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Molecular Structure of Diphenylchlorophosphine in the Gas Phase

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Abstract — The molecular structure of diphenylchlorophosphine was determined by gas-phase electron diffraction in combination with quantum-chemical calculations. The molecule has the C_1 symmetry with the following torsion angles around the P–C bonds: 140.2(3.1)° ($C^2P^1C^8C^9$) and –95.8(3.1)° ($C^8P^1C^2C^3$). The $ClPC^2$ and $ClPC^8$ bond angles are 101.9(4)° and 99.7°, respectively; the CPC bond angle is 103.1(1.3)°. The results of structural analysis agree with theoretical calculations of the geometry by the B3LYP/6-31G* and HF/6-31G* methods. The molecular geometries of some amines (fluoro- and chlorodiphenylamines) were calculated for comparison.

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Proceeding with studies of the structures of phenyl derivatives of phosphorus in the gas phase [1–3] with the aim to reveal regular trends in their geometric structures, we made an electron diffraction study of diphenylchlorophosphine and analyzed theoretically the conformations of fluorodiphenylamine and chlorodiphenylamine $XNPh_2$ (X = F, Cl). In the structural and conformational analysis we used the results of HF/6-31G*, B3LYP/6-31G*, and other calculations [4].

Structural analysis. As follows from theoretical calculations, the diphenylchlorophosphine molecule has the C_1 symmetry (Table 1, Fig. 1). Nevertheless, there are some features of the C_2 symmetry. The phosphorus atom lies in the plane of phenyl groups; the the exocyclic angles PC^2C^3 and PC^8C^9 (115°–116°), as well as the adjacent angles PC^2C^7 and PC^8C^{13} (125°–126°), are equal within 1° but distort the C_2 symmetry of the phosphorus–phenyl fragments. Furthermore, endocyclic angles CC(P)C and the opposite angles at the C^6 and C^{10} atoms are less than 120°. The ClPC angles also differ (by 2°). However, as shown by HF/6-31G* and B3LYP/6-31G* calculations, the main parameters such as the torsion angles $\tau(C^2PC^8C^9)$ and $\tau(C^8PC^2C^3)$ which define the molecular conformation as a whole are essentially different.

The structural analysis was performed on the basis of molecular intensity curves $sM(s)$ in the region of s 1.75–15.50 and 3.50–28.0 $Å^{-1}$. Figure 2 shows the composed experimental $sM(s)$ curve. Figure 3 shows the radial distribution curve $f(r)$ [Fourier transform of the composed $sM(s)$ curve]. In the $f(r)$ curve, all the main bond distances (C–H, C–C, P–C, P–Cl) are well resolved. The assignment of the remaining peaks presents no problem. In the refinement procedure, the bond angles in phenyl rings were taken from the HF/6-31G* calculations. This simplification is justified, because the calculated bond angles (HF/6-31G*, B3LYP/6-31G*) differ by only 0.1° (Table 1). The P–C and C–C bonds were refined by the group method using the theoretical differences. The required mean vibrational amplitudes u_{ij} were calculated using the theoretical force constants and were then refined with independent geometric parameters (Table 1). Table 2 compares the observed and calculated mean vibrational amplitudes. Some C···C amplitudes such as $C_1\cdots C_3$ and diagonal $C_1\cdots C_4$ amplitudes for the distances of 2.4 and 2.8 Å, and also C···H amplitudes in the phenyl rings are well known, and it is not necessary to include them in the refinement because in the preliminary stage of refinement they remained unchanged and led only to additional undesirable correlations with the more significant geometric parameters. Nevertheless, we observe several strong correlations between the geometric parameters; for example, there is a strong correlation |0.95| between the torsion angles $\tau(ClPC^2C^3)$ and $\tau(C^8PC^2C^3)$, and between the amplitudes of groups III and IV. Below we present the correlation matrix of diphenylchlorophosphine molecule [correlation coefficients ($\times 10^2$)].

