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Molecular Structure and Internal Rotation Potential of Dimethylphenylphosphine, According to Gas-Phase Electron Diffraction Data and Quantum-Chemical Calculations

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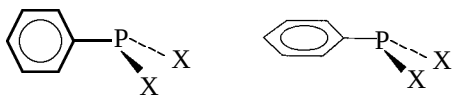
Abstract — Geometric parameters of dimethylphenylphosphine molecule were determined by gas-phase electron diffraction using a dynamic model in which the rotation of the PMe_2 group is treated as large-amplitude motion. Refinement of the structural parameters and parameters of the potential function was performed taking into account the geometry relaxation on the basis of HF/6-311++G** calculations. The internal rotation potential has a single minimum at φ 0° (φ is the angle between the bisector of the MePMe angle and the phenyl ring plane) and may be described by the function of the form $V(\varphi) = 0.5V_2(1 - \cos 2\varphi)$, where $V_2 = 0.38 \pm 0.36$ kcal mol^{-1}. The data obtained are compared with those for related molecules. Steric effects affect the geometry of the phenylphosphine molecule more significantly than does p–π interaction.

Experimental studies of internal rotation around the P–C_{Ph} bond in phenylphosphine derivatives are interesting for the analysis of the conjugation of phosphorus lone electron pair with the π system of the benzene ring [1]. In terms of this concept, the bisector conformer of the molecule X_2P–Ph (**A**), in which the bisector of the XPX angle lies in the plane of the benzene ring (φ 0°), has the geometry with the worst conditions for the conjugation, whereas the perpendicular conformer **B**, in which the bisector lies in the plane that is orthogonal to the benzene ring plane (φ 90°) has the optimal geometry for the conjugation. Thus, the occurrence of conjugation in the molecule should lead to the perpendicular conformation.



A **B**

Experimental studies show that the bisector conformation is realized in the phenylphosphine molecule [2] and the perpendicular conformation, in the aniline molecule [3, 4]. This fact suggests the occurrence of conjugation in the aniline molecule and its absence in the phenylphosphine molecule.

In the case of phenylphosphyne derivatives, the conformational preference is not obvious because, along with p–π interaction, the steric and polar interactions and also changes in geometry of bonds around the P atom under the action of substituents should be taken into account. Experimental data for these derivatives are limited and largely controversial, because they were mainly obtained using the static model (approximation of small harmonic vibrations) without taking into account large-amplitude motions. In particular, in the framework of this model Naumov *et al.* [5] interpreted the electron diffraction data for the dichlorophenylphosphine molecule and concluded that there are two conformers: the first with φ 0° (major) and the second with φ 90°, separated by a barrier of 1–3 kcal mol^{-1}, whereas, according to the data of photoelectron spectroscopy and quantum-chemical calculations [6], in this molecule the conjugation is negligible and hence only the bisector conformer with φ 0° should be present. Recently [7] we performed an electron diffraction study of dichlorophenylphosphine molecule using the dynamic model that takes into account large-amplitude motion and effects of relaxation, i.e., variations in the geometric parameters that accompany rotation around the P–Ph bond, on the basis of quantum-chemical calculations. It was found that the internal rotation potential has only one minimum at 0° and the perpendicular conformation corresponds to the potential maximum with the energy difference ΔE 0.57 ± 0.32 kcal mol^{-1}. In an electron diffraction study of difluorophenylphosphine molecule

performed by Burt *et al*. [8], the conformational equilibrium was not examined, and only the effective value of the torsion angle φ 31(2)° was obtained, giving no information on the form of the potential function.

The dimethylphenylphosphine molecule, $C_6H_5 \cdot PMe_2$, is also interesting for the analysis of the effects of mutual influence on the geometry of bonds at the P atom, because data on the conformation of this molecule are also contradictory.

