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Molecular Structure of Phenylphosphine and Its Analogs by Gas-Phase Electron Diffraction and Quantum-Chemical Calculations

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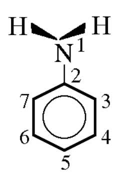
Abstract—The molecular structures of phenylphosphine and its analogs, aniline and phenylarsine, were studied by gas-phase electron diffraction and quantum-chemical methods. The geometry and force constants were calculated at the HF/6-31G and B3LYP/6-31G* levels of theory. Phenylphosphine and phenylarsine possess a bisector conformation with asymmetric phenyl rings. The main geometric parameters are as follows (r_a): P–C 1.833(6), C–C$_{av}$ 1.397(1)Å. The structures of molecules like X_2YPh (X = H, F, Cl; Y = N, P, As) were discussed.

The structure of phenylphosphine was studied previously [1]. The repeated structural analysis is motivated by the fact that *ab initio* calculations and normal-coordinate analysis provide more precise and correct data on molecular geometry and dynamic characteristics. In addition, in the present work we performed ab initio calculations for analogs of phenylphosphine, aniline (H_2NPh) and phenylarsine (H_2AsPh). It was also worthwhile to consider the molecular structures of compounds of this series from a common viewpoint.



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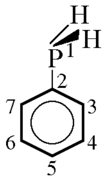

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Quantum-chemical calculation and normal-coordinate analysis. Table 1 presents the *ab initio* results for compounds H_2XPh [2]. Calculations in the framework of the density functional theory permit to reveal the effect of electron correlation on the calculation results. As follows from Table 1, the aniline molecule (**A**) unlike H_2PPh and H_2AsPh (**B**) possesses a C_s conformation with amino hydrogen atoms located on the same side of the phenyl ring plane. The symmetry of the phenyl ring in aniline is C_2. The calcu lated geometries agree well with the experimental ones obtained by microwave spectroscopy [4]. The phenyl groups in H_2PPh and H_2AsPh possess asymmetric structures, but the whole molecules have a symmetric bisector conformation with hydrogen atoms located on the opposite sides of the phenyl ring plane. Replacement of a hydrogen atom in benzene by an H_2Y (Y = N, P, S) group decreases the C–C$_{ipso}$–C bond angle by 1.3°–1.5°, as follows from the calculation results. At the same time, in aniline molecule, according to experimental data, this angle is unchanged (Table 1). The nitrogen atom which is more electronegative (3.0) than carbon (2.5) induces a positive charge on the ipso carbon atom (0.297 au), and the phosphorous and arsine atoms whose electronegativities are 2.1 and 2.0 induce negative charges on carbon atoms (–0.221 and –0.134 au, respectively). As a result, the C–C$_{ipso}$ bonds get slightly polarized.

The minimum on the potential curve of phenylphosphine (Fig. 1) corresponds to a conformation with l_p–P–C–C (φ) 0° (HF/6-31G*). The B3LYP/6-31G* results are slightly different. The energy minimum corresponds to a conformation with φ 20°. However, this conformation is preferred over that with φ 0° by 0.02 kcal/mol only. The latter calculation in fact points to a broad minimum from –20° to +20°. This is not a single instance. Thus, as shown in [5] with $Cl_3C(O)NH_2$ as an example, higher level *ab initio* calculations shift the minimum from 0° by 10–25°. For phenylarsine, both the methods assign the energy minimum to a conformation with φ 0°.

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Table 1. Geometric parameters of H_2XPh (X = N, P, As): bond lengths (Å) and bond angles (deg)[a]