Table 1. Experimental and calculated geometric parameters of diphenylchlorophosphine molecule and theoretical parameters for fluoro(chloro)diphenylamines (bond lengtths, Å; bond angles, deg)

Parameters	$ClPPh_2$ [a]				$HPPh_2$	$FNPh_2$	$ClNPh_2$
	B3LYP/6-31G*	B3LYP/6-311+G*	HF/6-31G*	Experiment	Experiment [2]	HF/6-31G*	HF/6-31G*
P^1–C^2	1.848	1.850	1.841	1.829 (1)	1.829 (4)	1.425 (NC)	1.429 (NC^2)
P^1–C^8	1.846	1.845	1.836	1.824 (1)	1.833 (4)	1.434 (NC)	1.434 (NC^8)
P–Cl	2.131	2.135	2.090	2.086 (1)	1.401 (PH)	1.388 (NF)	1.730 (NCl)
C^2–C^3	1.405	1.403	1.394	1.404 (1)	1.407 (1)	1.391	1.392
C^3–C^4	1.395	1.392	1.385	1.395 (1)	1.396 (1)	1.382	1.381
C^4–C^5	1.396	1.395	1.385	1.395 (1)	1.400 (1)	1.386	1.388
C^5–C^6	1.396	1.393	1.386	1.395 (1)	1.396 (1)	1.383	1.382
C^6–C^7	1.396	1.395	1.385	1.395 (1)	1.400 (1)	1.387	1.389
C^7–C^2	1.402	1.398	1.392	1.401 (1)	1.405 (1)	1.387	1.385
C^8–C^9	1.404	1.401	1.391	1.400 (1)	1.402 (1)	1.380	1.387
C^9–C^{10}	1.395	1.394	1.388	1.400 (1)	1.402 (1)	1.389	1.384
C^{10}–C^{11}	1.394	1.393	1.382	1.400 (1)	1.396 (1)	1.383	1.386
C^{11}–C^{12}	1.395	1.396	1.389	1.399 (1)	1.402 (1)	1.390	1.385
C^{12}–C^{13}	1.398	1.392	1.381	1.394 (1)	1.396 (1)	1.381	1.386
C^{13}–C^8	1.404	1.401	1.395	1.411 (1)	1.408 (1)	1.389	1.387
C–C_{av}	1.392	1.396	1.388	1.399 (1)	1.401 (1)	1.855	1.386
C–H_{av}	1.087	1.086	1.075	1.097 (2)	1.087 (5)		1.074
$P^1C^2C^3$	115.1	115.0	115.1	115.2 (2)	120.4 (6)	118.6 (NCC)	116.0 (NC^2C^3)
$P^1C^8C^9$	115.9	116.3	116.2	116.3 (2)	119.4	117.9 (NCC)	117.8 (NC^8C^9)
$C^2C^3C^4$	120.6	120.6	120.8	120.8	122.4	119.9	120.2
$C^3C^4C^5$	120.0	120.0	119.9	119.9	118.2 (20)	120.7	120.4
$C^4C^5C^6$	119.8	119.7	119.8	119.8	119.3 (12)	119.0	119.3
$C^5C^6C^7$	120.3	120.4	120.3	120.3	123.2 (14)	121.0	120.8
$C^6C^7C^2$	120.3	120.3	120.4	120.5	117.4 (15)	119.6	119.8
$C^7C^2C^3$	119.0	119.0	118.8	118.7	119.5 (6)	119.8	119.6
$C^8C^9C^{10}$	120.6	120.5	120.7	120.7		119.7	120.0
$C^9C^{10}C^{11}$	119.9	119.9	119.8	119.8		119.9	120.1
$C^{10}C^{11}C^{12}$	120.0	120.0	120.0	120.0		120.1	119.8
$C^{11}C^{12}C^{13}$	120.2	120.2	120.1	120.1		120.1	120.3
$C^{12}C^{13}C^8$	120.3	120.3	120.4	120.4		119.5	119.8
$C^{13}C^8C^9$	119.0	119.1	118.9	119.0		120.6	120.1
CPC	102.3	101.6	103.3	103.1 (13)	101.0 (20)	117.7 (CNC)	118.0 (CNC)
$ClPC^2$	101.3	101.5	101.7	101.9 (4)	98 [c] (HPC^2)	108.0 (FNC^2)	115.1 ($ClNC^2$)
$ClPC^8$	100.6	100.1	101.0	99.7 [b]	98 [c] (HPC^8)	106.1 (FNC^8)	111.7 ($ClNC^8$)
$\tau(C^2PC^8C^9)$	154.5	153.3	144.7	140.2 (31)	154 (7)	119.0 ($C^2NC^8C^9$)	140.0 ($C^2NC^8C^9$)
$\tau(C^8PC^2C^3)$	–95.1	–83.9	–93.4	–95.8 (31)	–65 (7)	–47.5 ($C^8NC^2C^3$)	–69.5 ($C^8NC^2C^3$)
$\tau(ClPC^2C^3)$	161.3	173.2	161.2	161.2 (36)		–167.6 (FNC^2C^3)	155.2 ($ClNC^2C^3$)

