THEORETICAL AND EXPERIMENTAL STUDIES OF IR AND NMR SPECTRA OF *gem*-2,2-DIAMINO-4,4,6,6-TETRAPHENOXY-1,3,5-*cyclo*-TRIAZA-λ^5-PHOSPHORINE

Lenka DASTYCHOVÁ[a1,*], Dalibor DASTYCH[a2], Pavel KUBÁČEK[b] and Milan ALBERTI[c]

[a] *Department of Chemistry, Faculty of Technology, Tomáš Baťa University in Zlín, náměstí T. G. Masaryka 275, 762 72 Zlín, Czech Republic; e-mail: [1] lenka.dastychova@email.cz, [2] dastych@gmail.com*

[b] *Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic; e-mail: kubacek@chemi.muni.cz*

[c] *Department of Physical Electronics, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic; e-mail: alberti@chemi.muni.cz*

Received August 9, 2010
Accepted September 14, 2010
Published online November 9, 2010

The vibrational spectra of *gem*-2,2-diamino-4,4,6,6-tetraphenoxy-1,3,5-*cyclo*-triaza-λ^5-phosphorine were studied using density functional theory. Selected vibrational bands were assigned to normal modes on the basis of DFT calculation with the ADF program package. The ^{1}H and ^{13}C NMR spectra, the higher order ^{31}P, $^{31}P\{^1H_{am.}(sel.)\}$ and $^{31}P\{^1H_{arom.}(sel.)\}$ NMR spectra were measured and the values of $^1J(C,H)$, $^2J(C,H)$ and $^2J(P_I,P_{II})$ were found. Nearly the complete spin system (ABB′$M_4X_4X_4'$) for the symmetry C_2 was simulated with the gNMR simulation program and the values of $^2J(P_I,H_{am.})$, $^4J(P_{II},H_{am.})$, $^4J(P_{II},H_{arom.})$, $^6J(P_I,H_{arom.})$ and $^6J(P_{II},H'_{arom.})$ were determined for the first time. The experimental NMR data were also compared with quantum chemical calculation results.

Keywords: NMR spectra; Vibrational spectra and assignment; Coupling constant; Simulation; DFT calculations; *gem*-2,2-Diamino-4,4,6,6-tetraphenoxy-1,3,5-*cyclo*-triaza-λ^5-phosphorine.

Cyclo-triaza-λ^5-phosphorines are well known compounds since 1834 when the first mixture of cyclic chlorophosphazene oligomers was prepared by the reaction of PCl_5 with ammonia[1,2]. $P_3N_3Cl_6$ with alternating phosphorus and nitrogen atoms in a cycle was suggested by Stokes sixty years later[3]. $P_3N_3Cl_4(NH_2)_2$ with a geminal structure[4] is the starting compound for a preparation of any tetrasubstituted alkoxy- and aryloxydiamino-*cyclo*-triaza-λ^5-phosphorines. The substitution reaction leads in the majority of cases to the formation of various nongeminal *cis*-[5,6] or *trans*-[6,7] derivatives with general formula $P_3N_3(OR)_4(NH_2)_2$ (R = Me, Et, *n*-Pr, *n*-Bu). The first com-

Collect. Czech. Chem. Commun. 2010, Vol. 75, No. 11, pp. 1125–1138

doi:10.1135/cccc2010101

pound in which Cl atoms have been substituted for -OR groups without migration of amino group was *gem*-$P_3N_3(OMe)_4(NH_2)_2$ [5]. Recently we succeeded in the preparation of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$ and determination of its crystal and molecular structure by X-ray diffraction (Fig. 1)[8].

The calculated IR spectra have been useful in the assigning of selected experimental bands in most cases. But only a few theoretical spectroscopic studies performed on *cyclo*-triaza-λ^5-phosphorines were published at this time[9,10] except for chloro derivatives[11–14]. Aryloxyamino-*cyclo*-triaza-λ^5-phosphorines are compounds with a wide variety of application such as precursors for flame retardant polymers[15], inhibitors of urease[16], etc. In the present work, the selected vibration bands in IR and Raman spectra are discussed. Quantum chemical computations of vibrational bands were carried out using the TZ2P basis set and a medium frozen core in ADF program.

Simulated ^{31}P NMR higher order spectra of several *cyclo*-triaza-λ^5-phosphorines have been reported[10,17,18]. ^1H and ^{31}P NMR spectra of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$ have been mentioned by Kajiwara[19], but these data are not in agreement with ^{31}P chemical shifts of known phenoxy[5,20–23] and amino[5,6,24] derivatives of *cyclo*-triaza-λ^5-phosphorines. The ^1H NMR data of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$ have been reported[25] as well, however, this work contained only a chemical shift of amino group.