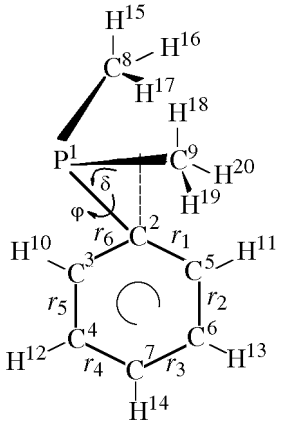
As follows from data on the Kerr effect, the *p*-tolyldimethylphosphine molecule exists in the bisector conformation [9]. Ratovskii *et al*. [10, 11] analyzed the UV spectra of dialkylphenylphosphines and concluded that in these molecules the *p*–π interaction is considerably weaker than in aromatic amines. They presumed the existence of two conformers with essentially different capability for *p*–π interaction. A ^{13}C NMR study of dimethylphenylphosphine molecule [12] showed that the difference in the chemical shifts between carbon atoms in *m*- and *p*-positions is temperature-independent. If there were a conformational equilibrium, this would suggest either small difference in the energy of the conformers or high barrier to internal rotation.

In our first electron diffraction study [13], we also examined the IR and Raman spectra of the dimethylphenylphosphine molecule to reveal the conformational equilibrium. We found that, at both fast and slow cooling of the sample, the positions and shapes of the bands remain unchanged, showing no evidence of the conformational equilibrium. From the electron diffraction data in terms of the dynamic model taking into account hindered internal rotation, we determined a nonparametric internal rotation potential by the method from [14]. It has two minima: the first at φ 0° (deeper) and the second at φ 90°. The energy difference for these two conformers is about 0.6 kcal mol^{-1} with barrier to internal rotation of 1.1 kcal mol^{-1}.

Previously [15] we noted that the main limitation of the algorithm from [14] is the lack of clear criteria for selection of the regularization parameter, which strongly affects the form of the potential function obtained. Furthermore, our study of the dichlorophenylphosphine molecule [7] revealed that, when determining a conformation of phenylphosphines, it is important to take into account relaxation effects; it also cast doubts on the existence of the perpendicular conformation which corresponds to the maximum of the internal rotation potential of the dichlorophenylphosphine molecule.

In this study we used new electron diffraction patterns of the dimethylphenylphosphine molecule, which were recorded at the Oslo University (Norway) on a Baltzers Eldigraph KD-G2 instrument at accelerating voltage of 40 kV and nozzle temperature of 22°C for two nozzle to plate distances: 498.7 and 248.7 mm. The scattering intensities were recorded in the range of scattering angles *s* 1.75–15.625 and 3.5–30.5 Å^{-1} using a scanner [16].

Parameterization. The molecular model and atom numbering are shown below. The rotation angle φ corresponds to the dihedral angle between the bisector of the MePMe angle the benzene ring plane. The angle φ describes deviation of the P–C bond from the bisector of the $C^3C^2C^5$ angle. The directions defining positive signs of these angles are show by arrows.



To describe rotation of the PMe_2 group, we used a dynamic molecular model taking into account the contributions to the scattering intensity *sM*(*s*) of all pseudo-conformations that arise in large-amplitude motion in accordance with their population determined from the rotation potential *V*(φ):

$$SM(s) = \int_{\varphi_{min}}^{\varphi_{max}} W(\varphi) sM(s, \varphi) d\varphi,$$
$$W(\varphi) = Q^{-1} \exp[-V(\varphi)/RT], \quad (1)$$

where *Q* is the normalization coefficient; *R*, universal gas constant; and *T*, absolute temperature.

In practice, the relaxation effects of changing of "local geometry" of the molecule during large-amplitude motion are usually neglected, assuming that bond lengths and bond angles remain unchanged for different conformations of the molecule. In our case, this assumption requires verification, because the molecule as a whole has the C_s symmetry only at the limits of

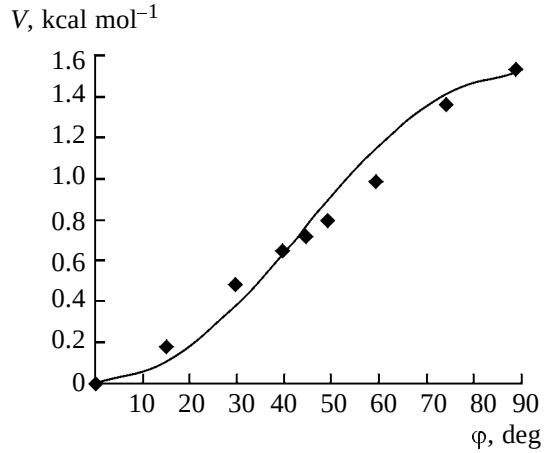


Fig. 1. (Points) Calculated values of internal rotation potential of dimethylphenylphosphine molecule and (solid line) their approximation with the function $V(\varphi) = 0.5V_2(1 - \cos 2\varphi)$.