Table 1. (Contd.)

Parameters	$ClPPh_2$ [a]				$HPPh_2$	$FNPh_2$	$ClNPh_2$
	B3LYP/6-31G*	B3LYP/6-311+G*	HF/6-31G*	Experiment	Experiment [2]	HF/6-31G*	HF/6-31G*
$\tau(ClPC^8C^9)$	–101.3	–102.6	–110.3	–115.0 [b]		–120.0 (FC^8C^9)	–83.3 (CNC^8C^9)
$\tau(ClPC^2C^7)$	162.2	–4.2	161.8	161.2 [b]		16.7 (FNC^2C^7)	–24.9 ($ClNC^2C^7$)
$\tau(ClPC^8C^{13})$	79.8	78.0	70.3	65.0 [b]		59.3 (FNC^8C^{13})	97.0 ($ClNC^8C^{13}$)
$\tau(l_pPC^2C^3)$			30.3	40.4 (33)	67		43.3
$\tau(l_pPC^8C^9)$			5.3	4.2 (34)	22		24.0
R factor, %				4.70			

[a] In parentheses for $ClPPh_2$ are δ values obtained by least-squares treatment. [b] Dependent parameters. [c] Fixed values.

Strong correlations between the torsion angles do not lead, as it is usually observed in such cases, to the incorrect observed value of $\tau(Cl_PC^1C^2)$ angle, because the least-squares program we use takes into account the correlations and excludes their influence. Analysis of the matrix of correlation coefficients allows us to select the optimal strategy of refinement of the geometric parameters. The final refined geometric parameters are presented in Tables 1 and 2.

It should be noted that the B3LYP/6-31G* method overestimates the P–Cl bond length (2.135 Å) as compared to the HF method. Taking into account the diffuse functions keeps the P–Cl bond length practically unchanged. Only the B3LYP method with enlarged basis set cc-pVTZ without diffuse functions gave results (2.117 Å) more consistent with the experimental P–Cl bond length. By the way, in [2] we estimated graphically the P–Cl bond length in the diphenylchlorophosphine molecule and obtained the bond length (2.083 Å) close to that determined experimentally in this study [2.086(1) Å]. In determination of the structural parameters by gas-phase electron diffraction, revealing small differences between similar parameters is more important than determining their absolute values. This, so-called MOCED approach is widely used in microwave spectroscopy and gas electron diffraction [5, 6].

Thus, an electron diffraction study shows that the conformation of the diphenylchlorophosphine molecule is close to that of the diphenylphosphine molecule [2]. Naturally, the chlorine atom affects the structural parameters. As follows from analysis of both theoretical and experimental structural data, in the $ClPPh_2$ molecule there is an intermolecular hydrogen

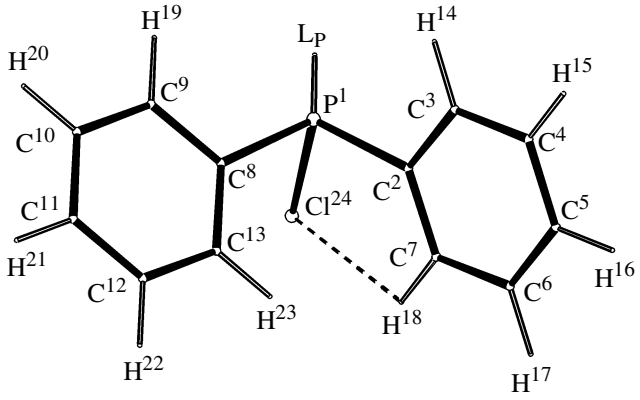

Fig. 1. Conformation of diphenylchlorophosphine molecule.