In this paper we report ^1H, ^{13}C, ^{31}P, $^{31}P\{^1H_{am.}(sel.)\}$ and $^{31}P\{^1H_{arom.}(sel.)\}$ NMR chemical shifts of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$ and the values of eight coupling constants, $^1J(C,H)$, $^2J(C,H)$, $^2J(P_I,P_{II})$, $^2J(P_I,H_{am.})$, $^4J(P_{II},H_{am.})$, $^4J(P_{II},H_{arom.})$, $^6J(P_I,H_{arom.})$ and $^6J(P_{II},H'_{arom.})$ (Table IV). The ADF program package together with gNMR simulation of the ^{31}P NMR spectrum supported the coupling constants. All the simulated phosphorus-hydrogen

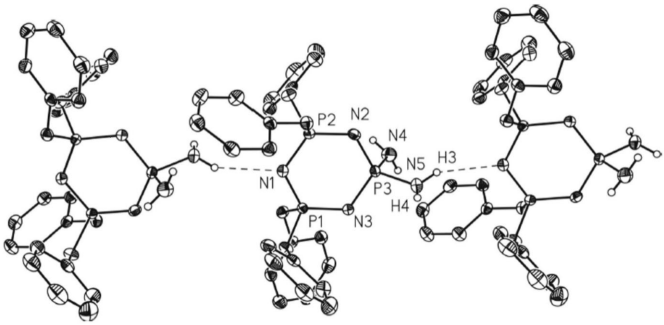


FIG. 1
Molecular structure of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$ with intermolecular hydrogen bonds. H atoms from phenyl rings are omitted for clarity. Elipsoids are drawn with 50% probability level[8]

coupling constants are apparently the only known phosphorus-hydrogen coupling constants of amino and phenoxy derivatives of *cyclo*-triaza-λ^5-phosphorines.

EXPERIMNETAL

Preparation of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$

The preparation of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$ was performed under dry nitrogen atmosphere using Schlenk technique by the reaction of C_6H_5ONa with *gem*-$P_3N_3Cl_4(NH_2)_2$ in tetrahydrofuran, as described earlier[8]. The crude product was several times recrystallized from dry diethylether.

Chemicals Used

The *gem*-$P_3N_3Cl_4(NH_2)_2$ was prepared from $P_3N_3Cl_6$ (BASF, Germany). Sodium phenoxide was prepared from phenol (Fluka Chemie AG, Switzerland) and metallic sodium wire (Ferak Berlin, Germany). Phenol, diethylether (Penta, Czech Republic) and tetrahydrofuran (Penta, Czech Republic) were purified and dried according to procedures by Perrin and Armarego[26]. $CDCl_3$, 99.1 atom% D (ISOSAR GmbH) was kept under dry argon and was not further purified.

Physical Measurements

The IR spectrum of the *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$ was measured in Nujol on an IFS 28 FT-IR Bruker spectrometer in the range of 4000–400 cm^{-1}. Resolution of this spectrometer is 2 cm^{-1} per point. Raman spectrum of solid sample was measured in Raman capillary using a Bruker IFS 55 Equinox apparatus in the range of 3500–0 cm^{-1}.

NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer operating at 500.134, 125.773 and 202.456 MHz for ^1H, ^{13}C and ^{31}P, $^{31}P\{^1H_{am.}(sel.)\}$ and $^{31}P\{^1H_{arom.}(sel.)\}$, respectively. The ^1H and ^{13}C NMR spectra were referred to tetramethylsilane, and ^{31}P, $^{31}P\{^1H_{am.}(sel.)\}$ and $^{31}P\{^1H_{arom.}(sel.)\}$ NMR spectra were referred to 85% H_3PO_4. The sample was dissolved in tetrahydrofuran or diethylether in a coaxial NMR cuvette system: the sample was in a Simax® tube (outer diameter 4.0 mm), inserted in Wilmad® NMR tube (outer diameter 5.0 mm). The space between the cuvettes was filled with D_2O for an external lock. To obtain ^{31}P, $^{31}P\{^1H_{am.}(sel.)\}$ and $^{31}P\{^1H_{arom.}(sel.)\}$ NMR spectra, the *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$ was measured as 5.2×10^{-2} M solution in $CDCl_3$ using Wilmad® NMR tube (outer diameter 5.0 mm) at the temperature 273 and 283 K. The spectra were recorded with spectral width of ~6000 Hz, time domain 32 kB, real transform size 32 kB, number of scans 2048, acquisition time 0.68 s, relaxation delay 3 s, flip angle 90°, a window function was not used. All the high-quality spectra were measured with resolution 0.077 Hz. The ^{31}P NMR spectrum was simulated by gNMR V4.1.2 program[27] at the spectral frequency 202.456 MHz.

