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Theoretical conformational analysis of organophosphorus compounds †

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Contents

I. Introduction 297
II. Conformational analysis of tri- and tetracoordinate phosphorus compounds 298
III. Conclusion 311

Abstract. Published data on the theoretical conformational analysis of acyclic tri- and tetracoordinate phosphorus compounds by quantum-chemical methods are generalised and systematised. Theoretical results are compared with experimental data for a wide range of such compounds. The main characteristics and fine conformational details of their structures are considered. The bibliography includes 221 references.

I. Introduction

The development of conformational analysis is associated primarily with the need to explain and predict the reactivity of molecules from their three-dimensional structures. Pioneering studies by Barton, published in 1950, marked the beginning of extensive progress in this field, which now covers virtually all areas of organic chemistry. Barton is the person to whom Eliel, Allinger, Angyal and Morrison dedicated their monograph 'Conformational Analysis',[1] and it remains a 'textbook' for researchers dealing with molecular structures. The well-known phrase of these authors states that a chemist who does not understand conformational analysis, does not understand organic chemistry.[1] Physical methods of investigating molecular structures and quantum-chemical calculations play an important role in this field of science.

However, theoretical conformational analysis of organoelement compounds remains poorly developed in spite of advances in quantum chemistry. In the cited monograph of Eliel *et al.*, the conformations of organoelement compounds were not even mentioned. For organophosphorus compounds (OPCs) in which the phosphorus atom has a coordination number of 3 or 4, the main geometric parameters of such molecules (bond angles, bond lengths, *etc.*) and the most important fundamental characteristics of their bonds with phosphorus (for example, polarity and polarisability) have not been determined at that time. This hinders the use of conventional methods of organic chemistry in studies of OPC structures in solution.

Pure conformational control of a particular reaction is rare. For organoelement, in particular, organophosphorus, compounds, such examples are especially lacking. The reactivities of geometric isomers which model a particular conformational situation have received much more attention. This is associated primarily with the synthesis of compounds in which an anchor group (often the *tert*-butyl group or a heterocyclic substituent) stabilises only one conformer. Most of these studies have been carried out on substituted cyclohexanes and their heteroanalogues. For organophosphorus compounds, with rare exceptions, theoretical investigations of the fine details of their three-dimensional and electronic structures were not carried out until the 1980s.

The conformational analysis of organophosphorus compounds has attracted attention because they are widely used and, as a consequence, there is a need to synthesise compounds possessing desired properties. A knowledge of the structures and fine conformational features of these compounds is also of importance in studies of their reaction mechanisms and the reactivities. In the 1970s and1980s, theoretical analysis of the general and specific features of the OPCs' spatial and electronic structures and comparisons of the results with the general concepts of organic chemistry became of importance.

The development of a methodology for the conformational analysis of complex organic and organoelement compounds, including OPCs, was a considerable step forward. This methodology was described in a review by Vereshchagin and Vulsfson [2] and proved to be very efficient in studies of the structures of a wide range of various compounds in solution, where most chemical reactions occur.

Numerous studies on the experimental conformational analysis of OPCs were performed in Kazan by researchers belonging to the schools founded by Academician B A Arbuzov and the Corresponding Member of the Russian Academy of Sciences A N Pudovik. These studies were carried out using various complementary physical methods (vibrational and photoelectron spectroscopy, NMR spectroscopy, X-ray diffraction analysis, the dipole moment method, Kerr effect measurements, Rayleigh scattering). The results of these studies were covered in several reviews.[3–8]

Attempts to provide a theoretical support for the abundant available experimental data on the conformations of organophosphorus compounds are scarce, although this problem has

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Table 1. The total energy (E) of the *cis* conformer of H_2POH and the energy difference between the conformers $\Delta E = E(trans) - E(cis)$ calculated by quantum-chemical methods at different levels of theory.[a]

