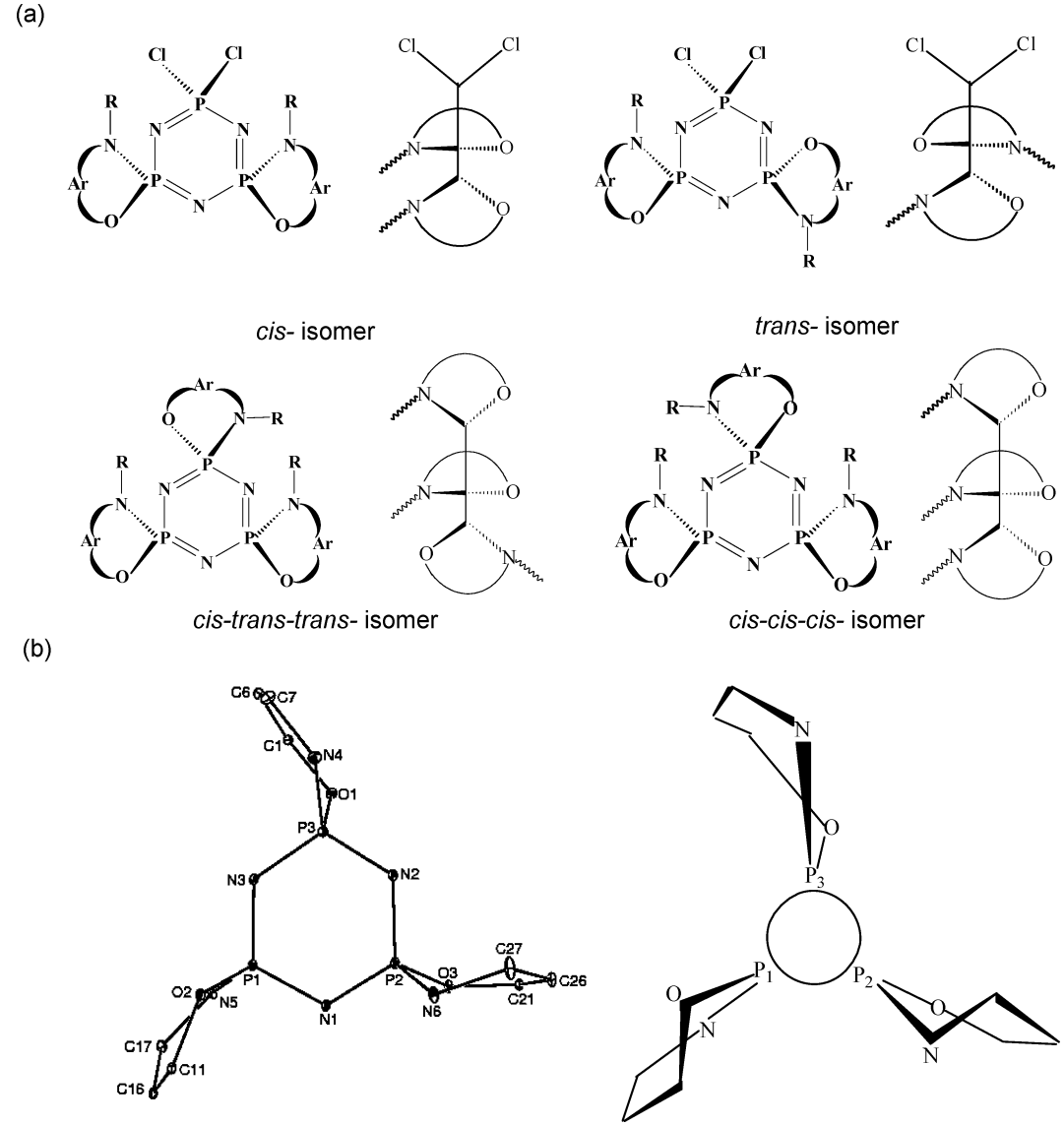


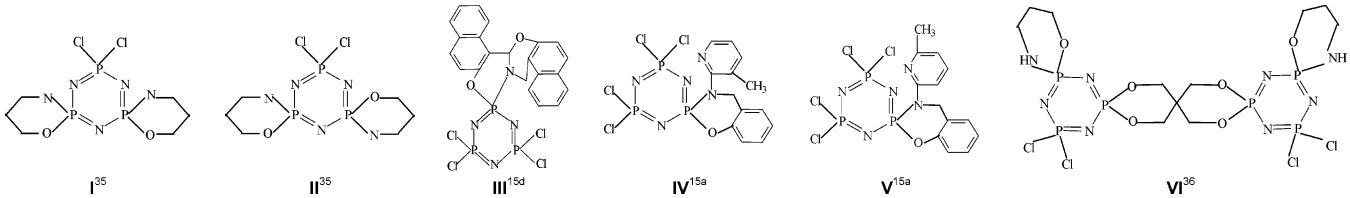
Figure 2. (a) The possible geometric isomers of di- (**5a** and **5b**) and trispirocyclic (**6a** and **6b**) phosphazene architectures. (b) The ORTEP diagram and the propeller view of **6a**.[29]

$^3J_{PH}$ = 13.1 Hz, NC*H*$_2$), 4.20 (dd, 2H, $^1J_{HH}$ = 6.50 Hz, $^3J_{PH}$ = 14.7 Hz, Ar−C*H*$_2$), 4.35 (dd, 2H, $^1J_{HH}$ = 6.60 Hz, $^3J_{PH}$ = 14.6 Hz, Ar−C*H*$_2$), 6.90−7.30 (8H, Ar-*H*). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 11.50 (NCH$_2$CH$_2$*C*H$_3$), 21.20 (NCH$_2$*C*H$_2$), 48.60 (Ar*C*H$_2$), 50.10 (N*C*H$_2$), 119.20 (t, $^3J_{PC}$ = 8.20 Hz, C_4), 124.30 (t, $^3J_{PC}$ = 7.80 Hz, C_2), 125.00 (C_6), 127.20 (C_5), 129.20 (C_7), 150.50 (t, $^2J_{PC}$ = 7.30 Hz, C_3).

6,6-Dichloro-bis{3-ethyl-3,4-dihydro-spiro[1,3,2-benzoxazaphosphorine}[2λ^5,4λ^5,6λ^5][1,3,5,2,4,6]-triazatriphosphorine (5b). A total of 3.50 g of **2** (23.17 mmol) in THF solution (75 mL) and triethylamine (5.00 mL) were slowly added to a stirred solution of 4.02 g of $N_3P_3Cl_6$ (11.6 mmol) in THF (75 mL) at room temperature. The mixture was stirred for 10 h, and the precipitated amine hydrochloride was filtered off. The solvent was evaporated, and the oily residue was crystallized from *n*-hexane ($CHCl_3$, R_f = 0.45). Yield: 1.50 g (43%). mp: 116 °C. Anal. Calcd for $C_{18}H_{22}N_5O_2P_3Cl_2$: C, 42.85; H, 4.36; N, 13.88. Found: C, 43.03; H, 5.07; N, 13.91. ESI-MS (fragments are based on ^{35}Cl, I_r %): *m*/*z* 504 ([(M−H)]$^+$, 6.7). FTIR (KBr, cm^{-1}): ν 3059;3026 (C−H arom.), 2972;2932 (C−H aliph.), 1259;1178 (P═N), 598;559 (P−Cl). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.32 (t, 6H, $^3J_{HH}$ = 7.15 Hz, NCH$_2$C*H*$_3$), 3.25 (m, 4H, $^3J_{HH}$ = 6.93 Hz, $^3J_{PH}$ = 13.6 Hz, NC*H*$_2$), 4.15 (m, 4H, $^1J_{HH}$ = 5.61 Hz, $^3J_{PH}$ = 14.1 Hz, ArC*H*$_2$), 7.05−7.40 (8H, Ar-*H*). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 13.18 (NCH$_2$*C*H$_3$), 42.83 (Ar*C*H$_2$), 48.05 (N*C*H$_2$), 119.32 (d, $^3J_{PC}$ = 3.90 Hz, C_4), 124.90 (d, $^3J_{PC}$ = 3.60 Hz, C_2), 125.0 (C_6), 127.34 (C_5), 129.32 (C_7), 151.20 (d, $^2J_{PC}$ = 3.7 Hz, C_3).