Computational Details

The quantum chemical calculations were carried out with the molecular ADF program, version 2008.01 [28–30]. Molecular geometry was optimized and the IR spectra were calculated with the core double zeta, valence triple zeta, doubly polarized basis set TZ2P and a medium frozen core in ADF model. The large basis set was used to achieve a good approximation for the infrared intensities. The calculation of IR spectrum was performed with no scaling factor. NMR calculations on the molecule were performed with the NMR [34] and CPL [35,36] modules of the ADF package, the XC functional BP [37,38] was used besides OPBE. The OPBE[31] functional combines OPTX (exchange)[32] and PBEc (correlation)[33]. We chose the OPBE functional because of faster and comparable good performance[31] as compared to hybrid functionals.

RESULTS AND DISCUSSION

Molecular Geometry

$P_3N_3(OC_6H_5)_4(NH_2)_2$ with geminal structure crystallizes in tetragonal system with space group $P4_1$. The cell dimensions are: a = 12.9555(18) Å, c = 15.029(3) Å, V = 2522.5(7) Å^3 (ref.[8]). Nitrogen atom between two $\equiv P(OC_6H_5)_2$ groups is involved in a rather weak hydrogen bond to a hydrogen atom of amino group of another molecule (Fig. 1).

The metrical parameters from X-ray[8] are in a good agreement with parameters from ADF calculation, except for a number of torsion angles around P–O and C–O bonds (Table I). The discrepancies are probably due to the intermolecular interactions in the crystalline state of the molecule. Selected metrical parameters are shown in Table I.

The geometry optimization with the used calculation method and the numerical integration accuracy to 5 digits corresponds to C_2 symmetry imposing no symmetry constraint. Under the C_2 constraint the final energy differs only by 0.01 eV. Within C_{2v} symmetry the geometry optimization arrived to the energy that is higher only by 0.4 eV even though some real dihedral angles within the P_3N_3 ring reach to 20°. All the geometry optimizations produced several imaginary frequencies; 4 in the case of C_2 point group in a range from 10 to 20 cm^{-1}. Several additional real low frequencies occurred as well. Most of those calculated soft normal modes correspond to the torsions around P–O and C–O bonds, however e.g. rocking of PN_2 in $P(NH_2)_2$ group is also included (40 cm^{-1}). The stereochemical nonrigidity of the molecule is bound not only to the phenoxy groups but to the easy distortions of the P_3N_3 ring that is planar and rigid, perhaps, only in $P_3N_3F_6$ [17,39].

TABLE I
Experimental and optimized geometry of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$; selected bond lengths and angles

Parameter	Experimental[a]	Optimized geometry (C_2)	Parameter	Experimental[a]	Optimized geometry (C_2)
Bond lenght, Å		ADF	Bond angle, °		
P1–N1	1.5889(13)	1.59	N3–P1–N1	118.06(7)	119.8
P1–O2	1.5977(11)	1.61	N3–P1–O1	110.49(6)	110.5
N1–P2	1.5945(13)	1.59	O1–P1–O2	98.13(6)	98.4
P3–N3	1.6111(13)	1.62	P1–N1–P2	120.00(9)	119.1
P3–N4	1.6459(16)	1.68	O4–P2–N1	110.60(6)	102.5
N4–H1	0.85(2)	1.02	N2–P3–N5	115.53(7)	104.1
O1–C11	1.4008(18)	1.39	N5–P3–N4	101.46(9)	98.6
O4–C14	1.4082(18)	1.39	P3–N4–H1	113.5(14)	110.9
			H1–N4–H2	110(2)	108.6
Dihedral angle, °			P3–N5–H3	117.9(14)	110.7
P1–N1–P2–N2	1.17(1)	–8.35	C11–O1–P1	123.31(9)	117.3
P1–N3–P3–N4	–98.13(1)	–137.80			
C11–O1–P1–O2	–175.98(1)	–171.06			
C12–O2–P1–O1	–62.88(1)	–57.78			
C23–C13–O3–P2	77.09(1)	79.17			

[a] Geometrical parameters determined by X-ray diffraction[8].

Vibrational Spectra and Assignments

The optimized geometry of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$ (C_2 symmetry) was used to calculate wavenumbers by DFT methods using TZ2P basis set. Most of the vibrational bands were assigned on the basis of DFT calculations to experimental bands in the measured IR (Fig. 2) and Raman spectra (Fig. 3). Experimental and calculated values of wavenumbers are in a good agreement with regard to a total number of atoms in the molecule (60 atoms) (Table II). Only discrepancies between experimental and theoretical stretching vibrations of NH_2 groups (3300–3500 cm^{-1}) were in interval from +3.58 to +5.27% due to a presence of intermolecular hydrogen bonds in the solid. The good visual correspondence between experimental and calculated IR spectra is perceptible from Fig. 2. The vibrational assignment is listed in Table II.