Method	Basis set	E (a.u.)	ΔE / kcal mol^{-1}
Hartree – Fock	3-21G(d)	−415.27576	−0.80
	6-31G	−417.22858	1.76
	6-31G(d)	−417.31424	0.11
	6-31 + G(d)	−417.319909	0.28
	6-31G(d,p)	−417.32531	0.12
	6-31 + G(d,p)	−417.331052	0.26
	6-311G(d,p)	−417.36867	−0.62
	6-311 + G(d,p)	−417.37360	0.09
	6-311G(2d,2p)	−417.380881	−0.56
	6-311 + + G(2d,p)	−417.383562	−0.05
	6-311 + G(2d,2p)	−417.384770	0.08
	6-311 + + G(2d,2p)	−417.384820	0.08
	6-311 + + G(3d,2p)	−417.389418	0.00
	6-311 + + G(3d,3p)	−417.389620	0.01
MP2	6-31G(d)	−417.596726	0.69
MP3	6-31G(d)	−417.613711	0.53
MP4	6-31G(d)	−417.618745	0.54
MP2	6-311 + + G(3d,2p)	−417.750979	0.22
B3LYP	6-31G(d)	−418.362668	0.72
B3LYP	6-31G(dp)	−418.371584	0.72
DFT/PBE	TZ2P	−418.184044	0.23

[a] V V Zverev, unpublished data.

Table 2. The total energy (E_{min}) of the *gauche* conformer of $H_2P(X)OH$ (X = O, S), the XPOH torsion angle (φ_{min}) and the rotation barrier $\Delta E = E(cis) - E_{min}$.[a]

Method	Basis set	E_{min} (a.u.)	φ_{min} / deg	ΔE (see [b])
$H_2P(O)OH$				
Hartree – Fock	3-21G(d)	−489.771315	0	0.000
	6-31G(d,p)	−492.226614	0	0.000
	6-31 + G(d,p)	−492.229600	10	0.002
	6-311G(d,p)	−492.284637	20	0.019
	6-311 + + G(d,p)	−492.326792	25	0.061
	6-311 + + G(2d,2p)	−492.290078	0	0.000
	6-311 + + G(3d,3p)	−492.317056	0	0.000
MP2	6-31G(d)	−492.678535	39	0.297
MP3	6-31G(d)	−492.683435	32	0.120
MP4	6-31G(d)	−492.694606	34	0.163
B3LYP	6-31G(d)	−493.615503	40	0.334
B3LYP	6-31G(d,p)	−493.624409	42	0.323
DFT/PBE	TZ2P	−493.403126	40	0.282
$H_2P(S)OH$				
Hartree – Fock	3-31G(d)	−810.771315	0	0.000
	6-31G(d,p)	−814.867500	0	0.000
MP2	6-31G(d)	−815.259610	22	0.048
B3LYP	6-31G(d)	−816.581483	26	0.059
DFT/PBE	TZ2P	−816.262590	21	0.050

[a] V V Zverev, unpublished data. [b] In kcal mol^{-1}.

attracted increased attention in recent years. It should be emphasised that we are referring to high-level *ab initio* calculations here, because semiempirical quantum-chemical methods have been used for several decades. In spite of the fact that each method is of limited application and should be used with caution,[9] in some cases the implementation of these methods is justified.‡ This is demonstrated with particular examples below.

It has been mentioned many times that *ab initio* calculations using the economical 3-21G* basis set are sufficient for theoretical studies of the various properties of organophosphorus compounds. However, the calculated energies of the *cis*, *trans* and *gauche* conformers of the H_2P-OH and $H_2P(O)OH$ molecules (Tables 1 and 2) show that this model is of limited application. In the case of a small energy difference between the conformers, successive extension of the basis set up to 6-311 + + G(2d,2p) is not accompanied by a monotonic change in the calculated properties (analogously to that observed for the total energy), and the inclusion of electron correlation data results in a substantial change in the relative stability of the conformers. Apparently, it follows that the conformational energies of OPCs, estimated by quantum-chemical calculations without analysis of the role of correlation effects, can differ substantially from experimental data. In our opinion, with their large number of approximations used to analyse intramolecular interactions, simplified orbital models deserve attention. In some cases, these models, derived by factorisation of the electron shells, were confirmed by photoelectron spectroscopy.[11–13]

