Vibrational spectra, conformations, and force constants of bis(dimethylamino)chlorophosphine and 2-chloro-1,3-dimethyl-1,3,2-diazaphospholane

S. A. Katsyuba, E. A. Filippova, R. R. Shagidullin, I. Kh. Shakirov, and O. N. Nuretdinova*

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan', Russian Federation.
Fax: +7 (843 2) 75 2253. E-mail: katsyuba@glass.ksu.ras.ru

Conformational analysis of the molecules of bis(dimethylamino)chlorophosphine and 2-chloro-1,3-dimethyl-1,3,2-diazaphospholane was carried out by the molecular mechanics method. According to calculations, both compounds are conformationally homogeneous, which is in agreement with the data of vibrational spectroscopy. The structural parameters found were used to calculate the frequencies and modes of normal vibrations, to analyze the IR and Raman spectra, and to estimate force constants for both diaminophosphines.

Key words: cyclic and acyclic diaminophosphines, conformations, normal vibrations, force constants.

Previously,[1] based on a study of vibrational spectra of bis(dimethylamino)chlorophosphine (**1**) and 1,3-dimethyl-2-chloro-1,3,2-diazaphospholane (**2**), we have shown that these compounds are conformationally homogeneous in the condensed phase. However, the structures of the conformers have not been determined; this precluded the possibility of comparing the results obtained by spectroscopy with the results of electron diffraction studies[2,3] of molecules **1** and **2** in the gas phase. The spectra of compounds have been reported only partially and have not been interpreted in detail.

In the present study, the force constants of molecules **1** and **2** and geometric characteristics of their equilibrium conformations were estimated using vibrational spectroscopy and molecular mechanics, and the vibrational spectra were completely interpreted.

Experimental

Compounds **1** and **2** were obtained by the reactions of the chlorides of the corresponding acids of trivalent phosphorus with amines in the presence of a base according to previously described procedures.[4] The physicochemical constants and parameters of the ^{31}P NMR spectra of these compounds coincided with the published data. IR spectra were recorded on a UR-20 spectrometer, and the Raman spectra were measured on a Coderg spectrometer with an LG-38 He—Ne-laser.

The frequencies and modes of normal vibrations were calculated in terms of the El'yashevich—Wilson GF method.[5] The initial values for the force constants of molecule **1** were transferred from the force field of the Me_2N-PCl_2 molecule (**3**);[6] then they were varied within the framework of the "damped" least-squares method.[7] The force constants of the methyl groups were not varied. A similar procedure was applied to molecule **2** with the only difference that the initial parameters were transferred from the force field of molecule **1**. Published data[2,3] for the lengths of valence bonds were used. The other geometric parameters of molecules **1** and **2** were calculated by the molecular mechanics method;[8] as this was done, the "immanent" torsion potential[8] of the >P—N< bond was assumed to have the following form:

$$U_{tor} = 0.5V[1 - \cos(2\varphi)],$$

where φ is the dihedral angle between the lone electron pair of the phosphorous atom and the plane of the dimethylamino group. The V value was chosen in such a way as to reproduce the experimental barriers to the internal rotation around the exocyclic >P—N< bond in the molecules of the phospholane series.[9] The $V = 6.0$ kcal mol^{-1} value found was also used in the calculations for molecules **1** and **2**. The other parameters were determined earlier.[8]

Results and Discussion

The potential surface for the internal rotation in molecule **1** calculated by the molecular mechanics method has one minimum corresponding to the symmetrical conformation shown in Fig. 1. In the case of compound **2**, the calculations predict two minima, one of which corresponds to the conformer shown in Fig. 2 and the other of which corresponds to its mirror image. Since the mirror isomers cannot be distinguished by spectral methods, the results of the simulation are in full agreement with the conclusion about the conformational homogeneity of molecules **1** and **2** based on the data of vibrational spectroscopy. Furthermore, the calculated geometric parameters of molecule **2** coincide to within the experimental error with the values found by X-ray electron diffraction.[3]