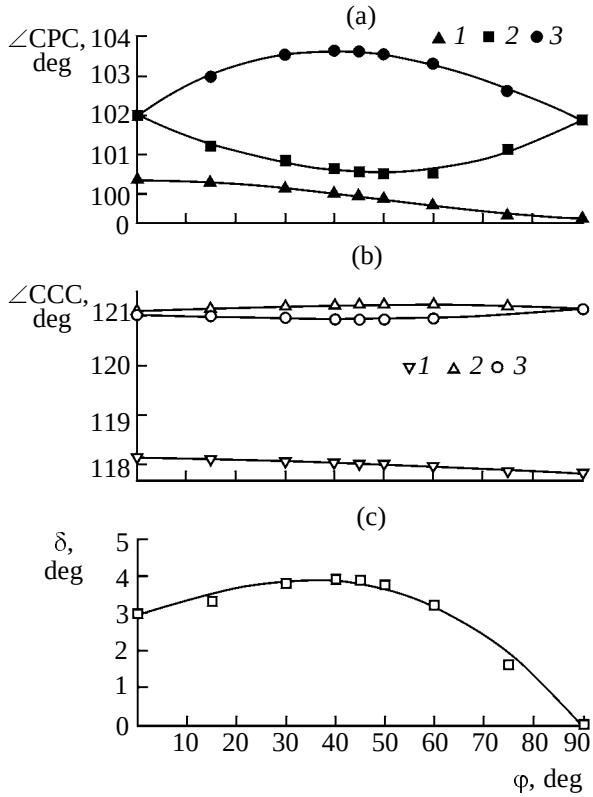


Fig. 2. Variation of the CPC and CCC bond angles and of angle δ in dimethylphenylphosphine molecule at internal rotation. Angles: (a) (*1*) C^8PC^9, (*2*) C^2PC^8, and (*3*) C^2PC^9; (b) (*1*) $C^3C^2C^6$, (*2*) $C^2C^3C^4$, and (*3*) $C^2C^5C^6$; (c) δ.

the interval from 0° to 90°. For intermediate conformations, considerable changes in the local symmetry of the PMe_2 group and δ angle are possible because of steric hindrance arising when the Me group is located near the benzene ring plane.

To calculate the relaxation effects of geometry during the internal rotation, we performed optimization of the geometric parameters at fixed values of φ 0°, 15°, 30°, 45°, 60°, 75°, and 90° at the HF/6-311++G** level, using the GAUSSIAN 98 program [17]. The internal rotation potential obtained (Fig. 1) has a single minimum corresponding to the bisector conformer, and the energy difference between the perpendicular and bisector conformers is 1.4 kcal mol^{-1}. The shape of the rotation potential $V(\varphi)$ may be satisfactorily approximated by the single term (V_2) of the even Fourier series:

$$V(\varphi) = \sum_{n=2k}^{N} \frac{V_2}{2}(1 - \cos n\varphi). \qquad (2)$$

The variations in the geometric parameters are given in Figs. 2 and 3. Their analysis shows that the P–C bond lengths change by 0.005–0.01 Å. The angles in the benzene ring change only slightly; however, the angles at the P atom change by 1°–2°, and δ changes from 0° to 4°. Thus, changes in the geometry of the dimethylphenylphosphine molecule during internal rotation are significant, and the geometry relaxation should not be neglected in structural analysis. Taking into account the relaxation effects, it is possible to describe correctly the changes in the symmetry of the molecule at different values of φ, e.g., passing from six nonequivalent C–C bond lengths to three bond types at φ 90° (Fig. 3) and also changes in δ (Fig. 2), which is 4°–5° at φ 0°–60° but is exactly 0° at φ 90° (assuming that deviations of the Ph–P fragment from planarity are small and can be neglected).