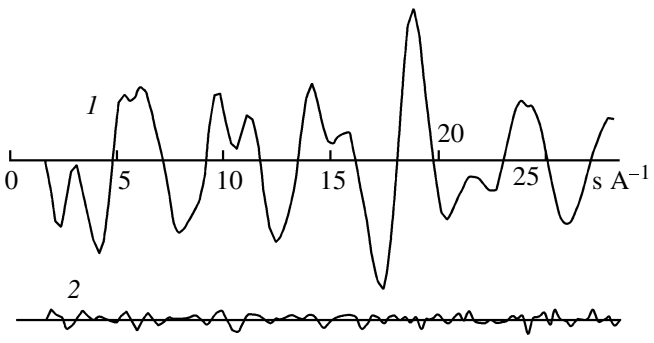

Fig. 2. Experimental molecular intensity curve of diphenylchlorophosphine molecule: (*1*) $sM(s)$ and (*2*) $\Delta sM(s) = sM(s)_{exp} - ksM(s)_{calc}$.

Table 2. Root-mean-square vibrational amplitudes of diphenylchlorophosphine molecule, Å

Bond	r_{ij}	u_{ij}(exp.) [a]		u_{ij}(theor.) [b]	Bond	r_{ij}	u_{ij}(exp.)		u_{ij}(theor.)
P–C	1.83	0.060 (2)		0.057	$C^2\cdots C^{11}$	5.30	0.152 (7)		0.186
C–C	1.40	0.049 (3)		0.048	$C^2\cdots C^{12}$	5.18	0.169 (7)		0.203
P–Cl	2.086	0.061 (2)		0.060	$C^3\cdots C^{10}$	5.16	0.256 (7)		0.289
$P\cdots C^3$	2.74	0.075 (3)		0.075	$C^3\cdots C^{12}$	5.68	0.353 (7)		0.387
$P\cdots C^7$	2.88	0.083 (3)		0.083	$C^4\cdots C^{13}$	5.86	0.338 (7)		0.371
$P\cdots C^9$	2.75	0.083 (3)		0.083	$C^5\cdots C^8$	5.36	0.168		0.201
$P\cdots C^{13}$	2.87	0.078 (3)		0.078	$C^6\cdots C^{10}$	5.49	0.611 (7)	III	0.645
$C^2\cdots C^5$	2.81	0.067 (3)		0.067	$C^7\cdots C^{11}$	5.75	0.526 (7)		0.560
$C^2\cdots C^8$	2.86	0.108 (3)		0.108	$C^7\cdots C^{12}$	5.95	0.518 (7)		0.551
$C^3\cdots C^6$	2.78	0.067 (3)		0.067	$C^4\cdots Cl$	5.44	0.142 (7)		0.175
$C^4\cdots C^7$	2.79	0.066 (3)		0.066	$C^5\cdots Cl$	5.56	0.121 (7)		0.154
$C^8\cdots C^{11}$	2.81	0.067 (3)		0.067	$C^{11}\cdots Cl$	5.34	0.182 (7)		0.215
$C^9\cdots C^{12}$	2.80	0.068 (3)		0.068	$C^{12}\cdots Cl$	5.13	0.267 (7)		0.300
$C^{10}\cdots C^{13}$	2.80	0.068 (3)		0.068	$C^2\cdots Cl$	3.04	0.110 (10)		0.100
$P\cdots C^4$	4.07	0.074 (3)		0.074	$C^7\cdots Cl$	3.25	0.160 (10)		0.150
$P\cdots C^6$	4.16	0.081 (3)		0.081	$C^8\cdots Cl$	3.00	0.121 (10)	IV	0.111
$P\cdots C^{10}$	4.07	0.080 (3)		0.080	$C^9\cdots Cl$	3.35	0.351 (10)		0.341
$P\cdots C^{12}$	4.15	0.076 (3)		0.076	C···C	2.42	0.059 (10)		[b]
$C^2\cdots C^{10}$	4.42	0.218 (3)	I	0.218	C···C	2.80	0.067 (10)		[b]
$C^2\cdots C^{13}$	4.12	0.223 (3)		0.223	C···H	2.16	0.101 (10)		[b]
$C^3\cdots C^9$	3.98	0.237 (3)		0.237	C···H	2.42	0.099 (10)		[b]
$C^3\cdots Cl$	4.34	0.175 (3)		0.175	C···H	3.89	0.100 (10)		[b]
$C^{13}\cdots Cl$	4.06	0.357 (3)		0.357					
$P\cdots C^5$	4.63	0.080 (3)		0.078					
$P\cdots C^{11}$	4.63	0.080 (3)		0.078					
$C^3\cdots C^{13}$	4.65	0.369 (3)		0.368					
$C^4\cdots C^8$	4.85	0.211 (3)		0.209					
$C^4\cdots C^9$	4.91	0.270 (3)		0.268					
$C^6\cdots C^8$	4.86	0.320 (3)		0.318					
$C^7\cdots C^{10}$	4.61	0.593 (3)	II	0.591					
$C^7\cdots C^{13}$	5.05	0.513 (3)		0.511					
$C^6\cdots Cl$	4.62	0.155 (3)		0.153					
$C^{10}\cdots Cl$	4.61	0.329 (3)		0.327					