NH stretching modes, ν(NH₂): Highest values of wavenumbers (in a region from 3310 to 3473 cm^{-1}) were assigned to $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ vibrations in agreement with calculated values. Discrepancies between the experimental and theoretical stretching vibrations of NH_2 groups (3300–3500 cm^{-1}) are situated in interval from +3.58 to +5.27%, and may be caused by presence of intermolecular hydrogen bonds in the crystal structure (Fig. 1). The hydrogen bonding involving NH and CH groups has been considered as the reason for shifts of the experimental $\nu(NH_2)$ vibrational modes to the lower values[40,41]. This assignment of stretching vibrations is also in a good agreement with experimental values of $\nu(NH_2)$ in amino-*cyclo*-triaza-λ^5-phosphorines, e.g. $P_3N_3Cl_5NH_2$ (3246 and 3346 cm^{-1})[24].

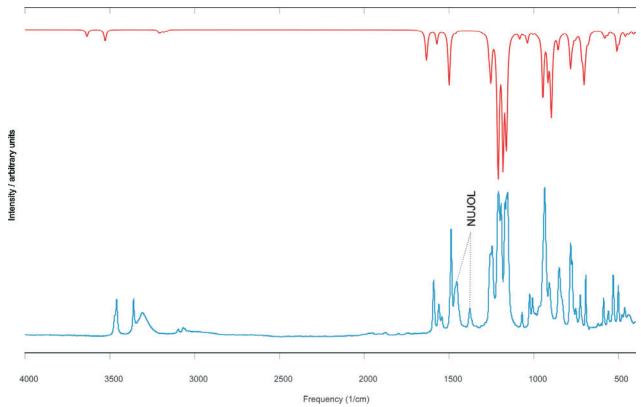


FIG. 2
Measured (lower) and calculated (upper) IR spectra (4000–400 cm^{-1}) of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$. Vibrational bands of the nujol were smoothed away for clarity in interval from 2870 to 2950 cm^{-1}

TABLE II
Selected observed and calculated vibrational wavenumbers ($\tilde{\nu}$) of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$

Experimental IR $\tilde{\nu}$, cm^{-1}	Experimental Raman $\tilde{\nu}$, cm^{-1}	Calculated ADF/TZ2P $\tilde{\nu}$, cm^{-1}	Assignment
3473 sh		3602	$\nu_{as}(NH_2)$
3463 w		3600	$\nu_{as}(NH_2)$
3363 w		3497	$\nu_s(NH_2)$
3310 w		3494	$\nu_s(NH_2)$
3098–3041 vw	3071 s	3125–3153	20 ν_s(CH)
1591 m	1592 m, brd	1611–1620	8 $\delta(NH_2)$
1560 w		1557	$\delta(NH_2)$
1542 vw		1556	$\delta(NH_2)$
1488 s		1484–1487	8 δ(CH)
1256 sh	1257 vw	1250	δ(PN) + δ(CO)
1246 s		1240	δ(PN) + δ(CO)
1207 vs	1207 vw	1201	ν(CO)
1193 vs		1197, 1193	ν(CO)
1169 vs	1170 sh	1169	ν(Pn) + δ(CH)
1161 vs	1162 w	1155–1148	8 δ(CH)
1153 vs	1151 w	1155–1148	8 δ(CH)
1069 w		1071, 1073	4 δ(CH)
1024 m	1028 w	1025–1028	4 ν(CC)
1008 m	1008 vs		$\rho(NH_2)$[a]
935 vs		936	ν(PO) + $\rho(NH_2)$
909 m			
		886, 889	ν(PO) + ν_{as}(NPN)(exo) + δ(PNH) + δ(CH)
			δ(CH)
		890	ν_{as}(NPN)exo
850 m	852 vw, brd	847	ν(PO) + $\rho(NH_2)$
783 s	785 vw, brd	740–780	4 δ(CH)
774 m		740–780	4 δ(CH)
752 w		748	δ(PN)*
478 vw		486	δ(OPO)*
	463 vw	456	τ(PN)*

[a] Assigned according to $P_3N_3Cl_5NH_2$ [24] and with *gem*-$P_3N_3Cl_4(NH_2)_2$ [42]. * The value is in agreement with literature data of *spiro*[2,2′-biphenoxy]-4,4,6,6-tetrachloro-1,3,5-*cyclo*-triaza-λ^5-phosphorine[9].

δ*(NH$_2$) and* ρ*(NH$_2$) vibrations*: Experimental and theoretical δ(NH$_2$) vibration bands are in a quite good agreement, despite the hydrogen bonds existing in a crystal structure (see Table II), and also correspond very well to known literature data of $P_3N_3Cl_5NH_2$ (δ(NH$_2$) 1546 cm^{-1})[24]. The discrepancies between the experimental and theoretical δ(NH$_2$) vibrations are situated in interval from +0.25 to +1.79%. The ρ(NH$_2$) vibration (1008 cm^{-1}) was assigned after a comparison with $P_3N_3Cl_5NH_2$ (ρ(NH$_2$) 1015 and 1051 cm^{-1})[24] and with *gem*-$P_3N_3Cl_4(NH_2)_2$ (ρ(NH$_2$) 1025 cm^{-1})[42].