The present review is the first to summarise data on the internal rotation about single bonds of phosphorus obtained by calculation, and these data are compared with experimental results. The review covers organophosphorus compounds containing at least one P–C or P–XR bond (X = O, S, N; R is a hydrocarbon substituent), in which phosphorus has a coordination number of 3 (P^{III}) or 4 (P^{IV}). The structures of low-coordinate phosphorus compounds (see Refs 14–25) and phosphorus-containing heterocycles[26–31] are beyond the scope of this review. Metal complexes containing OPCs are also not included in the review, because this large and specific area of organophosphorus chemistry deserves a separate analysis.

The review summarises the results of theoretical conformational analyses of OPCs performed primarily in the last 10–15 years and covers inclusively data published up to mid-2003. In addition, the most important and high-priority studies and reviews in the field of experimental and theoretical conformational analysis of organophosphorus compounds published earlier are considered.

II. Conformational analysis of tri- and tetracoordinate phosphorus compounds

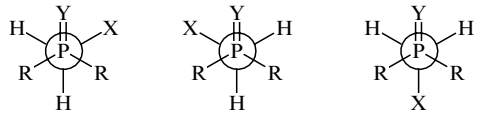
1. Internal rotation about P–C(sp^3) bonds

The first reviews[5,8] on the conformations of acyclic organophosphorus compounds, in which the P^{III} and P^{IV} atoms are bound to various organogen atoms, were published 20 years ago. The results analysed in these reviews were obtained primarily by experimental methods and semiempirical quantum-chemical calculations (in rare cases, by *ab initio* calculations for a few simple molecules). Conformational studies in this field were accompanied by generalisation and critical analysis of the considerable amount of experimental data obtained by gas electron diffraction, X-ray diffraction analysis, IR, UV, Raman and NMR spectroscopy and quantum-chemical calculations. Along with these general physical methods, a comparison and analysis of experimental dipole moments, the dipole moments calculated according to the vector-additive scheme (hereafter, the dipole moment method) and data on electric-field-induced birefringence (hereafter, the Kerr effect method) play an important role in conformational studies. Photoelectron spectroscopy also makes a great contribution to investigations of conformational equilibria.

‡ In particular, the results of conformational analysis of a wide range of cyclic systems by *ab initio* (HF/3-21G) and semiempirical (AM1) quantum-chemical calculations and the molecular mechanics method (MM2) were compared in the study,[10] and it was concluded that calculations by different methods gave similar results. However, calculations by the AM1 method, though adequately predicting the molecular conformation, gave erroneous estimates of the relative stabilities of the conformers.

The main characteristic features of internal rotation about P–C(sp^3) bonds in OPCs were revealed. The internal rotation about the P–C(sp^3) bond has a threefold barrier due to the tetrahedral environment of the carbon atom involved in this bond. From the very beginning, conformational analysis of OPCs assumed that the staggered *gauche* or *trans* conformations with respect to the P–C(sp^3) bond were the most stable,[5] by analogy with the C(sp^3)–C(sp^3) bond (although the eclipsed *cis* conformation was initially also considered because of a lack of data). The Newman projections of the stable conformations of OPCs are shown below.[5]

According to current opinion, staggered *gauche* (synclinal) or *trans* (antiperiplanar) conformations with respect to the P–C(sp^3) bond are favourable for most OPCs.



g_1 g_2 t

This situation occurs regardless of the coordination state of the phosphorus atom (P^{III} or P^{IV}) and the presence of one, two or three such bonds in OPC molecules. At the same time, specific interactions (for example, intramolecular hydrogen bonding) and conjugation effects (for example, in the O=P–O–Si bond system) can stabilise the eclipsed *cis* (synperiplanar) conformation.