Parameter	H_2NPh			H_2PPh				H_2AsPh	
	HF/6–31G*	B3LYP/6–31G*	experiment MW [3]	HF/6–31G*	B3LYP/6–31G*	experiment (present work, r_a)		HF/6–31G*	B3LYP/6–31G*
						scheme 1	scheme 2		
$X–C^2$	1.397	1.401	1.402(2)	1.844	1.854	1.833(4)	1.833(6)	1.941	1.957
$C^2–C^3$	1.393	1.405	1.397(3)	1.390	1.392	1.399 (1)	1.399 (1)	1.388	1.399
$C^3–C^4$	1.383	1.393	1.394(4)	1.389	1.397	1.399	1.399	1.389	1.398
$C^4–C^5$	1.386	1.397	1.386(4)	1.382	1.395	1.392	1.392	1.382	1.394
$C^5–C^6$	1.386	1.397	1.386(4)	1.389	1.397	1.398	1.398	1.389	1.398
$C^6–C^7$	1.383	1.393	1.394(4)	1.382	1.395	1.391	1.391	1.382	1.394
$C^7–C^2$	1.393	1.405	1.397(3)	1.396	1.394	1.405	1.405	1.393	1.402
C–H	1.076	1.087	1.082(4)	1.076	1.087	1.122(10)	1.122(10)	1.076	1.087
Œ–H	0.997	1.013	1.001(1)	1.404	1.425	[1.404]	[1.404]	1.525	1.546
ŒC^2C^3	120.6	120.7	119.4(2)	118.2	117.8	[118.2]	119.8 (30)	118.4	117.9
$C^2C^3C^4$	120.4	120.5	120.1(2)	120.8	120.8	[120.8]	122.4	120.9	120.8
$C^3C^4C^5$	120.9	120.8	120.7(1)	119.9	120.0	[119.9]	117.7(40)	119.9	119.9
$C^4C^5C^6$	118.8	118.9	118.9(1)	119.8	119.7	[119.8]	120.7(20)	119.8	119.7
$C^5C^6C^7$	120.9	120.8	118.9(1)	120.1	120.2	[120.1]	121.4[b]	120.0	120.1
$C^6C^7C^2$	120.4	120.5	120.7(1)	120.7	120.7	[120.7]	118.8[b]	120.8	120.7
$C^7C^2C^3$	118.7	118.6	120.1(1)	118.5	118.6	[118.5]	119.0[b]	118.5	118.7
CCH	120.0	120.0	119.7(3)	120.0	120.0	120.0	120.0	120.0	120.0
HXH	110.6	111.1	113.1(2)	94.7	93.0	[94.7]	[94.7]	93.0	90.1
$\tau(H^{13}XC^2C^3)$	155.7	156.5	37.5(2)[c]	–131.8	–153.5	[–131.8]	[–131.8]	–133.0	–134.2
$\tau(H^{14}XC^2C^3)$	26.8	26.4		131.8	112.3	[131.8]	[131.8]	133.0	134.2
$\tau(XC^2C^3C^4)$	177.7	177.2	180.0	180.0	179.9	[180.0]	[180.0]	180.0	180.0
R factor, %						6.48	6.36		

[a] In brackets are assumed values. [b] Dependent parameters. [c] Dihedral angle between the phenyl ring and HNH planes.

Moreover, quantum-chemical calculations permitted us to determine the force field of the molecules, IR and Raman frequencies and mean vibration amplitudes. Analysis of the Raman spectra of phenylarsine and phenylphosphine led the authors of [6, 7] to conclude that the molecules possess a C_s conformation. The authors assumed for the phenyl ring a C_2 symmetry. However, this conclusion contradicts *ab initio* results.

Tables 2 and 3, together with experimental IR and Raman frequencies, present theoretical ones. In the normal-coordinate analysis of phenylphosphine, the following factors were used for scaling force constants: 0.79 (P–H, HPH), 0.82 (C–H), 0.77 (C–C), and 0.81 for the rest force constants. The scaling factors for phenylarsine were as follows: 0.85 (As–C), 0.82 (As–H), 0.77 (C–C), 0.815 (C–H), 0.74 (AsCH, HAsH), 0.79 (CCH), 0.81 (CCC), and 1.0 (out-of-plane and torsion vibrations). In general, the agreement between experimental and calculated frequencies is satisfactory.