ν*(PN) and* δ*(PN) vibrations*: Only two bands consistent with δ(PN) and τ(PN) vibration types were found (Table II). Other PN ring vibrations are strongly mixed with different vibrational modes in all cases as seen in Table II.

A number of vibrational bands were also assigned to stretching and deformation of CH and CO groups (Table II). The other assigned theoretical values, except wavenumbers of groups containing atoms which are bonded by a hydrogen bridge (vibrations of NH$_2$ and CH atom groups), are in a much better agreement with the experimental spectra and the discrepancies do not exceed 0.55% (Table II).

δ*(CH) vibrations*: The calculated values are found in interval of several cm^{-1} as well as by several more types of normal vibrations: ν$_s$(CH), δ(NH$_2$), ν(CC) (see Table II). As results from DFT calculations, it is possible to differ for δ(CH) eighth vibrations δ(*ortho*-CH) and eight vibrations δ(*meta*-CH) (calc. 1155–1148 cm^{-1}) and four vibrations corresponding to vibrational motion of CH groups in *para*-position (calc. 1071, 1073 and 740–780 cm^{-1}), in a good agreement with experimantal data (Table II).

Experimental NMR Data

The title compound was characterized by ^{1}H, ^{13}C, ^{31}P and ^{31}P{^{1}H} NMR spectra. The obtained experimental data are in Table III.

Simulation of the ^{31}P NMR Spectrum by gNMR

The simulation of the ^{31}P NMR spectrum was performed for the ABB'M$_4$X$_4$X$_4$' spin system inclusive of all phosphorus atoms (as ABB'), hydrogens from both amino groups (as M$_4$) and *ortho*-protons from phenoxy groups (as X$_4$X$_4$').

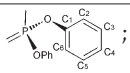
≡***P****(NH$_2$)$_2$ multiplet*: A difference between linewidths of P$_I$ resonance signal in ^{31}P{^{1}H$_{am.}$(sel.)} and in ^{31}P NMR spectra (Fig. 4), and between linewidths of the identical signal in ^{31}P{^{1}H$_{arom.}$(sel.)} and ^{31}P NMR spectra, respectively, shows an existence of coupling with protons of the amino groups and with

ortho-protons from phenoxy groups. The simulated multiplet is presented in Fig. 4, the calculated values of $^2J(P_I,H_{am.})$ and $^6J(P_I,H_{arom.})$ are given in Table IV.

≡***P(OC$_6$H$_5$)$_2$ multiplet***: The splitting of signals in the $^{31}P\{^1H\}$ NMR spectrum proved that P_{II} atoms are not magnetically equivalent (Fig. 4). After this the simulation confirmed that all *ortho*-protons are not magnetically equivalent, because the simulation for spin system ABB'M_4X_8 was not suc-

TABLE III
Experimental chemical shifts (δ) and coupling constants (*J*) of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$

Atom	δ, ppm (multiplet)	^1J(C,H), Hz	^2J(C,H), Hz	$^2J(P_I,P_{II})$, Hz	$\nu_{1/2}$, Hz
NH_2	2.7 s[b]				~13
$H_{arom.}$	7.2 m[b]				
C_1[a]	153.0 s[c]				~12
$C_{2,6}$[a]	130.2 dd[c]	161	8		
$C_{3,5}$[a]	122.4 d[c]	162			~16
C_4[a]	125.2 dt[c]	161	7		
P_I[d]	20.1 t[b]			~68	
P_{II}[d]	10.8 d[b]			~68	

[a] Numbering of carbon atoms: 

; [b] diethylether; [c] tetrahydrofuran; [d] P_I = **P**$(NH_2)_2$, P_{II} = **P**$(OC_6H_5)_2$.

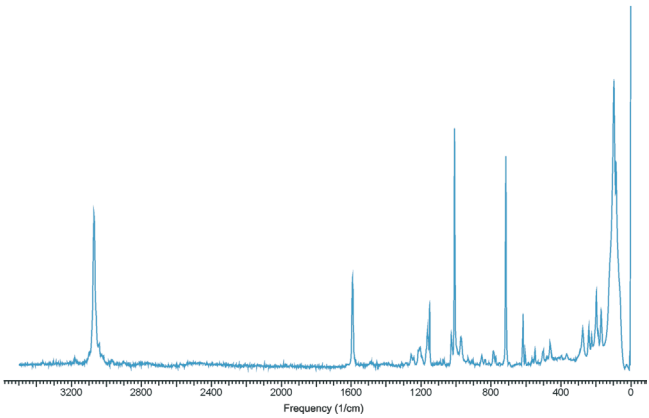


FIG. 3
Raman spectrum of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$ (3500–0 cm^{-1})

cessful as it was expected. On this account, *ortho*-hydrogens were divided in two groups of magnetically nonequivalent atoms and two coupling constants were simulated: $^4J(P_{II},H_{arom.})$ and $^6J(P_{II},H'_{arom.})$. The values of simulated coupling constants are given in Table IV. A linewidth difference in the resonance signal in $^{31}P\{^1H_{am.}(sel.)\}$ and $^{31}P\{^1H_{arom.}(sel.)\}$ NMR spectra is only 0.1 Hz. However, it indicates a coupling with protons from amino groups. Thus it was possible to include the $^4J(P_{II},H_{am.})$ in the simulation and to find its approximate value (see Table IV).