tris{3,4-Dihydro-spiro[1,3,2-benzoxazaphosphorine}[2λ^5,4λ^5,6λ^5-[1,3,5,2,4,6]triazatriphosphorine (6a). A solution of **1** (5.75 g, 34.8 mmol) in THF (75 mL) and triethylamine (5.00 mL) were slowly added to a stirred solution of 4.03 g of $N_3P_3Cl_6$ (11.6 mmol) in THF (75 mL) at ambient temperature. The mixture was refluxed for 18 h and the precipitated amine hydrochloride filtered off. The solvent was evaporated under reduced pressure and the oily residue chromatographed [sillicagel, eluent THF/toluene (1:3)]. The product was crystallized from benzene ($CHCl_3$, R_f = 0.48). Yield: 2.20 g (38%). mp: 133 °C. Anal. Calcd for $C_{30}H_{39}N_6O_3P_3$: C, 57.69; H, 6.25; N, 13.46. Found: C, 57,74; H, 6.83; N, 13.43. ESI-MS (I_r %): *m*/*z* 624 ([M$^+$], 43.4); ([(M−H)]$^+$, 100.0). FTIR (KBr, cm^{-1}): ν 3073;3046 (C−H arom.), 2959;2866 (C−H aliph.), 1244;1180 (P═N). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.94 and 0.98 (t, 6H and 3H, $^3J_{HH}$ = 7.36 Hz, NCH$_2$CH$_2$C*H*$_3$), 1.67 (m, 6H, $^3J_{HH}$ =

Table 3. ^{31}P NMR (decoupled) Spectral Data, α and α′ Angles (deg), and Δ(P−N) Values[a]



I[35] **II**[35] **III**[15d] **IV**[15a] **V**[15a] **VI**[36]

compound	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**	**6a**	**6b**
spin system	AX_2	AB_2	AX_2	AX_2	A_2B	A_2B	AB_2	AX_2
δ (PCl_2)	23.40 ($^2J_{PP}$ = 58.5)	18.80 ($^2J_{PP}$ = 45.2)	23.70 ($^2J_{PP}$ = 56.4)	24.03 ($^2J_{PP}$ = 56.2)	28.60 ($^2J_{PP}$ = 64.5)	28.60 ($^2J_{PP}$ = 63.8)		
δ (PON)	4.54 ($^2J_{PP}$ = 58.5)	16.70 ($^2J_{PP}$ = 45.2)	5.60 ($^2J_{PP}$ = 56.4)	4.95 ($^2J_{PP}$ = 56.2)	12.70 ($^2J_{PP}$ = 64.5)	12.30 ($^2J_{PP}$ = 63.8)	18.20; 18.70 ($^2J_{PP}$ = 52.8)	5.03; 23.71 ($^2J_{PP}$ = 56.3)
NPN (α)[b]	115.05(2)		113.45(0.35)	113.97(14)	115.18(15)			
NPN (α′)	102.50(2); 102.26(19)		103.50(4); 103.38(0.36)	102.77(15)	101.79(15); 102.85(15)			
a/*b*[c]	1.6005(4)/ 1.55125(4)		1.5925(7)/ 1.55475(7)	1.5960(3)/ 1.5530(3)	1.5825(3)/ 1.5620(3)			
Δ (P−N)[d]	0.049		0.037	0.043	0.020			
analogous compounds[e]	**I**[35]	**II**[35]	**III**[15d]	**IV**[15a]	**V**[15a]	**VI**[36]		
δ (PON)	12.0	12.30	1.60	5.15	1.66	12.94		
NPN (α)	115.70(2)	115.18(14)	115.03(17)	116.38(11)	116.45(14)	116.30(7)		
NPN (α′)	105.90(2)	102.60(2)	101.03(14)	100.30(9)	101.66(13)	102.90(7)		
Δ(P−N)	0.017	0.020	0.041	0.026	0.019	0.011		

[a] δ (PCl_2), α, and α′ values for $N_3P_3Cl_6$ are 19.30 ppm, 118.30(2)°, and 101.20(2)°,[37] respectively. [b] Average values have been taken into account for endocyclic angles. [c] *a* and *b* = the average lengths of two adjacent P−N bonds (Å). [d] Δ(P−N) = *a* − *b* (the choice of which of the two bond lengths are subtracted from each other is somewhat arbitrary, but Δ(P−N) must be consistent for the set of compounds discussed and compared). [e] The analogous compounds taken from the literature are as shown in the figure at the top of this table.

7.40 Hz, NCH_2CH_2), 3.08 (m, 6H, $^3J_{HH}$ = 7.50 Hz, $^3J_{PH}$ = 11.7 Hz, NCH_2), 4.22 (m, 6H, $^1J_{HH}$ = 6.59 Hz, $^3J_{PH}$ = 13.8 Hz, Ar−CH_2), 6.80−7.30 (12H, Ar-*H*). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 11.50 and 11.60 ($NCH_2CH_2CH_3$), 21.10 and 21.40 (NCH_2CH_2), 48.40 and 48.60 ($ArCH_2$), 49.60 and 49.80 (NCH_2), 118.30 and 118.60 (d, $^3J_{PC}$ = 4.50 Hz, C_4), 122.50 and 122.60 (C_2), 123.90 and 124.30 (C_6), 126.30 and 126.40 (C_5), 127.90 and 128.00 (C_7), 151.10 and 151.40 (C_3).