Structural analysis of phenylphosphine. The geometric parameters were refined by least-squares on the basis of experimental molecular intensity curves *sM*(*s*) (Fig. 2) using a modified norwegian

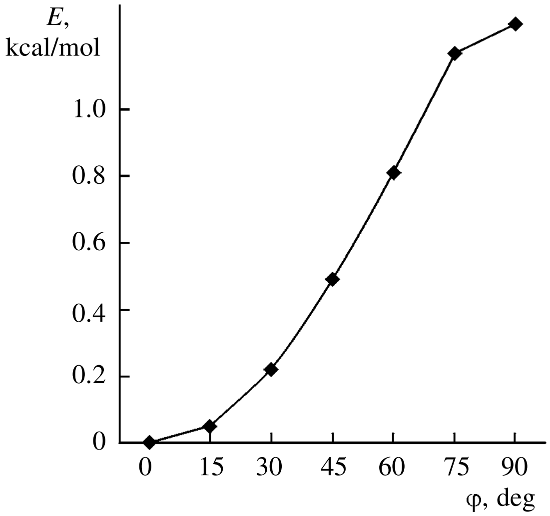

Fig. 1. Potential function of H2PPh (HF/6-31G*).

Table 2. Normal-coordinate analysis of phenylphosphine

HF/6-31G* calculation					Experiment (liquid)					
					Raman spectrum					IR spectrum, cm^{-1} [6]
cm^{-1}	I_{IR}	I_{Raman}	ρ	*PED*[a]	cm^{-1} [6]	I_{Raman}	ρ	cm^{-1} [5]	I_{Raman}	
3068	22	284	0.11	$99\nu_{CH}$	3058	10	*p*	3051	20 *p*	3065 s
3060	46	12	0.66	$97\nu_{CH}$						
3052	14	83	0.66	$96\nu_{CH}$	3019	1	–	3028	2	3050 w
3043	0.1	104	0.75	$94\nu_{CH}$						
3037	1	20	0.75	$91\nu_{CH}$						3010 sh
2303	114	192	0.10	$98\nu_{PH}$	2288	14	*p*	2285	18	2288 c
2293	143	130	0.75	$94\nu_{PH}$						
1590	0.1	22	0.69	$55\nu_{CC} + 13\alpha_{CCH}$	1587	14	*p*	1587	9 *dp*	1587 s
1571	2	7	0.74	$61\nu_{CC} + 18\alpha_{CCH}$	1571	sh	–	1571	2	1571 sh
1481	7	2	0.35	$25\nu_{CC} + 64\alpha_{CCH}$	1478	0.5	–	1481	1	1480 s
1434	19	0.3	0.74	$26\nu_{CC} + 59\alpha_{CCH}$	1437	0.5	–	1434	1	1436 s
1322	5	0.4	0.74	$69\alpha_{CCH}$	1328	w	–	1326	1	1327 w
					1284	0.5	–			1295 m
1190	5	0.3	0.24	$29\nu_{CC} + 53\alpha_{CCH}$	1187	3	0.39	1184	3 *p*	1185 w
1169	0.6	5	0.57	$18\nu_{CC} + 68\alpha_{CCH}$	1161	3	0.86	1157	4	1162 v.w
1117	44	40	0.73	$93\alpha_{HPH}$	1117	5	0.19	1107	7 *p*	1107 m
1087	0.1	6	0.44	$47\nu_{CC} + 18\nu_{PC}$						
1075	10	3	0.67	$62\nu_{CC}$	1073	3	0.62	1070	3	1070 s
1049	0.0	0.4	0.61	$65\nu_{CC}$	1026	10	0.08	1028	1	1022 m
1017	0.0	0.1	0.75	$72\gamma_{CH} + 13\tau_{CC}$			–	1022	8	
1002	0.5	9	0.11	$28\nu_{CC} + 30\alpha_{CCC}$	1002	20	0.19	998	14 *p*	998 m
995	0.2	0.0	0.75	$74\gamma_{CH} + 15\tau_{CC}$						988 w
965	2	30	0.11	$64\nu_{CC}$	970	sh	–	984	1	968 w
948	0.0	0.2	0.75	$72\gamma_{CH}$	913	1	0.84	916	1	
869	8	20	0.75	$70\alpha_{CPH}$				852	2	850 m
865	2	8	0.75	$63\gamma_{CH} + 16\alpha_{CPH} + 11\tau_{CC}$						
823	70	11	0.71	$86\gamma_{CPH}$	823	7	0.26	826	6 *p*	824 s
730	80	0.3	0.75	$79\gamma_{CH}$	722	3	*dp*	720	3 *dp*	720 v.s
690	9	1	0.75	$36\gamma_{CH} + 15\gamma_{PC} + 42\tau_{CC}$	692	6	0.19			
679	0.9	10	0.12	$29\nu_{PC} + 25\alpha_{CCC}$				689	6 *p*	692 s.m
609	0.0	5	0.75	$63\alpha_{CCC} + 18\alpha_{CCH}$	619	4	0.85	617	4 *dp*	
446	2	0.8	0.75	$53\gamma_{PC} + 26\tau_{CC} + 10\gamma_{CH}$	443	2	0.70	445	2 *dp*	443 m
405	0.0	0.1	0.75	$65\tau_{CC} + 20\gamma_{CH}$						
376	9	11	0.31	$59\nu_{PC}$	392	12	0.26	392	8 *p*	390 w
246	0.4	0.9	0.67	$85\alpha_{PCC}$	249	2	0.86	249	2 *dp*	
164	0.1	8	0.75	$38\gamma_{PC} + 41\tau_{CC}$	176	10	0.86	176	6	
65	6	5	0.75	$89\tau_{PC}$	55[b]	w				