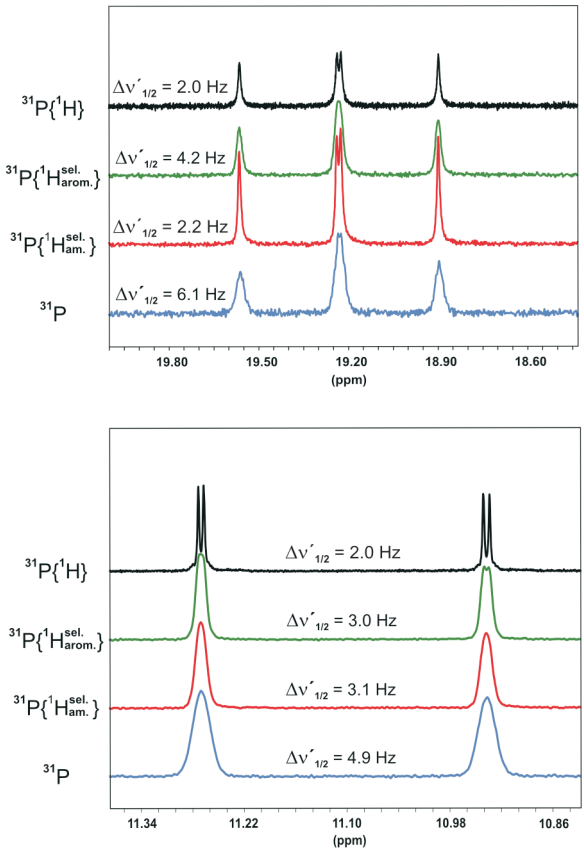


FIG. 4
^{31}P, $^{31}P\{^1H\}$, $^{31}P\{^1H_{am.}(sel.)\}$ and $^{31}P\{^1H_{arom.}(sel.)\}$ NMR spectra of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$ (5.2×10^{-2} M solution in $CDCl_3$, 0.077 Hz per point, measured at 283 K). The average linewidth ($\Delta\nu'_{1/2}$) of doublet of doublets in $^{31}P\{^1H\}$ NMR spectrum was counted as an average linewidth of two doublets ($\Delta\nu'_{1/2}$ = 2.0 Hz)

The coupling constants $^2J(P_I,P_{II})$, $^2J(P_I,H_{am.})$, $^4J(P_{II},H_{am.})$ and $^4J(P_{II},H_{arom.})$ were also calculated by ADF program package, and the NMR [34] and CPL [35,36] modules were used. The calculations were performed using OPBE and BP functionals. The calculated and the simulated coupling constants are conformable. A better agreement was achieved for $^2J(P_I,P_{II})$, $^2J(P_I,H_{am.})$ when BP functional was used as you can see in Table IV. Unfortunately, few experimental values afford no deeper discussion of the performance of used functionals and the calculational error, as well. The ^{31}P NMR spectrum is the higher order spectrum, although a difference of chemical shifts of both multiplets is 24 times higher than a value of $^2J(P_I,P_{II})$.

TABLE IV
Chemical shifts (δ) and coupling constants (*J*) of *gem*-$P_3N_3(OC_6H_5)_4(NH_2)_2$ determined by simulated ^{31}P NMR spectrum and by ADF calculations for a spin system ABB′$M_4X_4X_4'$

Atom[a]	δ, ppm	Spin–spin coupling	$J_{sim.}$, Hz	$J_{ADF/OPBE}$, Hz	$J_{ADF/BP}$, Hz
P_I	10.08	$^2J(P_I,P_{II})$	68.7	56.0	60.8
P_{II}	19.46	$^2J(P_I,H_{am.})$	2.5	0.7	1.2
		$^4J(P_{II},H_{am.})$	1.4	from –1.7 to –0.3	from –0.8 to –0.2
		$^4J(P_{II},H_{arom.})$	~0.2	from –0.1 to –0.1	from –0.2 to –0.2
		$^6J(P_I,H_{arom.})$	~0.2		
		$^6J(P_{II},H'_{arom.})$[b]	~0.6		

[a] P_I = $\mathbf{P}(NH_2)_2$, P_{II} = $\mathbf{P}(OC_6H_5)_2$; [b] $H'_{arom.}$: *ortho*-hydrogens from phenoxy groups which are bonded on the second (magnetically nonequivalent) P_{II} atom.