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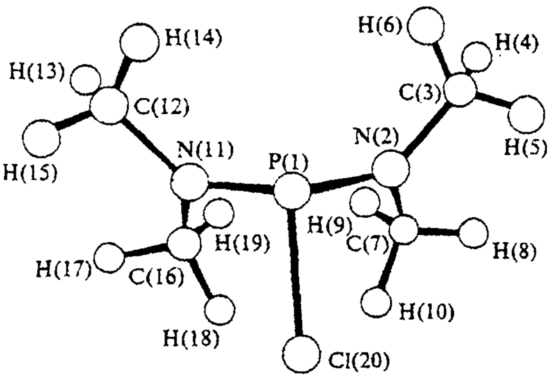

Fig. 1. Equilibrium configuration of molecule **1**.

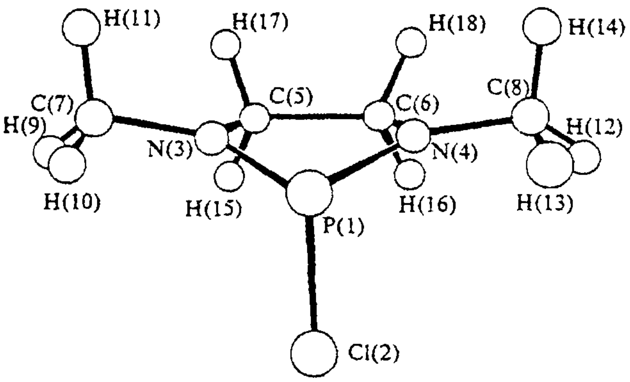

Fig. 2. Equilibrium configuration of molecule **2**.

However, our conclusion that molecule **1** is symmetrical does not agree with the results of another study,[2] according to which the orientations of the two dimethylamino groups with respect to the plane that comprises the nitrogen and phosphorus atoms are markedly dissimilar. Thus the following values for the angles of rotation of the Me_2N groups with respect to the axis orthogonal to this plane were reported:[2] $\varphi_1 = -14.1 \pm 5.6°$ and $\varphi_2 = 65.6 \pm 3.4°$. According to our calculations, $\varphi_1 = -27°$ and $\varphi_2 = 27°$. In the calculations of the frequencies and modes of the normal vibrations of molecule **1**, we assumed that its conformation corresponds to that shown in Fig. 1.

The calculated and experimental vibration frequencies for compound **1** are compared in Table 1. It should be noted that in the region of frequencies higher than 650 cm^{-1}, the spectra of compounds **1** and **3** are almost identical (see Ref. 6 and Table 1 in this work). The