4,4,6,6-Tetrapyrrolidino-tris{3,4-dihydro-spiro[1,3,2-benzoxazaphosphorine}[2λ⁵,4λ⁵,6λ⁵][1,3,5,2,4,6]triaza-triphosphorine (6b). A solution of **2** (5.27 g, 34.8 mmol) in THF (75 mL) and triethylamine (5.00 mL) were slowly added to a stirred solution of 4.03 g of $N_3P_3Cl_6$ (11.6 mmol) in THF (75 mL) at room temperature. The mixture was refluxed for 16 h and the precipitated salt filtered off. The solvent was evaporated, and the oily residue was purified with column chromatography with a THF/toluene (1:5) mixture as the eluent. The product was crystallized from chloroform/*n*-heptane (1:1) ($CHCl_3$, R_f = 0.50). Yield: 2.70 g (51%). mp: 114 °C. Anal. Calcd for $C_{27}H_{33}N_6O_3P_3$: C, 55.67; H, 5.67; N, 14.43. Found: C, 56.00; H, 5.83; N, 14.52. ESI-MS (I_r %): *m*/*z* 582 ($[M^+]$, 29.3); ($[(M-H)]^+$, 81.4). FTIR (KBr, cm^{-1}): ν 3080;3038 (C−H arom.), 2970;2866 (C−H aliph.), 1244;1176 (P═N). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 1.25 (t, 9H, $^3J_{HH}$ = 7.20 Hz, NCH_2CH_3), 3.20 (m, 6H, $^3J_{HH}$ = 6.82 Hz, $^3J_{PH}$ = 13.4 Hz, NCH_2), 4.30 (d, 6H, $^3J_{PH}$ = 15.6 Hz, Ar−CH_2), 7.00−7.35 (12H, Ar-*H*). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 13.00 (NCH_2CH_3), 42.80 (d, $^2J_{PC}$ = 4.50 Hz, $ArCH_2$), 47.90 (d, $^2J_{PC}$ = 3.55 Hz, NCH_2), 118.60 (d, $^3J_{PC}$ = 8.3 Hz, C_4), 123.80 (d, $^3J_{PC}$ = 7.30 Hz, C_2), 125.0 (C_6), 127.30 (C_5), 129.70 (C_7), 149.90 (d, $^2J_{PC}$ = 8.80 Hz, C_3).

X-ray Crystal Structure Determinations. Colorless crystals of **3a**, **4a**, **4b**, and **5a** were grown by dissolving the compounds in hot acetonitrile, *n*-hexane, *n*-heptane, and *n*-hexane, respectively, and allowing the solutions to cool slowly. Selected bond lengths and angles are given in Table 1, and crystallographic details are listed in Table 2. The crystallographic data were recorded on an Enraf Nonius CAD4 diffractometer using Cu Kα radiation (λ = 1.54184 Å) at *T* = 296 K for **3a** and **4a** and a Rigaku R-AXIS RAPID-S diffractometer using Mo Kα radiation (λ = 0.71073 Å) at *T* = 296 K for **4b** and **5a**. Absorption corrections by ψ scan[26] (for **3a** and **4a**) and multiscan[27] (for **4b)** were applied. Structures were solved by direct methods (SHELXS-97)[28] and refined by full-matrix least-squares against F^2 using all data (SHELXL-97).[28] All non-H atoms were refined anisotropically. The H atom positions are as follows: [all except H4A and H4B] (for **3a**), [all] (for **4a**), [H8A, H8B, H9A, H9B, H9C] (for **4b),** and [all] (for **5a**) were calculated geometrically at distances of 0.93 (CH) and 0.97 (CH_2) and 0.96 Å (CH_3) from the parent C atoms; a riding model was used during the refinement process, and the U_{iso}(H) values were constrained to be $1.2U_{eq}$ (for CH and CH_2) and $1.5U_{eq}$ (for CH_3). H4A and H4B (for **3a**) and the other H atoms (for **4b)** were located in difference syntheses and refined isotropically.

Results and Discussion

Synthesis. The novel spirocyclic phosphazene derivatives (**3a**−**6b**; Chart 1) have been obtained from the reactions of N/O donor-type N-alkyl-*o*-hydroxybenzylamines (**1** and **2**) and *o*-hydroxynaphthylamine (**3**) in THF. The reactions of $N_3P_3Cl_6$ with the bifunctional reagents (**1**−**3**) seem to be regiospecific because only the spirocyclic architectures have formed (Scheme 1). The reactions of 1 equiv of $N_3P_3Cl_6$ with 1 equiv of **1**, **2**, and **3** in THF with triethylamine as the HCl acceptor produce monospirocyclic phosphazene derivatives

(26) *X-AREA*, version 1.18; *X-RED*, version 1.04; Stoe & Cie: Darmstadt, Germany, 2002.
(27) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A.* **1968**, *24*, 351−359.
(28) Sheldrick, G. M. SHELXS-97; SHELXL-97; University of Göttingen: Göttingen, Germany, 1997.

4a, **4b**, and **3a**, respectively. The tetrakis-pyrrolidinophosphazene derivative, **3b**, has been isolated from the reaction of **3a** with the excess of pyrrolidine. When the reactions have been carried out with 2 equiv of **1** and **2**, dispirocyclic phosphazene skeletons (**5a** and **5b**) have been obtained. In addition, when 3 equiv of **1** and **2** have been added at room temperature, the dispiro isomers (**5a** and **5b**), which are the major products, besides the minor trispiro derivatives (**6a** and **6b**), have been obtained. Whereas, when the reactions have been carried out in THF by refluxing for 18 h, the trispirocyclic derivatives (**6a** and **6b**) have become the major products. The yields obtained for the reactions were variable depending on mono-, di-, and trisubstitution of the products. Monospirocyclic phosphazene derivatives, **3a**, **4a**, and **4b**, have been obtained with yields in a range of 59−86%; dispirocyclic phosphazenes, **5a** and **5b**, have been obtained with a relatively small yield of 40%, and trispirocyclic derivatives, **6a** and **6b**, have yields ranging between 38 and 51%. Although the ansa derivatives[16] were expected to form, no ansa products have been isolated in this study. The crystallographic and preliminary CSA results showed that compounds **5a** and **5b** are trans (racemic) mixtures (Figure 1); in addition, **6a** and **6b** are expected to exist as cis−trans−trans- or cis−cis−cis-geometric isomers, and both of them are found to be in cis−trans−trans configurations (Figure 2).

IR and NMR Spectroscopy. The FTIR spectra of the spirophosphazene derivatives (**3a**−**6b**) exhibit two medium-intensity absorption signals at 3070−3050 cm^{-1} and 3040−3020 cm^{-1} attributed to asymmetric and symmetric stretching vibrations of the Ar−H protons. Spirophosphazene derivatives display intense bands between 1259 and 1176 cm^{-1} attributed to $\nu_{P=N}$ bonds of the phosphazene ring.[14a] The characteristic ν_{NH} stretching bands of N-alkyl-*o*-hydroxybenzylamines disappear in the FTIR spectra of **4a**, **4b**, **5a**, **5b**, **6a**, and **6b**, while the corresponding bands appear at 3227 and 3194 cm^{-1} for **3a** and **3b**, respectively. As expected, two kinds of ν_{PCl} absorption peaks, namely, asymmetric and symmetric vibrations, have arisen for the partly substituted spirophosphazenes (**3a**, **4a**, **4b**, **5a**, and **5b**) at 598−555 and 559−506 cm^{-1}.

The ^{1}H-decoupled ^{31}P NMR spectral data of the phosphazene derivatives are listed in Table 3. According to the spectral data, all of the compounds have spiro architectures. The spin systems are interpreted as simple AX_2, A_2B, and AB_2 from the ^{31}P NMR spectra of (**3a**, **4a**, **4b**, **6b**), (**5a**), and (**3b**, **5b**, and **6a**), respectively. The spin systems of **6a** and **6b** are AB_2 and AX_2, respectively, indicating that only cis−trans−trans-geometric isomers are isolated (Figure 2b). According to Figure 2b, the orientation of the two N-propyl-spiro rings of **6a** are the same, whereas that of the other is different; hence, the whole molecule looks like a propeller where the chemical environment of P1 is different from those of P2 and P3.