[a] Table 2 and 3 present *PED* ≥ 10%. (I_{IR} and I_{Raman} are Infrared and Raman intensities, (v.s) very strong, (s) strong, (m) medium, (w) weak, (sh) shoulder, (ρ) depolarization ratio, (*p, dp*) polarized and depolarized frequencies, respectively. (ν, α, γ, τ) Stretching, in-plane, out-of-plane, and torsion vibrations, respectively. [b] A weak line at 55 cm^{-1} is observed.

computer program [8]. The g_{ij} functions necessary for calculation of theoretical $sM(s)$ curves were found using the tables [9]. The independent parameters of the molecule are the bond distances P–C, C–C, P–H, and C√, the bond angles PC^2C^3, $C^2C^3C^4$, $C^3C^4C^5$, $C^4C^5C^6$, CCH, HPH, and HPC, and the torsion angle φ. In accordance with the *ab initio* results, we refined the bisector conformation assuming a planar phenyl

Table 3. Normal-coordinate analysis of H_2AsPh

HF/6–31G*					Experiment [5]			
cm^{-1}	I_{IR}	I_{Raman}	ρ	*PED*	IR spectrum, cm^{-1}	Raman spectrum		
						cm^{-1}	I_{Raman}	ρ
3058	25	285	0.10	$92\nu_{CH}$	3065 m			
3050	46	17	0.75	$88\nu_{CH}$	3050 m	3055	20	*p*
3042	12	84	0.69	$93\nu_{CH}$	3025 sh			
3033	–	99	0.74	$97\nu_{CH}$				
3027	0.9	18	0.75	$97\nu_{CH}$	3010 w	3004	2	*p*
2086	159	147	0.75	$99\nu_{AsH}$	2089 m	2087		*p*
2085	122	210	0.10	$99\nu_{AsH}$				
1584	–	20	0.71	$55\nu_{CC} + 13\alpha_{CCH}$		1579	8	0.76
1566	1	7	0.74	$61\nu_{CC} + 18\alpha_{CCH}$	1582 s			
1474	7	3	0.29	$25\nu_{CC} + 62\alpha_{CCH}$	1482 s	1480	1	*p*
1420	18	0	0.72	$29\nu_{CC} + 60\alpha_{CCH}$	1435 m	1436	1	*p*
1312	5	0	0.75	$69\alpha_{CCH}$	1320 w	1329	1	
1178	2	0	0.40	$34\nu_{CC} + 44\alpha_{CCH}$	1187 m	1186	2	0.36
1160	0.7	5	0.53	$19\nu_{CC} + 72\alpha_{CCH}$	1156 w	1157	2	0.86
1092	2	8	0.66	$77\gamma_{CH} + 10\tau_{CC}$	1088 m	1087	3	0.18
1075	6	2	0.67	$72\nu_{CC}$	1025 m	1028	5	0.09
1070	0.5	0.5	0.56	$76\gamma_{CH} + 14\tau_{CC}$				
1065	–	0	0.75	$47\nu_{CC} + 12\nu_{AsC}$				
1043	–	0	0.75	$53\alpha_{CCC}$				