Table 1. Characteristics of the vibrational spectra of compound **1**

IR (liq.), ν/cm^{-1}	Raman (liq.) ν/cm^{-1}	Raman (liq.) *I* (rel.u.)	Raman (liq.) ρ [a]	Calculations ν/cm^{-1} [b]	Calculations Assignment[c]
3001 w	3000	0.2	0.8		
				2985 (4)	ν_{as}Me
2970 w	2970	sh			
2933 s	2933	1.9	0.29	2932 (2)	ν_{as}Me
2920 sh	2922	sh		2930 (2)	ν_{as}Me
2889 s	2887	1.6	0.3		
2870 sh					
2842 m	2840	1.5	0.1	2840 (4)	ν_{as}Me
2799 s	2795	1.3	0.09		
1478 m	1478	1.6	0.79	1473 (2)	δ_{as}Me
1460 sh				1465 (2)	δ_{as}Me
				1460 (2)	δ_{as}Me
1450 s				1457 (2)	δ_{as}Me
	1435	2.3	0.84	1440 (2)	δ_sMe
1410 w	1408	0.4	0.84	1431 (2)	δ_sMe
1280 sh				1288	rMe, νPN − ν_sNC (A′)
1271 s	1275	0.6	0.3	1280	rMe, νPN − $\nu_s NC_2$ (A″)
1243 vw	1245	vw			
1192 s	1185	vw		1173	$\nu_{as}NC_2$, rMe (A′)
1167 vw					
1140 w	1140	vw	0.8	1144	$\nu_{as}NC_2$, rMe (A″)
1095 w	1090	vw		1096	rMe (A″)
1082 vvw				1089	rMe (A′)
1061 m	1060	0.6	0.8	1033	rMe (A′)
				1032	rMe (A″)
1029 vvw				1010	rMe (A′)
				1009	rMe (A″)
980 vs	980	0.9	0.8	972	$\nu_s NC_2$ − νPN, rMe (A″)
960 vvs	960	0.7	0.8	965	$\nu_s NC_2$ − νPN, rMe (A′)
698 s	695	w.sh		699	$\nu_s NC_2$ + νPN (A″)
671 m	670	10	0.12	665	$\nu_s NC_2$ + νPN (A′)
448 m.br	490	vw		499	νPCl, rNC_2 (A′)
415 m.br	410	0.9	0.4	428	νPCl, δPN_2 (A′)
				427	δNP_2, ωNC_2 (A″)
	385	0.6	0.4	384	rNC_2, ωNC_2 (A″)
				380	νPCl, ωNC_2 (A′)
	335	6.7	0.25	324	νPCl, δNC_2 (A′)
				317	rNC_2, δNC_2 (A″)
	292	5.2	0.3	288	ωNC_2, χMe (A′)
				287	ωNC_2, χMe (A″)
	125	3.7	dp	144	ωNC_2 (A″)
				106	δPN_2 (A′)
				99	χPN (A″)
				53	ωNC_2 (A′)

[a] ρ is the degree of depolarization, p is polarized line, dp is depolarized line. [b] The multiplicity of the vibration degeneracy is given in parentheses. [c] The symmetry of the vibration is given in parentheses. Types of vibrations: ν, stretching; δ, deformation; r, rocking; τ, twisting; χ, torsional; ω, wagging; s, symmetrical; as, asymmetrical.

Table 2. Characteristics of the vibrational spectra of compound **2**

IR (liq.),	Raman (liq.)			Calculations	
ν/cm^{-1}	ν/cm^{-1}	*I* (rel.u.)	ρ[a]	ν/cm^{-1} [b]	Assignment[c]
3015 w					
2970 sh	2973	0.63	dp	2989 (2)	ν_{as}Me
2930 s	2940	1.0		2930 (2)	ν_{as}Me
	2885	sh		2896	$\nu_{as}CH_2$ (A′)
				2884	$\nu_{as}CH_2$ (A″)
2870 s	2872	0.95	p	2871	ν_sCH_2 (A′)
				2867	ν_sCH_2 (A″)
2810 s	2812	0.74	p	2836 (2)	ν_sMe
1490 sh					
1485 m	1480	sh		1469 (2)	δ_{as}Me
1465 m	1473	1.05		1466 (2)	δ_{as}Me
1455 sh					
1442 m	1442	0.83	0.8	1418 (2)	δ_sMe
1428 sh	1430	0.74	0.5		
	1370	0.43	0.5	1363	δCH_2 (A′)
1340 m	1342	0.46	0.8	1342	δCH_2 (A″)
1325 sh					
1260 sh	1260	sh	dp	1266	ωCH_2 (A″)
	1250	0.16	p	1248	ωMe, νPN (A′)
1235 s	1238	0.18	p	1219	νN—Me, τCH_2 (A′)
1217 s				1214	νN—Me, τCH_2 (A″)
1205 w.sh	1205	0.29	dp	1205	ν_{as}PNMe, τCH_2 (A″)
1180 vw	1180	0.33	p	1183	ν_{as}PNMe, τCH_2 (A′)
1148 s				1168	$\nu N—CH_2$, rMe, ωCH_2 (A′)
	1125	0.16	0.7	1112	$\nu N—CH_2$, rMe, ωCH_2 (A″)
1080 vw	1085	0.08	0.8	1079	rMe (A″)
1055 w				1070	rMe (A′)
1030 s	1030	0.95	0.4	1017	rMe, νCC (A′)
1010 m	1012	sh	dp	1011	rCH_2 (A″)
946 s	948	0.2	0.7	941	$\nu N—CH_2$ (A″)
918 vw					
880 vw					
855 br.sh	855	0.14	0.8	859	$\nu N—CH_2$, νCC (A′)
	830	0.03		827	rCH_2 (A′)
706 m	710	10	0.08	711	ν puls. (A′)
692 m	692	sh		694	νPN (A″)
595 w	597	1.05	0.86	602	ring δ (A″)
490 m	490	1.84	0.34	490	νPCl, rPCl (A′)
	392	1.26	0.3	393	νPCl (A′)
	355	1.1	0.83	350	rN—Me in plane (A″)
	310	sh		313	rNMe out-of-plane, χ vib. (A″)
	300	2.95	p	301	ring δ (A′)
	268	2.79	0.25	260	rN—Me sh. (A′)
	245	br.sh		210	χ Me (A″)
				197	χ Me (A′)
				188	χ Me, ring δ (A′)
				155	rNMe out-of-plane χ Me (A″)
	112	3.0	0.6	111	rN—Me out-of-plane (A′)
				97	rPCl (A″)