Two P atoms in disubstituted spirocyclic phosphazenes (**5a** and **5b**) and three P atoms in trisubstituted spirocyclic phosphazenes (**6a** and **6b**) are expected to be stereogenic phosphorus atoms. Compounds **5a** and **5b** are expected to exist as cis- or trans-geometric isomers and to be cis (meso)

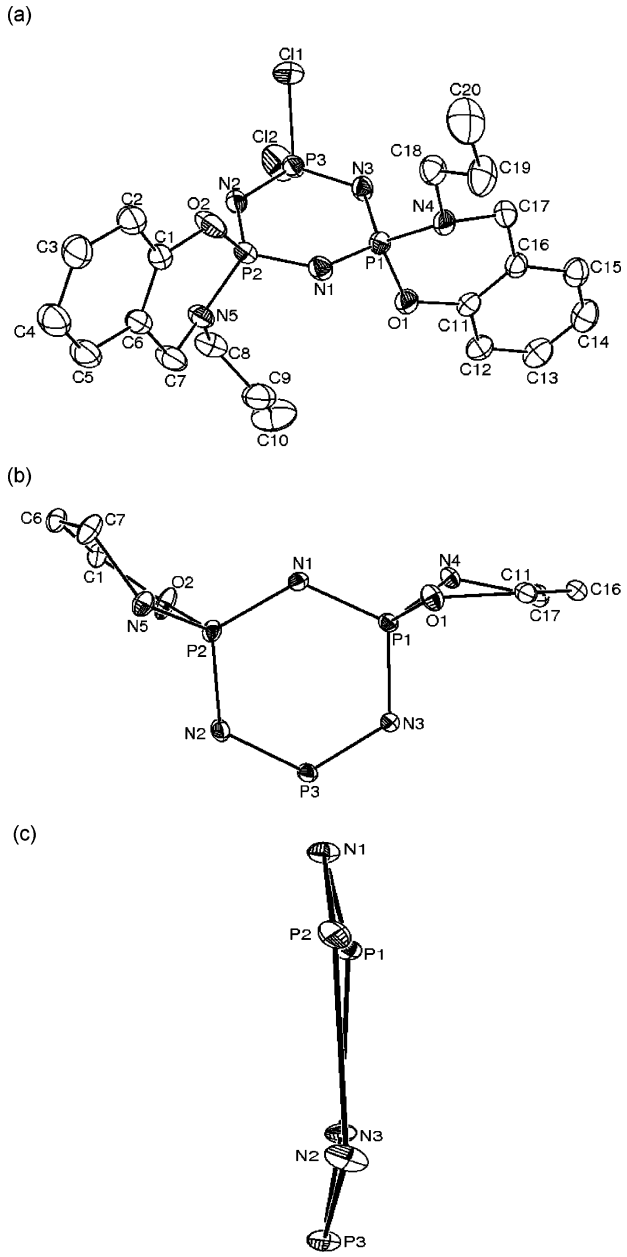


Figure 3. (a) An ORTEP-3[38] drawing of **5a** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The conformations of (b) the six-membered macro-ring and (c) the phosphazene ring are also given.

or trans (racemic) mixtures. The crystallographic and preliminary CSA results showed that both of the compounds (**5a** and **5b)** are racemic (Figures 1 and 3). In addition, compounds **6a** and **6b** are also expected to exist as cis−trans−trans- or cis−cis−cis-geometric isomers. Both of them are found to be in cis−trans−trans forms according to the ORTEP diagram of **6a**[29] (Figure 2b) and the ^{31}P NMR spectra of **6a** and **6b**, as mentioned above.

(29) The crystallographic data for compound **6a** do not fulfill the requirements of the checkCIFF program, but some of the data were used in this study for Figures 2 and 3 only: empirical formula, $C_{30}H_{39}N_6O_3P_3$; Fw, 624.58; crystal system, monoclinic; space group, $P2_1/n$; a(Å), 10.7295(9); b(Å), 14.8160(8); c(Å), 20.6592(15); α(deg), 90; β(deg), 103.312(6); γ(deg), 90; N2−P2−N1 = 118.11(16); N1−P1−N3 = 116.04(15); N2−P3−N3 = 116.32(16); N6−P2−O3 = 102.08(16); N5−P1−O2 = 101.40(14); N4−P3−O1 = 100.25(16).