[a] Brackets denote groups of amplitudes. [b] Theoretical u_{ij} values were not refined.

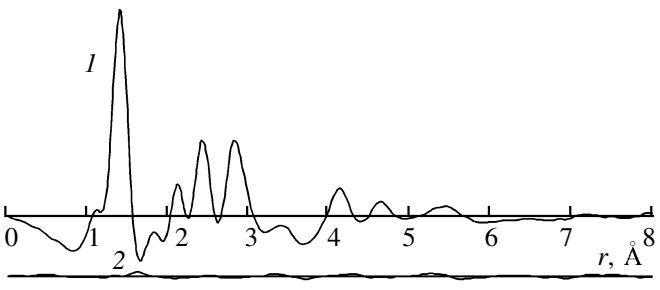

Fig. 3. Experimental radial distribution curve of diphenylchlorophosphine molecule: (*1*) $f(r)$ and (*2*) $\Delta f(r) = f(r)_{exp} - krf(r)_{theor}$.

bond Cl···H[18]. The PLATON 98 program [7] predicts the existence of the hydrogen bond C^7–H···Cl with the following parameters: $r(C^7–H)$ 1.085 Å, r(H···Cl) 2.722 Å, $r(C^7\cdots Cl)$ 3.268 Å, and ∠C–H···Cl 110.8°; these parameters only slightly differ from the observed values. Indeed, considering the van der Waals radii of carbon (1.78 Å), chlorine (1.80 Å), and hydrogen atoms (1.17 Å), we see that the H–Cl distance, so-called hydrogen bond, is only 0.25 Å shorter than their sum. Generally, the influence of the hydrogen bond should lead to elongation of the C–H[17] bond. However, because of the small energy of the hydrogen bond as compared to that of the C–H bond, this is not observed.

	Parameter	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	U^1	U^2	U^3	U^4	U^5	U^6	U^7
R^1	P–C	100																
R^2	C–C	–6	100															
R^3	C–Cl	18	–5	100														
R^4	C–H	15	17	–20	100													
R^5	$\angle C^1C^2C^3$	–25	1	–3	3	100												
R^6	$\angle CPC$	–31	–13	–3	–4	–6	100											
R^7	$\tau(C^8PC^2C^3)$	7	3	0	3	–19	8	100										
R^8	$\tau(C^9C^8PC^2)$	–1	–4	5	–16	3	9	–19	100									
R^9	$\angle ClPC^2$	–16	0	–6	7	15	13	0	–41	100								
R^{10}	$\tau(ClPC^2C^3)$	7	–5	3	4	20	4	95	–18	39	100							
U^1	u(P–C)	8	–14	29	0	0	–3	0	1	–1	0	100						
U^2	u(C–C)	6	–7	11	–20	–11	–3	–3	9	–3	–6	16	100					
U^3	u(P–Cl)	–25	–7	–4	–30	0	8	–4	6	2	–4	–18	13	100				
U^4	u I	–8	3	–4	4	37	1	–30	–8	2	–33	0	3	0	100			
U^5	u II	–1	0	2	–3	1	–3	16	–2	19	19	2	4	0	–8	100		
U^6	u III	–4	0	–1	–6	2	14	32	30	–69	–49	0	4	2	16	–17	100	
U^7	u IV	19	2	2	1	–41	35	13	16	–58	–3	0	0	–6	–6	–15	49	100