1017	32	37	0.69	$76\gamma_{CH}$	1000 m	1003	20	*p*
998	2	6	0.07	$26\nu_{CC} + 45\alpha_{CCC} + 17\alpha_{CCH}$	984 w			
968	3	34	0.11	$96\alpha_{HAsH}$	964 m	965	1	
964	0.3	0	0.75	$58\nu_{CC} + 16\alpha_{CCC}$				
924		3	0.75	$79\gamma_{CH} + 10\tau_{CC}$	910 w	909	1	
829	0.9	18	0.75	$32\alpha_{CAsH} + 40\gamma_{CH} + 10\tau_{CC}$	842 m	842	w	
753	62	16	0.61	$28\alpha_{CAsH} + 10\gamma_{CH}$	738 s	735	1	*dp*
732	76	3	0.75	$68\alpha_{CAsH}$	711 w	710	2	0.40
717	15	2	0.75	$94\alpha_{CAsH}$	692 s	687	0.5	
657	0.7	9	0.11	$22\nu_{CAs} + 38\nu_{CC}$	675 m	670	4	0.24
608	0.1	5	0.75	$64\alpha_{CCC}$	620 w	621	2	0.86
478	2	0.8	0.75	$49\gamma_{AsC} + 26\tau_{CC} + 10\gamma_{CH}$	440 w	437	1	*dp*
433	–	–	0.75	$60\tau_{CC} + 27\gamma_{CH}$				
289	8	10	0.29	$68\nu_{CAs}$		292	10	0.39
214	0.1	0	0.69	$85\alpha_{AsCC}$		237	0.5	
165	0.3	9	0.75	$37\gamma_{CAs} + 42\tau_{CC}$		162	8	0.86
88	1			$87\tau_{AsC}$				

ring and the PCCC torsion angle of 180°. Such parameters as P–H, HPH, and CCH were not refined and fixed on the HF/6-31G* values. Principal mean vibration amplitudes were also refined. Individual C–C bond distances were refined, as is common with parameters close in value, by the group method using the following corrections dCC_{ij} to the base parameter C^2–C^3: d_{34} (–0.0003 Å), d_{45} (–0.0076 Å), d_{56} (–0.0007 Å), d_{67} (–0.0078 Å), and d_{72} (0.0062 Å). The latter values were taken from the HF/6-31G* calculation.

Two schemes were used in calculations. In the first the PCC and CCC bond angles were fixed. In the second these parameters were refined. The results of structural analysis are given in Table 1. Table 2 lists the mean vibration amplitudes u_{ij}. As seen from Table 1, the standard deviations of the CCC bond

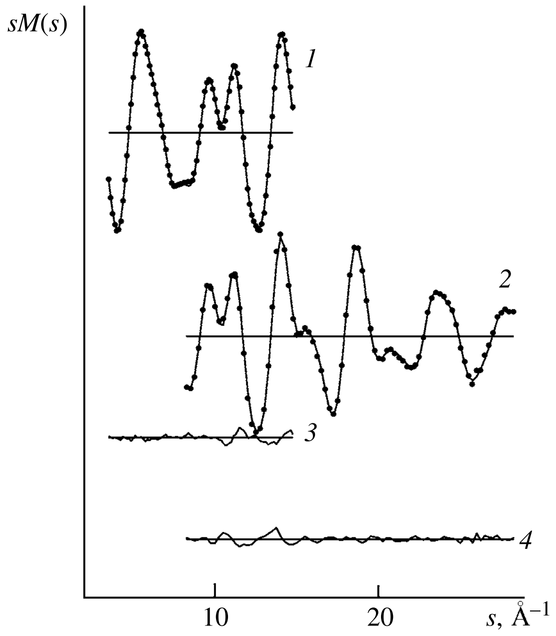

Fig. 2. (*1, 2*) Molecular intensity curves. (Points) Experiment and (solid lines) calculation. (*3, 4*) $\Delta = sM(s)_{\text{exp}} - ksM(s)_{\text{calc}}$.