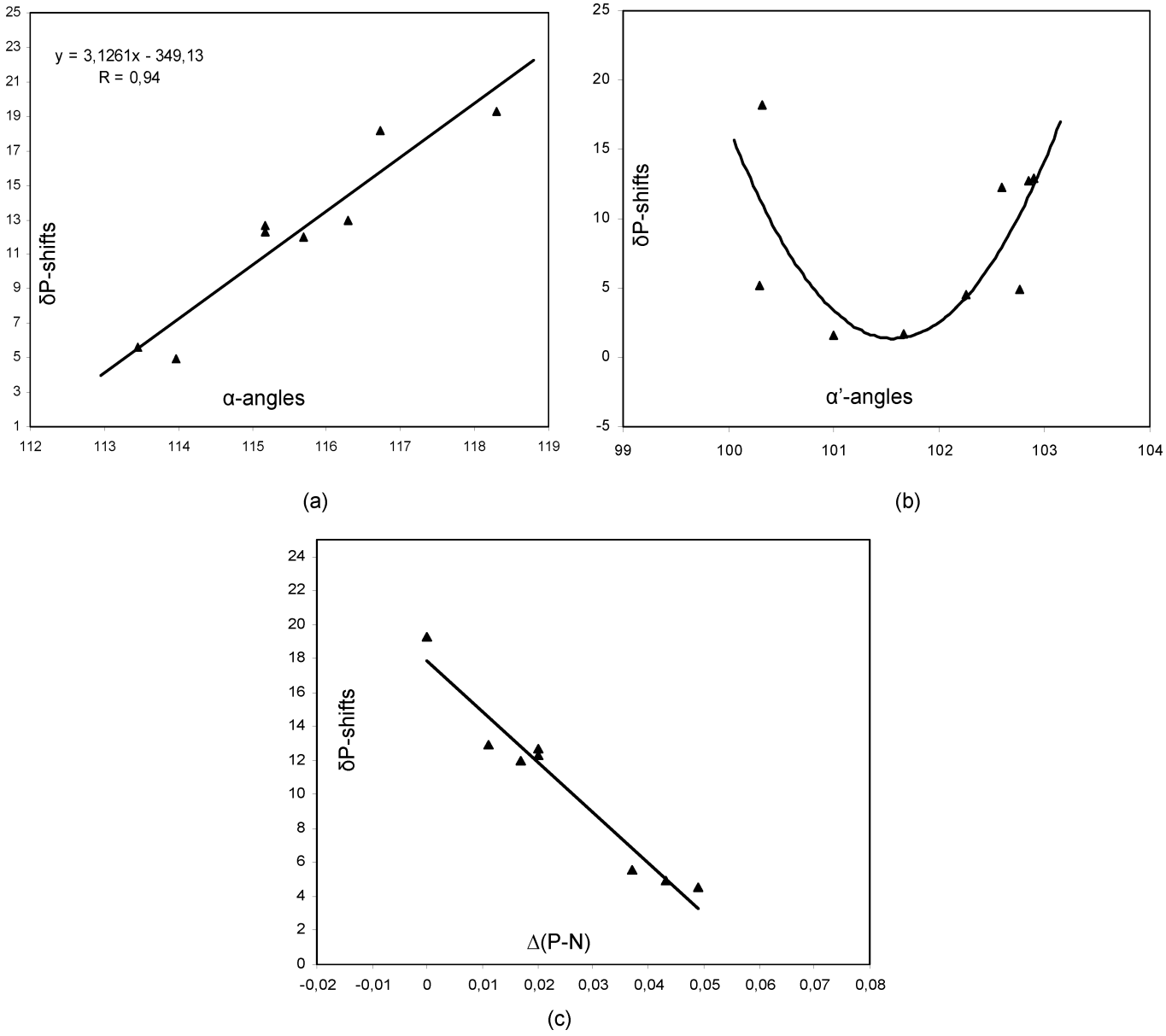


Figure 4. Plot of δ shifts against (a) endocyclic α angles, (b) exocyclic α′ angles, and (c) △(P−N) parameters of N/O donor-type phosphazene derivatives.

The endocyclic α and exocyclic α′ bond angles of the phosphazene derivatives are given in Table 3. The variations in the bond angles depending on the steric hindrances of exocyclic groups and electron-releasing and -withdrawing capacities of small or bulky substituents have previously been reported.[13c,14d,16] It was observed that relatively small changes in exocyclic bond angles of nonspirocyclic phosphazene derivatives caused large changes in ^{31}P NMR chemical shifts.[30] In the case of analogous spirocyclic phosphaza lariat ethers, linear trends have been observed for the relationship between endocyclic NPN (α) bond angles and δP shifts.[31] Parts a and b of Figure 4 were depicted for α and α′ bond angles versus the δP shifts of the spirocyclic phosphazenes synthesized in this study (**3a**, **4a**, **4b**, **5a**, **6a**, and $N_3P_3Cl_6$, which is known as the standard compound in the field of phosphazene chemistry) and the analogous compounds taken from the literature (**I**,[35] **II**,[35] **III**,[15d] **IV**,[15a] **V**,[15a] and **VI**[36]; Table 3). The trend observed for α and α′ angles (Figures 4a and 4b) is in good agreement with those of Shaw,[30] Labarre,[31a] and Bilge et al.[31b] It was observed that there is a linear relationship between the endocyclic NPN (α) angles and δP shifts, similarly as it was for phosphaza lariat ethers,[31b] while for the exocyclic NPO (α′) angles, the points are accumulated on the left- and right-hand sides of the curve (Figure 4b) that passes through a minimum. The linearity fits the relationship supporting the validity of the equation given as follows: $\delta P = 3.1261\alpha - 349.13$. According to the regression line, the values of α angles can be estimated and compared with those obtained from the X-ray data (experimental value). It is well-known that solvent interactions alter the δP shifts, whereas the intra- and intermolecular interac-

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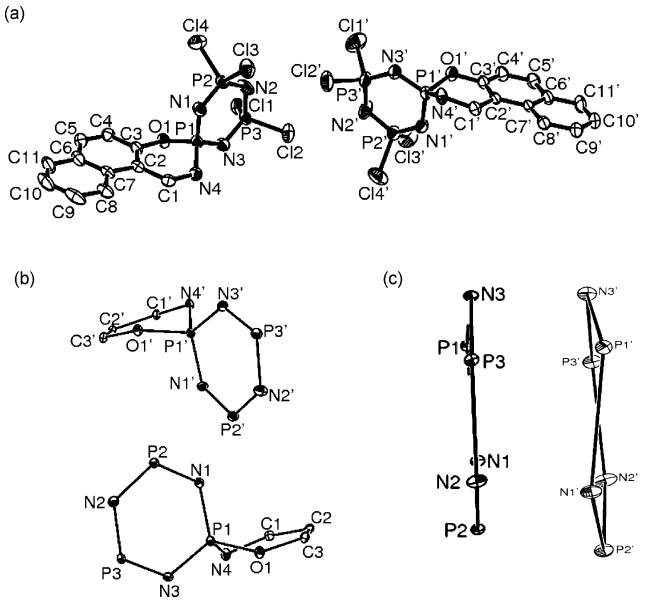

Figure 5. (a) An ORTEP-3[38] drawing of **3a** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The conformations of (b) the six-membered macroring and (c) the phosphazene ring are also given

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Table 4. Hydrogen-Bond Geometry (Å, deg) for **3a**

D−H···A[a]	D−H	H···A	D···A	D−H···A
N4−H4A···N1′[i]	0.890(33)	2.180(36)	3.049(6)	165.18(3.37)
N4′-H4B···N1[ii]	0.793(67)	2.278(65)	3.066(6)	172.44(6.26)

[a] Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, -y, 1-z$.

tions, as well as the hydrogen bonds, may affect the α angles. The point for **3a** (Table 3) deviates from linearity in Figure 4a. The experimental and calculated α values for **3a** are 115.05° and 113.13°, respectively. Compound **3a** contains two independent molecules in the asymmetric unit (Figure 5). The deviation appears likely to be caused by the packing in the unit cell which contains intermolecular hydrogen bonds (Table 4). In summary, it is crucial to analyze NMR measurements and X-ray crystallographic data together to interpret the results accurately.

The electron-releasing or -withdrawing power of spiro groups or substituents bonded to the phosphorus atoms of the N_3P_3 ring, Δ(P−N) (electron density transfer parameters: the difference between the bond lengths of two adjacent P−N bonds that form part of the same three-centered P−N−P island in a cyclophosphazene ring),[32] are given in Table 3. The relationship between the Δ(P−N) values of **3a**, **4a**, **4b**, **5a**, $N_3P_3Cl_6$, **I**, **II**, and **VI** versus the chemical shifts (δP_{NPO}) appears to show a linearity (Figure 4c) implying that the observations have been quantitative by the introduction of this correlation. The quantitative relationships between the substituent electronegativity and δP shifts in phosphazene chemistry were also proposed and discussed in the literature.[32]

In all of the phosphazene architectures, the ^1H and ^{13}C signals have been assigned on the basis of chemical shifts, multiplicities, and coupling constants. The assignments have been made unambigously by two-dimensional heteronuclear-correlated experiments (HETCOR) using delay values corresponding to ^1J(CH) and by HMBC using delay values corresponding to ^2J(CH), ^3J(CH), and ^4J(CH) between the carbons and protons (Table 5 of the Supporting Information). The HETCOR and HMBC spectra of **3a** and **4a** are depicted in Figures 6 and 7 (all of the ^{13}C and ^1H NMR assignments have been written on the spectra) as examples of *o*-hydroxynaphthyl- and N-alkyl-*o*-hydroxybenzylamine-phosphazene derivatives, respectively.