The simulation of ^{31}P NMR spectrum proved a nontrivial problem, due to six-bond interactions with small values of coupling constants (Table IV). It must be pointed out that $^2J(P_I,H_{am.})$ especially, as well as the other simulated phosphorus-hydrogen coupling constants are apparently the only known phosphorus-hydrogen coupling constants of amino and phenoxy derivatives of *cyclo*-triaza-λ^5-phosphorines, respectively, because the splitting is not usually directly visible in NMR spectra of such compounds as *cyclo*-triaza-λ^5-phosphorines.

CONCLUSIONS

Metric parameters and vibrational frequencies of *gem*-2,2-diamino-4,4,6,6-tetraphenoxy-1,3,5-*cyclo*-triaza-λ^5-phosphorine were calculated using DFT calculations with ADF program package. Most of the vibrational bands were

assigned on the basis of DFT calculations. Experimental and calculated values of wavenumbers are in a good agreement with regard to a total number of atoms in the molecule (60 atoms). Only discrepancies between experimental and theoretical values for NH_2 vibrations were in interval from +3.58 to +5.27% ($\nu(NH_2)$) and from 0.25 to 1.79% ($\delta(NH_2)$), respectively, due to the presence of intermolecular hydrogen bonds. The calculation of IR spectrum was performed with no scaling factor.

^1H, ^{13}C, ^{13}C APT, ^{31}P, $^{31}P\{^1H_{am.}(sel.)\}$ and $^{31}P\{^1H_{arom.}(sel.)\}$ NMR spectra were measured, and corresponding chemical shifts and coupling constants were obtained (Table III). The simulation of ^{31}P NMR spectrum was performed for ABB′$M_4X_4X_4'$ spin system, the value of $^2J(P_I,P_{II})$ was refined on, and $^2J(P_I,H_{am.})$, $^4J(P_{II},H_{am.})$, $^4J(P_{II},H_{arom.})$, $^6J(P_I,H_{arom.})$ and $^6J(P_{II},H'_{arom.})$ were simulated (Table IV). $^2J(P_I,P_{II})$, $^2J(P_I,H_{am.})$, $^4J(P_{II},H_{am.})$ and $^4J(P_{II},H_{arom.})$ were also calculated by ADF program using OPBE and BP functionals. The calculated and simulated coupling constants are conformable. A better agreement was achieved for $^2J(P_I,P_{II})$, $^2J(P_I,H_{am.})$ when BP functional was used, but few experimental values did not allow to discuss deeper the performance of used functionals and the calculational error, as well.

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic (Grant No. MSM0021622411), Academy of the Sciences of the Czech Republic (KAN 101630651) and Ministry of Industry and Trade of the Czech Republic (Project FR-TL1/413 in program TIP).

REFERENCES

1. Rose H.: *Ann. Chem.* **1834**, *11*, 131.
2. Liebig J., Wöhler F.: *Ann. Chem.* **1834**, *11*, 139.
3. Stokes H. N.: *J. Am. Chem. Soc.* **1895**, *17*, 497.
4. De Ruiter B., Winter H., Wilting T., van de Grampel J. C.: *J. Chem. Soc., Dalton Trans.* **1984**, 1027.
5. Fincham J. K., Parkes H. G., Shaw (née Gözen) L. S., Shaw R. A.: *J. Chem. Soc., Dalton Trans.* **1988**, 1169.
6. Fincham J. K., Hursthouse M. B., Parkes H. G., Shaw (née Gözen) L. S., Shaw R. A.: *J. Chem. Soc., Chem. Commun.* **1985**, 252.
7. Fincham J. K., Hursthouse M. B., Parkes H. G., Shaw (née Gözen) L. S., Shaw R. A.: *Acta Crystallogr., Sect. B: Struct. Sci.* **1986**, *42*, 462.
8. Dastychová L., Žák Z., Alberti M., Taraba J.: *Acta Crystallogr., Sect. E: Struct. Sci.* **2007**, *63*, o3500.
9. Menendez J. R., Carriedo G. A., Garcia-Alonso F. J., Clavijo E., Nazri M., Aroca R.: *J. Raman Spectrosc.* **1999**, *30*, 1121.
10. Voznicová R., Alberti M., Taraba J., Dastych D., Kubáček P., Příhoda J.: *Collect. Czech. Chem. Commun.* **2007**, *72*, 1407.