[a—c] See notes in Table 1.

calculations show that not only the vibration frequencies but also the vibration modes of both molecules coincide. Since molecule **1**, unlike **3**, contains two dimethylamino groups, the number of normal vibrations that involve predominantly the Me_2N group is twice that observed for molecule **3**. However, many vibration modes are degenerate; therefore, the expected doubling of the number of spectral peaks does not occur (see Table 1). Only those bands and lines that are caused predominantly by the $\nu_{as}NC_2$ (1192/1140 cm^{-1}) and ν_sNC_2 (980/960 and 698/671 cm^{-1}) vibrations are "split," and this "splitting" is mostly due to the kinematic interaction between the two dimethylamino groups.

The simulated spectrum is in satisfactory agreement with the experimental spectrum in the range of frequencies above 650 cm^{-1} even without variation of the initial approximation of the force field of molecule **1** obtained using the force field of molecule **3**. The fact that the force constants of the Me_2NP groups are close indicates indirectly that the conformations of the dimethylamino groups in molecules **1** and **3** are similar, because changes in the conformations of phosphorus-containing fragments normally change their potential fields (see, for example, Ref. 10). Thus, the orientations of the two dimethylamino groups in molecule **1** are virtually identical. This corresponds to the results of our conformational calculations (see Fig. 1) but is inconsistent with the nonsymmetrical conformation of molecule **1** proposed using the electron diffraction data.[2] This disagreement might be due to several reasons. It cannot be ruled out that allowance for the vibrational effects in the interpretation of electron diffraction patterns could have changed qualitatively the results of the study cited[2] (see, for example, Ref. 11) and, thus, these results would be brought in agreement with our calculations. It is also possible that the mechanical model of the molecule[8] does not take into account some specific intramolecular interactions that actually disturb the symmetry of molecule **1**. If we accept this hypothesis, which is supported by NQR data,[12] then we will have to assume that the vibrational frequencies and force constants of the dimethylamino groups at the phosphorus atom depend

Table 3. Force constants of compounds **1** and **2** ($\times 10^6$ cm^{-2})[a]