The protons of the benzylic moieties give rise to doublets and multiplets for (**3a**, **3b**, **4a**, **4b**, **6b**) and (**5a**, **5b**, and **6a**), respectively. The geminal Ar$C\boldsymbol{H_2}$N protons of **5a**, **5b**, and **6a** are not equivalent to each other; hence, the spectra of these compounds show two groups of complex signals with small separations, ca. 0.15 ppm. The signals of methyl protons of **4a**, **4b**, **5a**, **5b**, and **6b** are observed as triplets at the range of 0.94−1.30 ppm, whereas those of **6a** are observed as two separate triplets at 0.94 and 0.98 ppm. One of them belongs to six protons of two methyl groups and the other one to three protons of the other methyl group.

All of the possible carbon peaks are observed from the ^{13}C NMR spectral data as expected. The N$\boldsymbol{C}H_2$ signals of compound **3b** are confirmed by HETCOR experiments, which were $\delta = 46.3$ ppm for N$\boldsymbol{C}H_2$ (pyr) and $\delta = 41.2$ ppm for Ar$\boldsymbol{C}H_2$. Moreover, the aromatic carbons for the compounds were determined by using delays in two-dimensional HETCOR and HMBC experiments to emphasize the long-range couplings, either ^2J(CH), ^3J(CH), or ^4J(CH), between the carbons and protons (Figure 6; Table 5, Supporting Information). The expected coupling constants between aromatic C atoms and P atoms are observed for C_2, C_3, and C_4 in the compounds except for C_2 and C_3 of **6a**. These couplings [$^3J(PC_2)$, $^2J(PC_3)$, and $^3J(PC_4)$] give rise to doublets in the case of [**3a**, **3b**, **4a**, **4b**, **5b**, **6a** (C_1 only), and **6b**] and a triplet in the case of **5a**. The triplet observed for dispirophosphazene (**5a**) may be due to the second-order effects, which have previously been observed.[33] Vicente and co-workers[34] have reported a new way to estimate the *J*(PC) coupling constants between the external transitions of the triplet. As the peaks of the nonprotonated carbon atoms disappear in DEPT spectra, the carbons of aromatic rings in all of the spirophosphazene derivatives have been determined. Meanwhile, with both the HETCOR and HMBC results being taken into account, the possible conformations of **3a** and **4a**

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(33) (a) Finer, E. G.; Harris, R. K.; Bond, M. R.; Keat, R.; Shaw, R. A. *J. Mol. Spectrosc.* **1970**, *33*, 72−83. (b) Shaw, R. A. *Phosphorus Sulfur Silicon* **1989**, *45*, 103−136.

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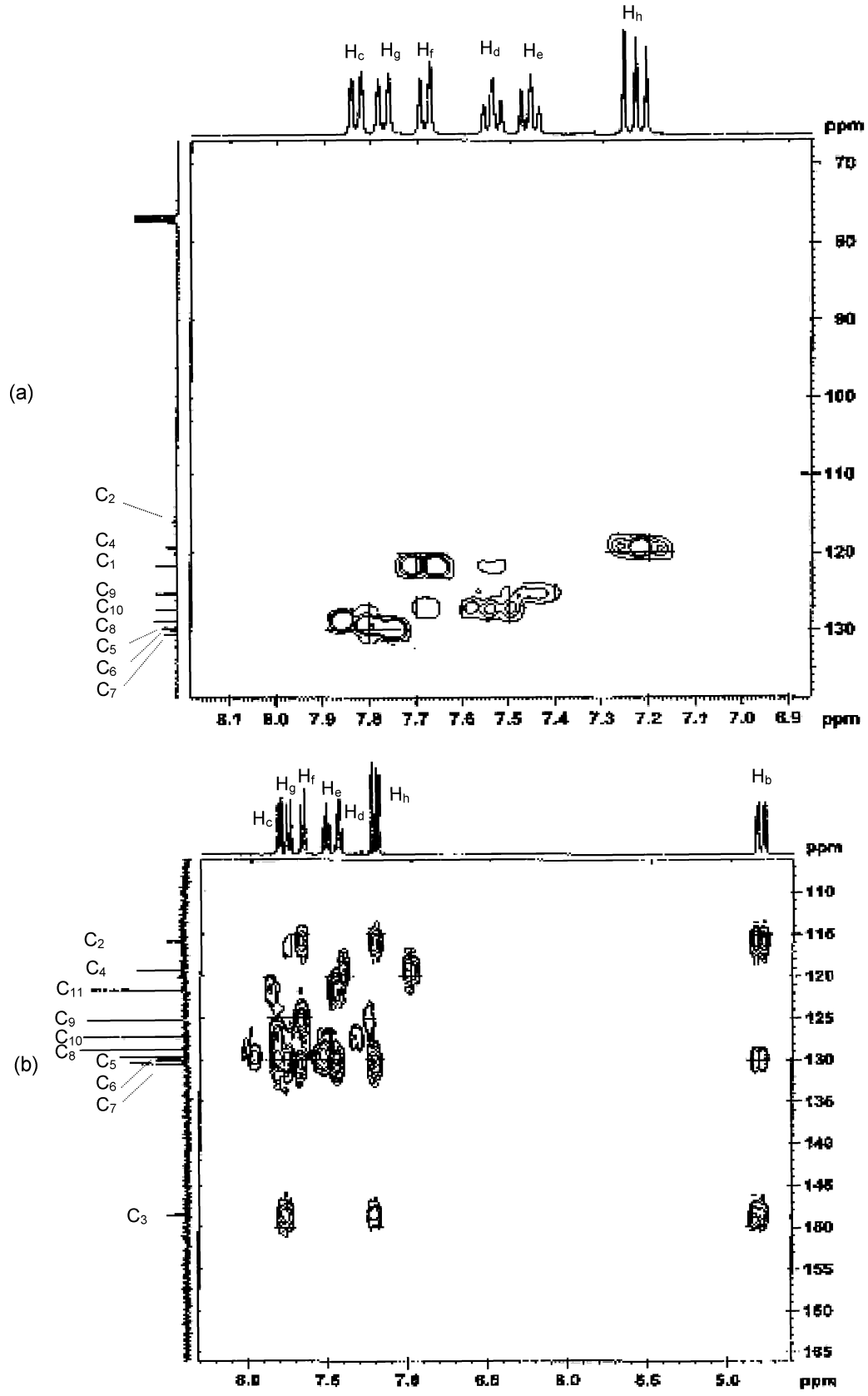

Figure 6. The HETCOR (a) and HMBC (b) spectra of compound **3a**.

in the $CDCl_3$ solution are depicted in Figure 8a and b as examples, showing that the structures in the solution and the solid states are in accordance.