11. Huvenne J. P., Vergoten G., Legrand P.: *J. Mol. Struct.* **1980**, *63*, 47.
12. Painter P. C.: *Appl. Spectrosc.* **1982**, *36*, 265.
13. Elass A., Vergoten G., Dhamelincourt P., Becquet R., De Jaeger R.: *Electron. J. Theor. Chem.* **1997**, *2*, 1.
14. Kandemirli F.: *Phosphorus Sulfur Silicon Relat. Elem.* **2003**, *178*, 2331.
15. Nader B. S., Kar K. K., Morgan T. D., Pawloski C. E., Dilling W. L.: *Trib. Trans.* **1992**, *35*, 37.
16. Medina R., Sullivan J. M.: U.S. 4,618,691 (1985); *Chem. Abstr. 103*, 177, 559.
17. Kapička L., Dastych D., Richterová V., Alberti M., Kubáček P.: *Magn. Reson. Chem.* **2005**, *43*, 294.
18. Hägele G., Engelhardt M., Boenigk W.: *Simulation und Automatisierte Analyse von Kernresonanzspektren*. VCH, Weinheim 1987.
19. Kajiwara M., Kurachi Y.: *Polyhedron* **1983**, *2*, 1211.
20. Reuben J.: *Magn. Res. Chem.* **1987**, *25*, 1049.
21. Abou Ali S., Herrmann E., Thomas B.: *Z. Chem.* **1984**, *24*, 133.
22. Allcock H. R., Evans T. L., Fuller T. J.: *Inorg. Chem.* **1980**, *19*, 1026.
23. Kretschmann M., Diefenbach U.: *Z. Anorg. Allg. Chem.* **1998**, *624*, 335.
24. Alberti M., Břínek J., Marek J., Toužín J.: *Z. Anorg. Allg. Chem.* **1997**, *623*, 637.
25. McBee E. T., Okuhara K., Morton C. J.: *Inorg. Chem.* **1966**, *5*, 450.
26. Perin D. D., Armarego W. L. F.: *Purification of Laboratory Chemicals*, 3rd ed. Pergamon Press, Oxford 1988.
27. Budzelaar P. H. M.: *gNMR*, V4.1.2. Adept Scientific plc., Letchworth 1995–2001.
28. te Velde G., Bickelhaupt F. M., van Gisbergen S. J. A., Fonseca Guerra C., Baerends E. J., Snijders J. G., Ziegler T.: *J. Comput. Chem.* **2001**, *22*, 931.
29. Fonseca Guerra C., Snijders J. G., te Velde G., Baerends E. J.: *Theor. Chem. Acc.* **1998**, *99*, 391.
30. Baerends E. J., Autschbach J., Bérces A., Bickelhaupt F. M., Bo C., Boerrigter P. M., Cavallo L., Chong D. P., Deng L., Dickson R. M., Ellis D. E., van Faassen M., Fan L., Fischer T. H., Fonseca Guerra C., van Gisbergen S. J. A., Götz A. W., Groeneveld J. A., Gritsenko O. V., Grüning M., Harris F. E., van den Hoek P., Jacob C. R., Jacobsen H., Jensen L., van Kessel G., Kootstra F., Krykunov M. V., van Lenthe E., McCormack D. A., Michalak A., Neugebauer J., Nicu V. P., Osinga V. P., Patchkovskii S., Philipsen P. H. T., Post D., Pye C. C., Ravenek W., Rodriguez J. I., Ros P., Schipper P. R. T., Schreckenbach G., Snijders J. G., Solà M., Swart M., Swerhone D., te Velde G., Vernooijs P., Versluis L., Visscher L., Visser O., Wang F., Wesolowski T. A., van Wezenbeek E. M., Wiesenekker G., Wolff S. K., Woo T. K., Yakovlev A. L., Ziegler T.: *ADF*, version 2008.01. SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam 2008. For the current version, see http://www.scm.com/Downloads/Welcome.html.
31. Swart M., Ehlers A. W., Lammertsma K.: *Mol. Phys.* **2004**, *102*, 2467.
32. Handy N. C., Cohen A. J.: *Mol. Phys.* **2001**, *99*, 403.
33. Adamo C., Barone V.: *J. Chem. Phys.* **1998**, *108*, 664.
34. Schreckenbach G., Ziegler T.: *J. Phys. Chem.* **1995**, *99*, 606.
35. Autschbach J., Ziegler T.: *J. Chem. Phys.* **2000**, *113*, 936.
36. Autschbach J., Ziegler T.: *J. Chem. Phys.* **2000**, *113*, 9410.
37. Becke A. D.: *Phys. Rev. A* **1988**, *38*, 3098.
38. a) Perdew J. P.: *Phys. Rev. B* **1986**, *33*, 8822; b) Erratum: Perdew J. P.: *Phys. Rev. B* **1986**, *34*, 7406.

39. Kapička L., Kubáček P., Holub P.: *J. Mol. Struct.: THEOCHEM* **2007**, *820*, 148.
40. Treu Filho O., Pinheiro J. C., da Costa E. B., Kondo R. T., de Souza R. A., Nogueira V. M., Mauro A. E.: *J. Mol. Struct.: THEOCHEM* **2006**, *763*, 175.
41. Feki H., Ben Ahmed A., Fourati N., Abid Z., Minot C.: *J. Mol. Struct.: THEOCHEM* **2009**, *895*, 21.
42. Alberti M., Toužín J.: Unpublished results.