The IR and Raman spectra of diphenylchlorophosphine are given in [9]. The vibration frequencies were assigned in [9] on the basis of C_{2v} symmetry of the phenyl rings. We performed a normal-coordinate analysis for this molecule (Table 3). We should note two low frequencies, 28 and 22 cm^{-1}, assigned to the torsion vibrations around the P–C^2 (PED 78%) and P–C^8 (PED 74%) bonds. The corresponding torsion force constants are essentially different (0.067 and 0.036 mdyne Å, respectively). Unfortunately, the

Table 3. Normal-coordinate analysis of diphenylchlorophosphine molecule

Band no.	Calculated, HF/6-31G*				Experiment [a]			
	ν, cm^{-1}	I_{Raman}	I_{IR}	PED, [b] %	ν_{Raman}, cm^{-1}	I_{Raman}	ν_{IR}, cm^{-1}	I_{IR}
1	3063	102	6.6	88n(CH)			3070	s
2	3059	10.2	7.5	77ν(CH)				
3	3049	318	15.3	93ν(CH)	3060	12		
4	3046	75.1	54.7	82ν(CH)	3055	10	3050	sh
5	3038	69.4	25.1	97ν(CH)				
6	3030	91.3	25.4	89ν(CH)			3020	s
7	3029	108	2.2	87ν(CH)				
8	3025	86	1.3	89ν(CH)	3018	sh		
9	3022	37	0.3	96ν(CH)				
10	3009	24.4	3.3	90ν(CH)	3010	s	3010	s
11	1598	54	0.7	59ν(CC) + 13α(CCH)	1584	24		
12	1593	50	4	53ν(CC) + 14α(CCH)			1585	m
13	1575	5	0.3	54ν(CC) + 18α(CCH)				
14	1572	7.5	0.3	49ν(CC) + 21α(CCH)				
15	1494	0.6	7	23ν(CC) + 65α(CCH)				
16	1493	0.4	4.6	23ν(CC) + 65α(CCH)	1482	1	1481	s
17	1439	0.6	3	22ν(CC) + 55α(CCH)				
18	1437	1.6	7.9	22ν(CC) + 57α(CCH)	1437	1	1438	s
19	1331	0.9	8.3	63α(CCH)	1307	s	1328 s	m–s
20	1328	1.9	4.0	63α(CCH)			1275	m
21	1200	0.9	0.3	31ν(CC) + 55α(CCH)	1277	s	1237	s
22	1196	1.1	1	29ν(CC) + 65α(CCH)				

Table 3. (Contd.)