In this study we used an approach suggested previously in [7] and based on the well-known fact that, although numerical values of related geometric parameters calculated with different basis sets may differ appreciably, their difference does not noticeably depend on the level of calculation [18]. The calculated quantum-chemical values for each geometric parameter were approximated by the least-squares method using fifth-degree polynomials:

$$P(\varphi) = a_0 + \sum_{n=1}^{5} a_n\varphi^n. \qquad (3)$$

The polynomial coefficients a_n (n = 1, . . . 5) were used in structural analysis for calculating the geometric parameter $P(\varphi)$ of the conformer with angle φ; in so doing, the parameter a_0, independent of φ, was varied. For example, in the case of refinement of the P–C bond length (Fig. 3), such an approach is equivalent to the shift of the function $r(PC) = f(\varphi)$ along the $r(PC)$ axis. This provides preservation of the initial difference of the P–C bond lengths for any pair

of conformers. For each P–Me bond, we used the specific set of coefficients a_n, and the refined parameter a_0 was common, which follows from the symmetry considerations. In the case of δ, the variation of a_0 in the structural analysis does not provide the fulfillment of the boundary condition: δ 0° at φ 90°. Therefore, for δ we used function (4) in which the polynomial coefficients were found according to Eq. (3) and δ_0 was varied.

$$\delta(\varphi) = \frac{\delta_0}{a_0}\,(a_0 + \sum_{n=1}^{5} a_n\varphi^n). \qquad (4)$$

Variation in δ_0 is equivalent to the scaling of the initial function, which provides the necessary symmetry of the perpendicular conformer and preserves the shape of the function δ(φ) in the region of φ 0°–60° similar to the initial shape (Fig. 2).

In addition to the six types of C–C bonds, description of the geometry of the benzene ring should include three CCC bond angles. We chose the CC^3C, CC^2C, and CC^5C angles and approximated their calculated values by the appropriate equation. In order to ensure the equivalence of the CC^3C and CC^5C angles at φ 90° (Fig. 2), we fixed for them the difference of coefficients a_0 and varied only the parameter a_0 for the CC^3C angle. Thus, taking into account parametrization of the C–C bonds, to describe the geometry of the benzene ring we can use only three independent parameters: r(CC), ∠CC^2C, and ∠CC^3C, which describe correctly the changes in the symmetry of the benzene ring in the whole range of φ. Six types of C–C bonds and three CCC bond angles, necessary for describing the geometry of the ring at $0° \le \varphi \le 90°$, are degenerated into three types of C–C bonds and two CCC angles at φ 90°.

It is important that the approach described uses the most reliable quantum-chemical data on relative variations of the geometric parameters of the molecule, allowing variation of their absolute values which often depend on the level of theory. This approach also eliminates differences between the quantum-chemical (r_e) and electron diffraction (r_α) parameters having different physical sense.

Based on the results of quantum-chemical calculations, we made the following assumption in parametrization of the molecular geometry: (1) the C–H bond distances in the phenyl ring are equal; (2) the C_6H_5P fragment is planar and has the C_s symmetry; and (3) the CH_3 groups have C_{3v} local symmetry. To describe the geometry of the molecule, we used 12 geometric parameters: r(CC), $r(PC_{Me})$, $r(PC_{Ph})$, $r(CH_{Me})$, $r(CH_{Ph})$, ∠$C^3C^2C^5$, ∠$C^2C^5C^6$, ∠$C^2C^3C^4$, ∠$C_{Ph}PC_{Me}$, ∠$C_{Me}PC_{Me}$, ∠PCH, and δ. All the parameters except r(CH) and ∠PCH were expressed as functions of φ in accordance with Eqs. (3) and (4).