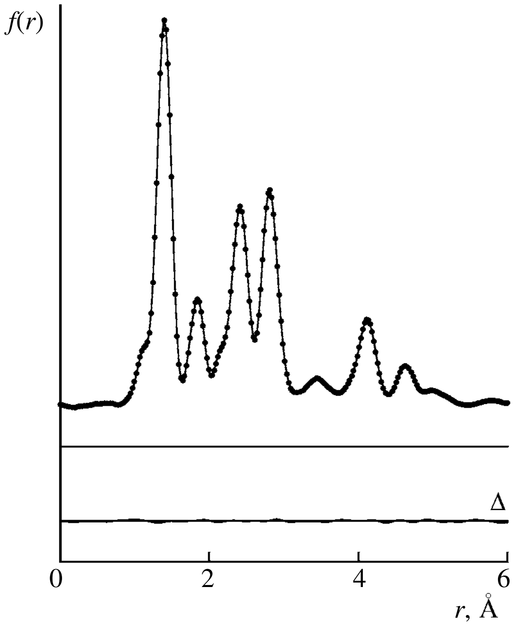

Fig. 3. Radial distribution curves. (Points) Experiment and (solid line) calculation.

angles are large, which results from strong correlations: $P^1C^2C^3/C^3C^4C^5$ $|0.96|$, $P^1C^2C^3/u(P\cdots C^4)$ $|0.83|$, $C^3C^4C^5/u(P\cdots C^4)$ $|0.78|$, $P^1C^2C^3/u(C^2\cdots C^4)$ $|0.92|$, $C^3C^4C^5/u(C^2\cdots C^5)$ $|0.90|$, and $u(P\cdots C^3)/uC^2\cdots C^4)$ $|0.86|$. For the same reason, the bond angles determined by scheme 2 are considered to be unreliable. The *R* factors by the two schemes diverge inconsiderably (0.3%). This testify correctness of the *ab initio* calculations. Figure 3 shows the radial distribution curve *f*(*r*); the assignment of the peaks on the *f*(*r*) curve is quite unambiguous.

Table 4. Principal mean vibration amplitudes of phenylphosphine, Å

Parameter	r_{ij}, Å	Calculation	Experiment[a]
P–C	1.83	0.052	0.052(5)
C–C	1.40	0.047	0.047(2)
C–H	1.12	0.077	0.075(10)
C···C	2.4	0.056	0.055(12)
C···C	2.8	0.062	0.058 (10)
$P\cdots C^3$	2.81	0.072	0.068
$P\cdots C^7$	2.83	0.069	0.065
$P\cdots C^4$	4.13	0.069	0.081 (10)
$P\cdots C^6$	4.11	0.067	0.079
$P\cdots C^5$	4.63	0.068	0.073(15)
$P\cdots H^{8,12}$	2.9	0.146	
$P\cdots H^9$	5.0	0.117	
$P\cdots H^{11}$	5.0	0.114	
$P\cdots H^{10}$	5.8	0.100	
C···H	2.16	0.099	0.077(15)
C···H	3.4	0.096	0.126(33)

[a] Values in parentheses are $3\delta_{\text{LS}}$

As noted above, the B3LYP/6-31G* calculation places the energy minimum of phenylphosphine on φ 20°. Refinement of geometric parameters with φ fixed at 20° led to the same results as for a symmetric conformation with φ 0°. This is not surprising. Experimentally conformational assessment of such molecules, even with invoking quantum-chemical calculations, is not unambiguous, since the *sM*(*s*) function is slightly contributed by rotation-dependent (P)H···C terms.