Band no.	Calculated, HF/6-31G*				Experiment [a]			
	ν, cm^{-1}	I_{Raman}	I_{IR}	PED, [b] %	ν_{Raman}, cm^{-1}	I_{Raman}	ν_{IR}, cm^{-1}	I_{IR}
23	1180	5.4	1.2	19ν(CC) + 66α(CCH)	1186	2.5	1182	s
24	1175	3.5	7.4	20ν(CC) + 74α(CCH)	1161	4	1158	m
25	1081	6.6	2.4	60ν(CC)	1099	s		
26	1080	7.9	8.2	62ν(CC)				
27	1076	10.4	24.9	18ν(PC) + 49ν(CC)				
28	1070	3.8	18.5	54ν(CC)			1096	vs
29	1059	0.3	0.4	71ν(CC)				
30	1053	0.5	2.6	66ν(CC)	1031	s	1068	sh
31	1013	0.2	0.1	56γ(CH) + 12τ(CC)			1025	m–s
32	1013	0.3	0	66γ(CH) + 11τ(CC)				
33	1003	13.6	0.3	34τ(CC) + 26α(CCC) + 14α(CCH)				
34	1001	16.2	0	29τ(CC) + 46α(CCC)	1001	20		
35	992	0.1	0.3	61ν(CH) + 12τ(CC)			997	
36	991	0.1	0	66ν(CH) + 12τ(CC)				
37	967	56	1.7	54τ(CC) + 21α(CCC)	975	s		
38	967	15	4.7	46τ(CC) + 17α(CCC)			970 s	
39	943	0.4	0.2	77γ(CH)	942 s			
40	940	0.3	1.5	75γ(CH)	916	s	917	
41	861	2	0.2	77γ(CH)			847 m	
42	859	2	0	77γ(CH)	843	s		
43	755	2.2	35.5	74γ(CH)	749	1	750 m	
44	751	0.7	28.3	75γ(CH)				
45	691	1.8	38.3	14γ(CP) + 42ν(CH) + 30τ(CC)	693	3	700 vs	
46	687	1.1	35.6	34γ(CH) + 23τ(CC)				
47	684	2.5	7.4	27ν(PC) + 18α(CCC)				
48	675	8.1	3.7	27ν(PC) + 23α(CCC)				
49	608	3.5	0.4	61α(CCC) + 19α(CCH)	621	4	617 m	
50	607	5.9	0.2	60α(CCC) + 10α(CCH)			555	
51	504	2.8	70	15ν(PCl) + 25γ(CP) + 22γ(CP)	504	7	503 s	
52	491	7.6	42	29ν(PCl) + 13α(ClPC) + 20γ(CP)				
53	458	8	40	44ν(PCl) + 10α(ClPC) + 13τ(CC)	458	5	462 m	
54	421	2	22	29ν(PC) + 11α(CPCl)	430	s	430 m	
55	401	0	0	60τ(CC) + 28γ(CH)	401	1		
56	399	0.8	6.4	46τ(CC) + 20γ(CH)				
57	397	2.3	22	35ν(PC)	401	1	404 s	
58	274	6.7	1.0	16ν(PCl) + 27α(PCC) + 20α(CPC)	285	8		
59	248	2.7	0.4	19ν(PC) + 36α(PCC) + 12α(CPC)	264	2		
60	220	2.9	1.9	16τ(CC) + 13α(CPC) + 16τ(CC)	232	2		
61	188	1.4	1.0	23α(PCC) + 17α(ClPC) + 17τ(CC)	202	1		
62	138	1.5	1.3	58α(ClPC) + 24α(PCC)				
63	95.8	6.3	0.9	59α(CPC)				
64	55.4	8.4	0.7	32α(CPC) + 30γ(PC)				
65	27.5	10.7	0.7	77τ(P–C)				
66	21.7	8.1	0.1	74τ(P–C) + 12α(CPC)				

[a] (I_{Raman}, I_{IR}) Band intensities: (vs) very strong, (s) strong, and (m) medium. [b] PED values making no less than 10% contribution are given; (ν, α, γ, τ) stretching, in-plane bending, out-of-plane bending, and torsion vibrations, respectively; the calculated frequencies are scaled.

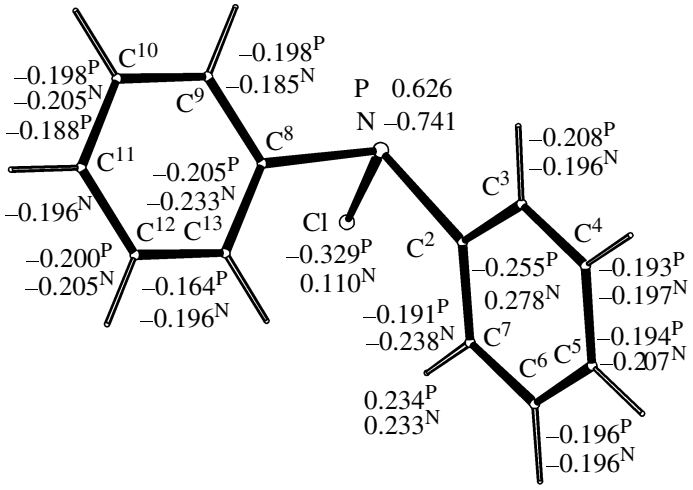

Fig. 4. Charges on atoms in diphenylchlorophosphine (superscript P) and diphenylchloramine (superscript N) molecules, as it follows from HF/6-31G* calculations.