Force constant[a]	**1**	**2**
K_{PCl}	2.8	3.3
K_{PN}	8.0	8.7
K_{N-C}	7.3	7.3
K_{C-C}	—	6.7
K_{CH}(Me)	7.92	7.92
K_{CH}(CH$_2$)	—	8.1
K_{NCC}	—	1.1
K_{NPN}	1.3	0.9
K_{NPCl}	2.1	1.2
K_{PNC}	1.0	1.0
K_{CNC}	1.31	1.31
K_{NCH}(Me)	1.05	1.05
K_{HCH}(Me)	0.71	0.71
K_{NCH}(CH$_2$)		0.94
K_{CCH}		1.0
K_{HCH}(CH$_2$)		0.64
H_{PN}^{PCl}	0.5	0.5
H_{PN}^{PN}	0.5	1.1
$H_{PN}^{NC(7)}$	0.1	0.1
$H_{PN}^{NC(5)}$	—	0.9
H_{CC}^{NC}	—	−0.3
$H_{NC(7)}^{NC(5)}$	—	0.5
h_{CH}^{CH}(CH$_2$)	—	0.1
h_{CH}^{CH}(Me)	−0.11	−0.11
A_{PCl}^{ClPN}	0.9	0.6
A_{PN}^{ClPN}	0.4	0.4
A_{PN}^{NPN}	0.3	0.3
A_{PN}^{PNC}	0.4	0.4
$A_{NC(7)}^{PNC(7)}$	0.4	0.4
$A_{NC(5)}^{PNC(5)}$	—	0.9
$A_{NC(5)}^{CNC}$	—	0.05
$A_{NC(7)}^{CNC}$	0.25	0.25
A_{NC}^{NCH}(Me)	0.6	0.6
A_{NC}^{NCH}(CH$_2$)	0.8	0.8
A_{CC}^{CCH}	—	0.3
A_{CH}^{HCH}(CH$_2$)	—	0.32
A_{CC}^{HCH}(Me)	0.4	0.4
l_{NPCl}^{NPCl}	0.8	0.6
l_{NPN}^{NPCl}	0.2	0.2
l_{PNC}^{PNC}	−0.35	−0.35
l_{NCC}^{PNC}	—	−0.35
$l_{NCH}^{PNC(7)}$	−0.2	−0.2
$l_{NCH}^{PNC(5)}$	—	−0.05
I_{NCH}^{NCC}	—	0.045
I_{NCH}^{NCH}(Me)	−0.03	−0.03
I_{NCH}^{NCH}(CH$_2$)	—	−0.01
I_{CCH}^{CCH}(CH$_2$)	—	−0.03
$I_{C(6)C(5)H(15)}^{C(5)C(6)H(17)}$	—	0.03

[a] Numbering of the atoms corresponds to that shown in Fig. 2.

rather slightly on their conformation. Otherwise, it would apparently be difficult to explain the facts that the spectra of compounds **1** and **3** are similar and that the force constants of the Me$_2$NP fragments, as noted above, can be transferred from one molecule to the other.

The vibrational spectra of **2** differ markedly from those of **1** (Table 2). Even the frequencies of the characteristic deformation and rocking vibrational modes of the methyl groups are different. The distinctive features of the spectra of compounds **2** are bands at 1370, 1342, and 830 cm^{-1} corresponding to the methylene groups and also bands at 855 and 597 cm^{-1} associated with ring vibrations. The most intense line in the Raman spectrum of compound **2**, as in the case of **1**, is due to the fully symmetrical vibration involving the PN bonds. However, this band shifts from 670 cm^{-1}, which is its position in the spectrum of **1**, to 710 cm^{-1}, whereas the frequency of the corresponding antisymmetrical vibrations (692 cm^{-1}) remains virtually constant.

The calculations show that the spectral differences between phosphines **1** and **2** are caused not only by kinematic factors. Some force constants of molecule **2** also differ from the corresponding parameters of **1**. It can be seen from Table 3 that the main differences between the potential fields are associated with the ClPN$_2$ fragment. Apparently, they are explained by the change in the hybridization of the P and N atoms on going from compound **1** to **2**. However, it cannot be ruled out that the change of the conformation of the NC$_2$ groups, which could influence the electronic interaction of these groups with the P^{III} atom, also plays some role.

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