Thus, our structural analysis revealed that phenylphosphine possesses a symmetric bisector conformation. As follows from Table 1, the calculated *r*(C–N) values for aniline are 1.397 and 1.401 Å. Both values are close to experiment [1.402(2) Å] but considerably smaller than the sum of the covalent radii of nitrogen and carbon (1.47 Å). This result can be attributed to interaction of the lone pair of N with π electrons of the phenyl ring. In methyl-, dimethyl-, and trimethylamines, such electron interactions are absent, and the C–N bond lengths, by electron diffraction and microwave data, are 1.47–1.45 Å [10], which is close to the

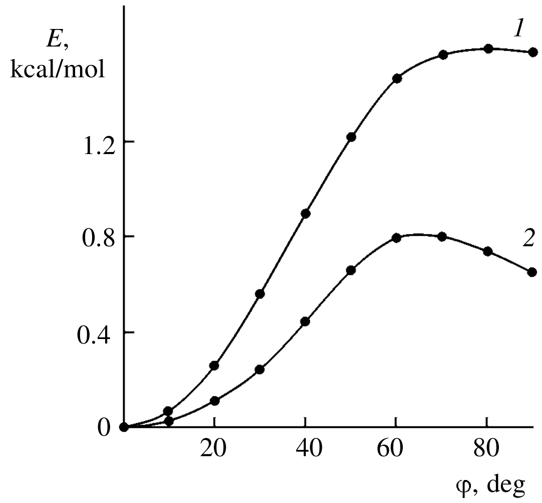

Fig. 4. Potential functions of F_2PPh calculated at the (*1*) HF/6–31G* and (*2*) B3LYP/6–31G* levels of theory.

sum of the covalent radii. Therewith, the mean bond angle at the nitrogen atom is about 110°. Drawing an analogy between methylamine and aniline, the C–N bond in the latter is shortened by 0.06 Å, which is much larger than the respective values in H_2PMe and H_2PPh (Δ_{P-C} 0.02 Å). In phenylphosphine and phenylarsine, the sums of the covalent radii are 1.843 and 1.968 Å. The experimental r(P–C) value [1.833(6) Å] is close to the sum of the covalent radii. In the bisector conformation of phenylarsine, π electrons and the phosphorus lone pair are orthogonal and do not interact. It can be assumed that r(As–C) in phenylarsine is 1.96 Å, which agrees with the results of structural studies of *o*-$ClC_6H_4AsCl_2$ {1.955(9) Å [11]}, *o*-$BrC_6H_4AsBr_2$ {1.954(17) Å [12]}, $C_6H_5 \cdot AsBr_2$ [1.952(11) Å], and *p*-$BrC_6H_4AsBr_2$ [1.967(14) Å] [13].

In conclusion, we present comparative data on the character of variation of the P–C bond length in the series X_2PPh (X = H, Cl, F) with the electronegativity of X (2.1, 3.0, and 4.0, respectively), r(P–C), Å: H_2PPh 1.833(6), Cl_2PPh 1.823(5) [14], and F_2PPh 1.809(7) [15]. As seen, the P–C bond shortens in going from an electron-donor substituent X to electron-acceptor. However, it is to be noted that the conformation of the fluorine-substituted phosphine is asymmetric, since the phenyl group is turned by 31° from the bisector conformation. To rationalize this fact, we calculated the potential function of F_2PPh by the HF/6–31G* and B3LYP/6–31G* methods (Fig. 4). The latter revealed two minima at 0° and 90°. The barrier to transition the minimum at 90° to that at 0° is as low as 0.2 kcal/mol. On the assumption that $\Delta S = 0$, the energy difference $\Delta E = E(\varphi = 90°) - E(\varphi = 0°) = 0.6$ kcal/mol, which corresponds to 0.27 and 0.73% conformer contents in the gas phase. According to the HF/6-31G* results, the minimum at 90° is almost absent. The barrier to the 90°–0° transition is 0.01 kcal/mol. We agree with Burt *et al.* [15] that the conformation with φ 31° corresponds to an effective conformation.

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