vibration spectra in the region below 200 cm^{-1} are absent. This region bears information about absorption by the central part of the molecule. On the whole, the calculated and observed vibration frequencies are in reasonable agreement. It is interesting to compare the structures of the $ClPPh_2$ and $ClNPh_2$ molecules. The results of a theoretical calculation for the $ClNPh_2$ molecule are given in Table 1. The main difference between the conformations of these molecules consits in the degree of pyramidality of the central N and P atoms. In the phosphine, the average bond angle at the P atom (102°) is appreciably smaller than that at the N atom (115°). Nevertheless, the degree of pyramidality at the N atom is also significant. The HF/6-31G* calculations and analysis using the PLATON program did not reveal a hydrogen bond in the $ClNPh_2$ molecule, although the Cl–H bond length is 2.66 Å and the Cl–H–C bond angle is 110°. We explain the lack of the hydrogen bond in the $ClNPh_2$ molecule by the difference in the charges on the Cl atoms in $ClNPh_2$ and $ClPPh_2$ molecules. Based on ab initio calculations, we compared the charges on the Cl, N and H atoms and found that the charge on the chlorine atom in the $ClNPh_2$ molecule is positive, in contrast to the negative charge in the $ClPPh_2$ molecule (Fig. 4). In the literature, the hydrogen bonding with the chlorine atom is usually demonstrated by the example of *o*-chlorophenol. An AM1 estimation of the energy of the Cl–H hydrogen bond showed that it is low (~2 kcal mol^{-1}) and that the chlorine atom has a negative charge (–0.019 au; charge on the H atom 0.229 au). This fact indicates that in the amine the charges on the Cl and N atoms are redistributed, with the charge on the Cl atom becoming positive, which precludes intramolecular hydrogen bonding. It can be assumed that in the $FNPh_2$ molecule, as the F atom is more electronegative than the Cl atom, the F–H hydrogen bond would be observed. However, this is not the case. An HF/6-31G* calculation of the geometry of the $FNPh_2$ molecule shows that the F–H distance (2.62 Å) is longer than the sum of the van der Waals radii of the F and H atoms (2.52 Å) and the F–H–C bond angle is 96°. Table 1 shows the calculated geometric parameters of the $FNPh_2$ and $ClNPh_2$ molecules (the atom numbering in amines and phosphines is similar).

Let us consider the atomic charge distribution in the trichloramine molecule. An HF/6-31G* calculation of the geometry of NCl_3 molecule shows that the ClNCl bond angle is 110.2° and, what is more important for this discussion, the charges on Cl atoms are positive (0.200 au). In the series of amines, the degree of pyramidality of bonds around N atoms depends on the nature of substituents: According to the experimental data, in the NH_3 molecule the HNH bond angle is 106.7°; in the NF_3 molecule the FNF angle is 102.4° [10]; in the NCl_3 molecule the ClNCl angle is 107.8° (ED + MW) [11, 12]; and the CNC angle is as large as 111° in the trimethylamine molecule [13] and 120° in the triphenylamine molecule [14]. To compare, the ClPCl angle in the PCl_3 molecule is 100.3° [15]. So large difference in the bond angles in phosphines and amines is due to the larger activity of the lone electron pair of the N atom as compared to that of the P atom.

EXPERIMENTAL

Electron diffraction patterns of gaseous diphenylchlorophosphine molecule (four plates for each

nozzele-to-plate distance, 498.53 and 248.71 mm) were recorded at 160°C on a Balzers electron diffraction unit in Oslo University. The electron wavelength was determined with benzene molecule. The electron intensities were measured with a scanner (IP-20030527). The sample for the investigation was purchased from Sigma.

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