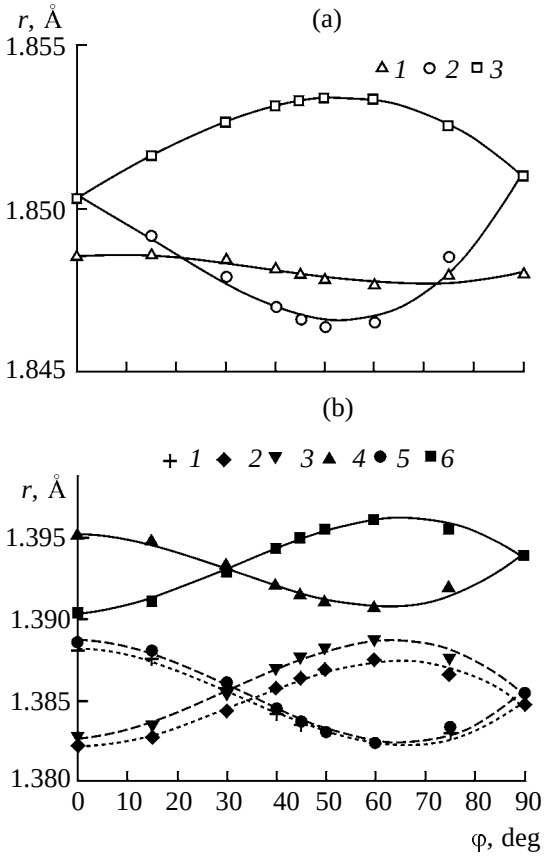


Fig. 3. Variation of the bond lengths in dimethylphenylphosphine molecule at internal rotation. Bonds: (a) (*1*) P–C^2, (*2*) P–C^9, and (*3*) P–C^8; (b) (*1*) C^5–C^2, (*2*) C^6–C^5, (*3*) C^7–C^6, (*4*) C^4–C^7, (*5*) C^3–C^4, and (*6*) C^2–C^3.

Calculation of the mean amplitudes and vibrational corrections. The results of normal mode analysis on the basis of the theoretical force field are in agreement with previous assignment of the fundamental vibration frequencies [13]. The frequency of the PMe_2 torsion vibration that was not observed previously in the IR and Raman spectra is, according to the calculated results, the lowest: ν_{54} 37 cm^{-1}. This vibration can be reliably separated from the other skeleton vibrations, because the closest frequency of the same symmetry, ν_{53} 128 cm^{-1}, is more than three times higher. Moreover, this vibration is characteristic and is not noticeably mixed with other vibrations. Its contribution to the potential energy is 73%.

The dependent geometric parameters were calculated in terms of the r_α structure taking into account the shrinkage corrections $\Delta r = r_\alpha - r_a$. The $sM(s, \varphi)$

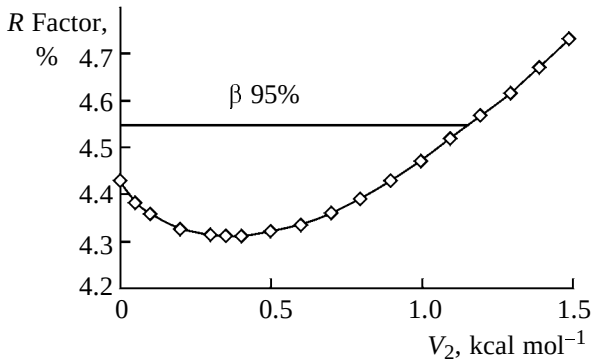


Fig. 4. Dependence of *R* factor on the height of rotation barrier V_2 and the confidence level.

were calculated with step Δφ 5° in the interval 0°–90°. In so doing, for each distance dependent on the rotational angle we used the vibrational corrections Δ*r*(φ) and amplitudes *u*(φ), obtained by interpolation of the corresponding values, calculated for φ 0°, 30°, 60°, and 90°, using Sipachev's method [19, 20].

Structural analysis. During refinement of the structural parameters, we also tested different zero approximations for *V*(φ), including models with a single minimum at φ 0° and 90°. When refining the parameters of the potential function, we found that all zero approximations converge to the single solution with V_2 0.38 kcal mol^{-1} for the bisector conformer with φ 0°.

The quantity V_2 is determined with a large uncertainty (rms deviation 0.12 kcal mol^{-1}), suggesting low sensitivity of the electron diffraction method to this parameter. This is also demonstrated by variations of the *R* factor for the fixed values of V_2 (Fig. 4). Variation of V_2 in the range 0–1.2 kcal mol^{-1} leads to the variation of the *R* factor by only 0.2%, which, according to the Hamilton criterion at 95% confidence level, is statistically insignificant. Thus, the shape of the potential function of internal rotation, i.e., position of the minimum, is determined sufficiently well, but the height of the barrier can be determined only with large uncertainty.

We also tested the model with nonparametric potential obtained in [13], which was approximated by the Fourier series with V_2 0.9 and V_4 0.5 kcal mol^{-1}. The *R* factor for this model was 4.69%, which is somewhat worse than that obtained by us for the final model (Table 1), though this difference is statistically insignificant. Thus, the presence of the perpendicular conformer cannot be revealed solely from electron diffraction data.