X-ray Structures of 3a, 4a, 4b, and 5a. The X-ray structural determinations of compounds **3a**, **4a**, **4b**, and **5a** confirm the assignments of their structures from spectro-

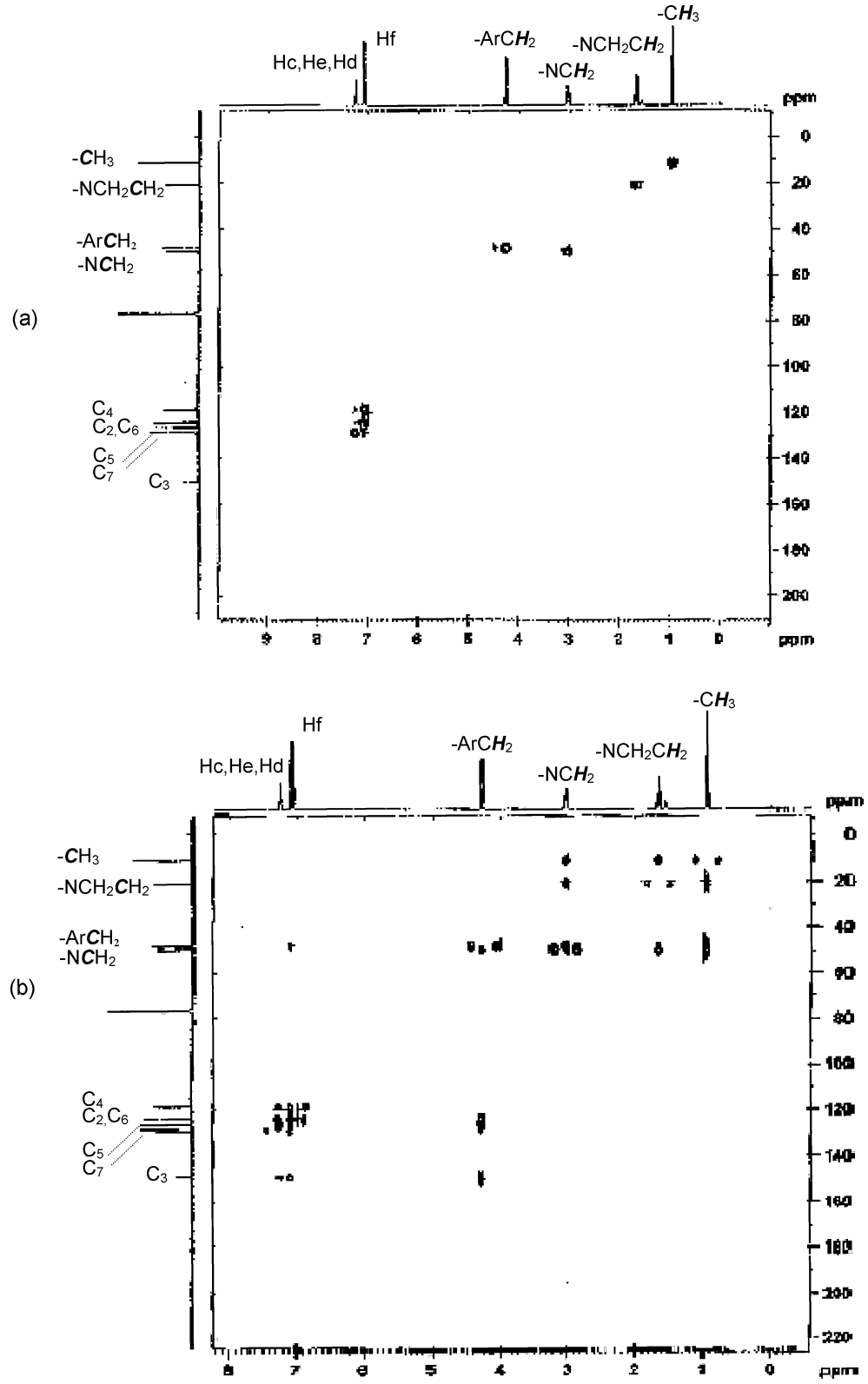

Figure 7. The HETCOR (a) and HMBC (b) spectra of compound **4a**.

scopic data. The molecular structures of **3a**, **4a**, **4b**, and **5a** along with the atom-numbering schemes are depicted in Figures 5, 9, 10, and 3, respectively. The asymmetric units of **3a** and **4a** contain two molecules. The phosphazene rings of **4a** and **4b** are planar (Figures 9b,c and 10b,c), having total puckering amplitudes[38] Q_T of 0.026(6), 0.071(6), and 0.014(3) Å, respectively. The phosphazene rings are not planar for **3a** (for primed molecule) and **5a** and are in twisted boat forms [Figure 5c, $\varphi_2 = -163.9(2)°$,and $\theta_2 = 113.5(3)°$; Figure 3c, $\varphi_2 = -143.4(8)°$ and $\theta_2 = 88.0(8)°$], while it is planar for the unprimed molecule of **3a** [Figure 5c, $\varphi_2 = -174.7(3)°$ and $\theta_2 = 137.8(2)°$], having total

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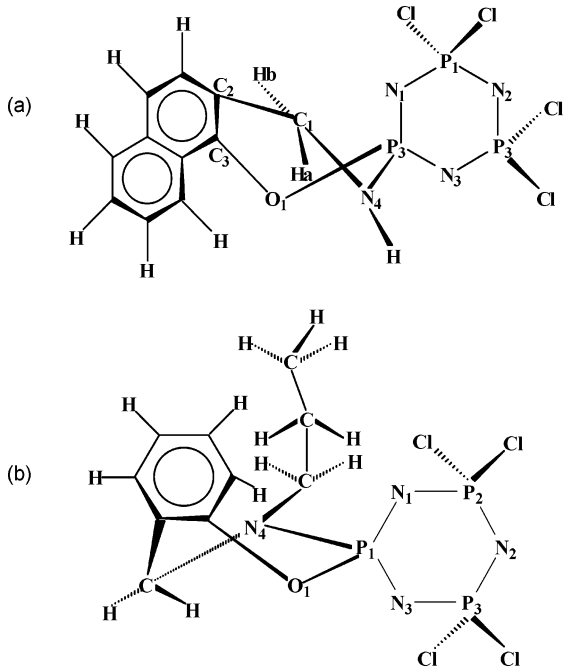

Figure 8. The possible stereoisomer structures of compounds (a) **3a** and (b) **4a** at ambient temperature in $CDCl_3$.

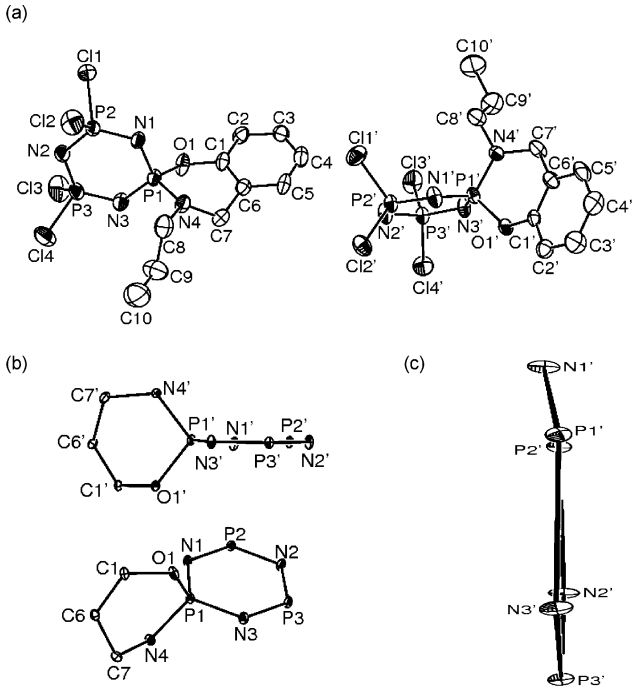

Figure 9. (a) An ORTEP-3[38] drawing of **4a** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The conformations of (b) the six-membered macroring and (c) the phosphazene ring are also given.