The molecular intensity *sM*(*s*) and radial distribution *f*(*r*) curves for the final set of structural parameters from Table 1 are presented in Figs. 5 and 6.

Table 1. Structural parameters[a] of the dimethylphenylphosphine molecule for the minimum of *V*(φ) at φ 0°

Parameter	r_a, Å; ∠$_\alpha$, deg		u_{calc}	u_{exp}	
P–C_{Ph}	1.846	(2)	0.052	0.067	(2)
P–C_{Me}	1.844		0.053	0.068	
C^2–C^3	1.410	(2)	0.047	0.054	(2)
C^2–C^5	1.396		0.047	0.053	
C^6–C^7	1.396		0.047	0.053	
C–C_{av}	1.401(2)				
C–H_{Ph}	1.097	(3)	0.077	0.096	(3)
C–H_{Me}	1.110		0.079	0.097	
∠$C_{Ph}PC_{Me}$	100.8(9)				
∠$C_{Me}PC_{Me}$	97.3(15)				
∠$C^3C^2C^5$	118.7(3)				
∠$C^2C^3C^4$	121.1[b]				
∠$C^2C^5C^6$	121.0[b]				
∠PCH	110.1(9)				
δ	3.9(6)				
V_2, kcal mol^{-1}	0.38 (36)				
Nonbonded distances					
C^3···P	2.135		0.071	0.072	
C^6···C^2	2.439		0.055	0.063	
C^4···C^2	2.441		0.055	0.063	(2)
C^5···C^3	2.418		0.056	0.064	
C^6···C^4	2.440		0.055	0.062	
C^7···C^3	2.406		0.055	0.063	
C^8···C^3	3.958		0.096	0.109	
C^9···C^5	3.282		0.135	0.149	
C^9···C^3	3.958		0.096	0.109	(6)
C^6···P	4.165		0.067	0.080	
C^4···P	4.094		0.069	0.083	
C^8···C^2	2.836		0.092	0.093	
C^8···C^5	3.019		0.135	0.136	
C^8···C^9	2.763		0.098	0.099	
C^9···C^2	2.836		0.092	0.093	(3)
C^5···P	2.883		0.068	0.069	
C^7···C^2	2.795		0.062	0.062	
C^5···C^4	2.803		0.062	0.063	
C^6···C^3	2.801		0.062	0.062	
C^8···C^6	4.579		0.155	0.170	(12)
C^9···C^6	4.579		0.155	0.170	
C^7···P	4.626		0.068	0.083	
C^8···C^7	5.328		0.146	0.167	
C^8···C^4	5.095		0.116	0.138	(30)
C^9···C^7	5.327		0.146	0.167	
C^9···C^4	5.095		0.116	0.132	
R Factor			4.31		

[a] Braces: refinement with fixed differences. Values in parentheses are trebled standard deviations and include systematic error. [b] Fixed values based on quantum-chemical calculations.

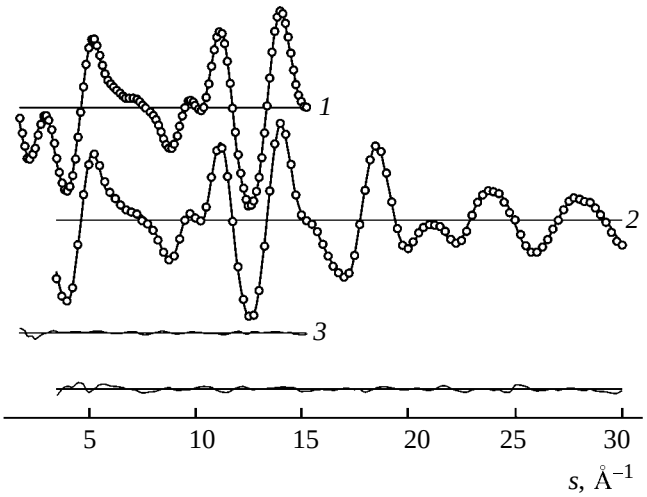


Fig. 5. (*1*, *2*) (Circles) Experimental and (solid lines) theoretical *sM*(*s*) curves; (*3*, *4*) the corresponding difference curves Δ(*s*).

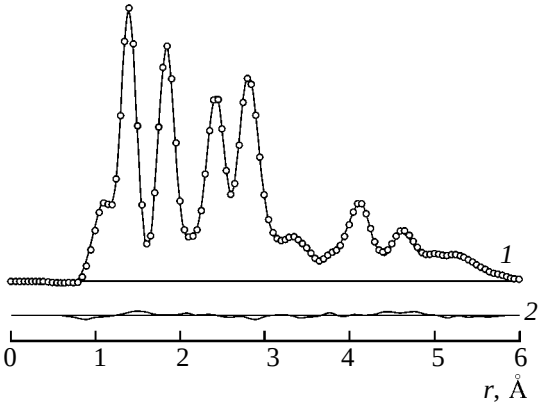


Fig. 6. (*1*) (Circles) Experimental and (solid line) theoretical (solid line) radial distribution curves *f*(*r*) and (*2*) difference curve Δ(*r*).

DISCUSSION

The data obtained (Table 2) show that, as compared to the previous study [13], the main parameters of the benzene ring and P–C bond lengths remain practically unchanged. The standard deviations for all the geometric parameters decrease. The PCH angle becomes usual and close to the tetrahedral value. Comparison of data for the phenylphosphine derivatives (Table 2) shows that the P–CMe and P–CPh bond lengths are equal within the errors of their determination and coincide with the P–C bond length in the trimethylphosphine molecule {r_g 1.847(3) Å [21]}. In aromatic amines, the C–N bond is appreciably (by 0.05 Å [22]) shorter than in aliphatic amines. This is usually attributed to the p–π conjugation. In phenylphosphines, such interaction is considerably weaker or absent at all.

More considerable influence on the P–CPh bond length is exerted by electronegative substituents at the P atom. For example, in difluoro- and dichlorophenyl-

Table 2. Main geometric parameters of dimethylphenylphosphine molecule

Parameter (Å, deg)	$PhPCl_2$, gas-phase electron diffraction [7][a]	$PhPF_2$, gas-phase electron diffraction [8][b]	$PhPMe_2$		
			gas-phase electron diffraction [13][c]	this work	
				gas-phase electron diffraction[a]	calculation[d]
P–X	2.060(3)	1.580(3)	1.844(5)	1.846(2)	1.850
P–C	1.823(5)	1.809(7)	1.845(9)	1.844(2)	1.848
$C–C_{av}$	1.387	1.392(3)	1.401(2)	1.401(2)	1.392
∠XPC	100.5(5)	98.8(11)	103.4(10)	100.8(9)	102.0
∠XPX	100.2(5)	102.3(12)	96.9(25)	97.3(15)	100.3
∠δ	4.6	0	0	3.9(6)	3.1
∠φ	0	31	0 and 90	0	0
∠PCH			115.2(31)	110.1(9)	109.2
V, kcal mol^{-1}	1.24(54)		1.08(17)	0.38(36)	1.5, 0.6[e]

[a] Dynamic model (r_a, $\angle_\alpha$) taking into account relaxation from quantum-chemical calculations. [b] Static model (r_a). [c] Dynamic model (r_a, $\angle_\alpha$) without relaxation. [d] HF/6-311++G**. [e] B3LYP/6-311G**.

phosphine molecules this length is 1.809(7) [8] and 1.823(5) Å [7], respectively, which is smaller than in the dimethylphenylphosphine molecule (Table 2).

The $C_{Me}PC_{Me}$ bond angle in the dimethylphenylphosphine molecule preserves its value as compared to the trimethylphenylphosphine molecule {98.3(3)° [21]}, but the $C_{Ph}PC_{Me}$ bond angle somewhat increases, probably owing to steric interactions (Table 2). It is interesting that, in the case of halogen derivatives, the bond angles at the P atom change in opposite directions: the XPX angle increases {100.2(5)° and 102.3(12)° for the dichloro- and difluorophenylphosphine molecules [7, 8], respectively}, and the XPC angle remains unchanged as compared to the trimethylphenylphosphine molecule. This is in contradiction with the Gillespie VSEPR theory [23], according to which the XPX angle should decrease with increasing electronegativity of substituent X.

The presence of the perpendicular conformer is not confirmed by the new data. These results agree well with quantum-chemical calculations and also with data of microwave spectroscopy for phenylphosphine [2] and with our data on the dichlorophenylphosphine molecule [7].

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