puckering amplitudes Q_T of 0.069(4), 0.142(4), and 0.154(2) Å, respectively. The six-membered rings A(P1/N4/C1/C2/C3/O1) and A′(P1′/N4′/C1′/C2′/C3′/O1′) (for **3a**), A(P1/N4/C7/C6/C1/O1) and A′(P1′/N4′/C7′/C6′/C1′/O1′) (for **4a**), A(P1/N4/C7/C6/C1/O1) (for **4b**), and A(P1/N4/C17/C16/C11/O1) and B(P2/N5/C7/C6/C1/O2) (for **5a**) are in twisted forms with total puckering amplitudes Q_T of 0.611(3) and 0.142(3) Å (for **3a**), 0.436(3) and 0.449(3) Å (for **4a**), 0.365-

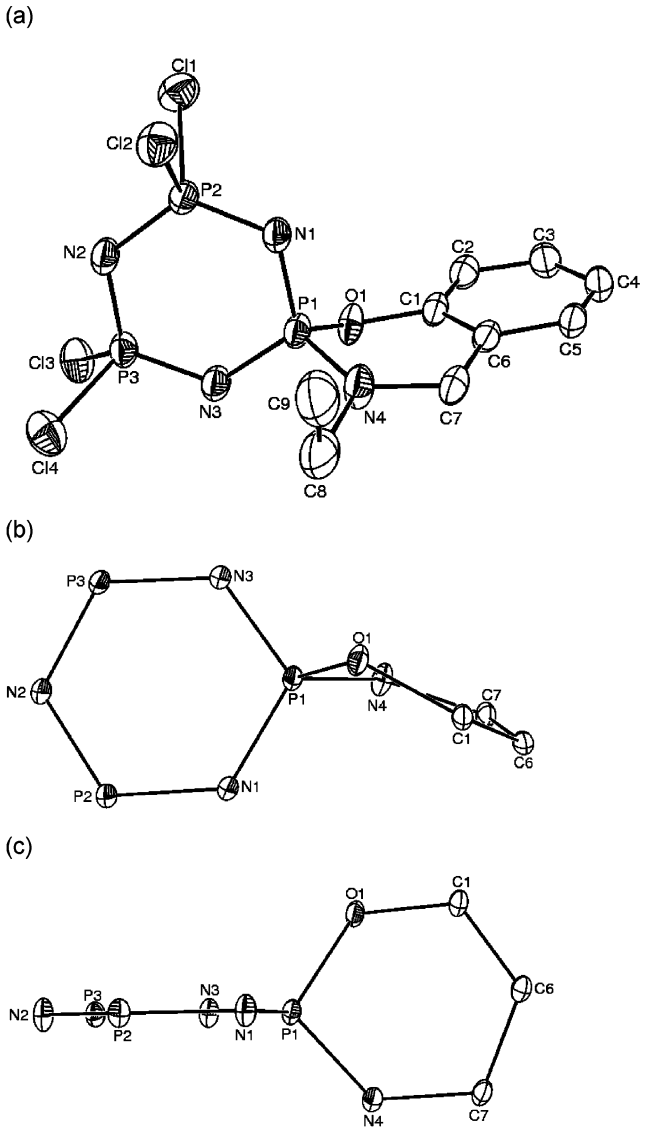

Figure 10. (a) An ORTEP-3[38] drawing of **4b** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The conformations of (b) the six-membered macroring and (c) the phosphazene ring are also given.

(2) Å (for **4b**), and 0.670(4) and 1.017(4) Å (for **5a**), respectively. In **5a**, a trans configuration has been established according to propyl groups, and the rings A and B are in *down* and *up* orientations.

In the unprimed molecule of **3a**, the phosphazene ring has a pseudo-mirror plane running through atoms N2 and P1. As can be seen from the packing diagram (given in the Supporting Information), the intermolecular N−H···N hydrogen bonds (Table 4) link the molecules into chains along the *a* axis, in which they may be effective in the stabilization of the crystal structure. In the packing diagrams of **4a**, **4b**, and **5a**, the molecules are stacked along the *a* axes of the unit cells.

The average P−N bond lengths in phosphazene rings are 1.586(4) (for **3a**) and 1.579(4) Å (for **3a′**), 1.575(7) (for **4a**) and 1.577(7) Å (for **4a′**), 1.581(3) Å (for **4b**), and 1.582(3) Å (for **5a**), which are shorter than the exocyclic P−N bonds of 1.601(4) (for **3a**) and 1.601(4) Å (for **3a′**), 1.630(8) (for

4a) and 1.609(7) Å (for **4a′**), 1.608(3) Å (for **4b**), and 1.645(3) and 1.635(3) Å (for **5a**). The electron back-donation also causes the shortening of the exocyclic P−N bonds according to the average P−N single bond of 1.683(5) Å.[40]

As can be seen from Table 1, in **3a**, **4a**, **4b**, and **5a**, α angles are narrowed, while α′ and β angles are expanded, considerably, according to the "standard" compound, $N_3P_3Cl_6$. In the "standard" compound,[37] α, α′, and β angles are 118.3(2), 101.2(1), and 121.4(3)°, respectively.

The sum of the bond angles around the spirocyclic-ring nitrogen atoms [359.6(6) and 356.8(7)° (N4 and N4′, for **4a**), 360.0(3)° (N4, for **4b**), and 345.3(3) and 356.1(3)° (N4 and N5, for **5a**) show the hybridization of N atoms, where the configuration around the N4 atom (for **5a**)] is pyramidal. Thus, the N4 atom for **5a** may represent a stereogenic center. Moreover, atoms (P1 and P2) for **5a** each have different attachments and thus are also expected to be stereogenic centers in the solid state. The absolute configuration of chiral phosphorus centers (P1 and P2) in **5a** can be designated as (*SS, racemic forms*), indicating that the Cahn−Ingold−Prelog[41] priority order of groups is POAr > $NPCl_2$ > NPOAr > NR.

Conclusions

N/O donor-type N-alkyl-*o*-hydroxy-benzyl- and *o*-hydroxynaphthylamines have led to the formation of mono- (**3a**, **4a**, and **4b**), di- (**5a** and **5b**), and tri- (**3b**, **6a**, and **6b**) spirocyclic phosphazene architectures via the condensation reactions of $N_3P_3Cl_6$. The substitution reaction of a mono-spirocyclic derivative (**3a**) with the excess of pyrrolidine has resulted in the tetrakis-pyrrolidino phosphazene (**3b**). The correlation between the endocyclic NPN and exocyclic NPO angles with δP shifts of the phosphorus atoms has been investigated. The variations of δP shifts depend on the steric and electronic factors of bulky substituents which change the α, α′, β, and γ angles of the phosphazene rings significantly. There is a linear trend between the NPN angles and δP shifts. This trend allows the prediction of α angles, taking into account the X-ray data, for the compounds for which the δP shift values are known, or vice versa. The relationship between Δ(P−N) (a measure of the electron-releasing or -withdrawing power of the spiro groups or substituents) and δP shifts has also been discussed. The crystallographic and preliminary CSA results show that compounds **5a** and **5b** are in trans (racemic) configurations, while **6a** and **6b** are in cis−trans−trans forms.

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Supporting Information Available: Additional figures giving crystal packing diagrams, Table 5, and X-ray crystallographic files in CIF format for compounds **3a**, **4a**, **4b**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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