The ratio of the various rotamers and the factors responsible for their stabilisation are determined by the balance between intramolecular repulsive and attractive forces, *i.e.*, from the sum of Coulombic interactions between the dipoles, steric and orientation interactions, intramolecular electronic effects, *etc*. It should be noted that the general and relative stabilities of favourable conformers are, with rare exception, independent of the aggregation state of the compounds under study (crystals, liquids or solutions). The conformations observed in crystals are almost always retained in liquid and solution states, although several staggered rotamers often co-exist in the liquid phase, and the conformational pattern becomes more diverse.

In the last 15 years, the relative stabilities of the conformations of organophosphorus molecules which differ in angle of rotation about the P–C(sp^3) bond, have been extensively studied by semiempirical and *ab initio* quantum-chemical methods.[32–44] In some studies,[34–36] the spectroscopic and structural data for phosphine oxides and phosphine sulfides were analysed using the semiempirical MNDO/H method, and the conclusion was drawn that this method provides a satisfactory general description of the geometry and various physicochemical characteristics of OPCs. The results of experimental conformational analysis (the temperature dependence of the conformational stability estimated by IR spectroscopy) agree closely with the results of theoretical conformational analysis (*ab initio* calculations) of the ethyldifluorophosphine obtained by Durig *et al*.[38,39] The staggered *gauche* and *trans* conformations are favourable for this compound, the energy difference being small (0.23 ± 0.02 kcal mol^{-1}).

Earlier experimental (IR and Raman spectra) conformational analysis and semiempirical calculations, carried out by this research group for the $ClCH_2PF_2$,[43] $EtP(S)Cl_2$ and $CD_3CH_2P(S)Cl_2$ molecules,[32] led to the same principal results. All these compounds are characterised by the staggered *gauche* (C_1 symmetry) and *trans* (C_s symmetry) conformations the *gauche* conformer being more stable. In the solid state, the latter conformer is the major one, whereas the *gauche* $\rightleftharpoons$ *trans* conformational equilibrium occurs in the liquid state; however, the *gauche* conformation is more stable (the energy difference is 0.60 kcal mol^{-1}).[32] The heights of the barriers to rotation about the P–C(sp^3) bond in $EtP(S)Cl_2$ (2.22 kcal mol^{-1}) and $CD_3CH_2P(S)Cl_2$ (2.71 kcal mol^{-1}) estimated in the cited study are consistent with the earlier data.

Ab initio calculations of the rotation about the P–C(sp^3) bond in carbanions stabilised by pentavalent phosphorus[37] demonstrated that in the presence of electronegative substituents, the rotation barriers are higher in compounds containing P=S groups, whereas in the presence of electropositive substituents, the rotation barriers are higher in compounds containing P=O groups. The results of X-ray diffraction studies and theoretical conformational analysis (*ab initio* and semiempirical calculations) of 1-alkoxyethyldiphenylphosphine oxide[33] are also in good agreement with each other.

A recent study of the $EtPH_2$ molecule[40] by *ab initio* methods using the HF, MP2, BLYP and B3LYP basis sets showed that internal rotation about the P–C(sp^3) bond gives rise to the two most stable conformers when the methyl group is in *trans* and *gauche* orientations relative to the lone electron pair of the P^{III} atom. The optimised structural parameters agree well with the data obtained by microwave spectroscopy. The results of gas electron diffraction and various *ab initio* calculations for bis(trichlorosilyl)-*tert*-butylphosphine are also in satisfactory agreement with each other,[42] although the structure is distorted and the environment of the silicon and carbon atoms deviates from the ideal tetrahedral coordination. The vibrational frequencies of methylphosphine CH_3PH_2 and its deuterated derivatives were calculated using the Gaussian 98 program (HF, MP2 and DFT/B3LYP/6-311G**), and the results compared with IR spectroscopic data.[44]

Theoretical conformational analysis of a wide range of typical (from the point of view of competition between Coulombic and steric interactions) substituted phosphine oxides $R^1R^2P(O)CH_2X$ ($R^1 = R^2$ = Me, Et, Pr^i, Bu^t, Ph; X = Me, CN, Ph, Cl) was carried out by the semiempirical PM3 method.[45,46] This method adequately reproduced the structural characteristics determined by gas electron diffraction and X-ray diffraction analysis for trialkylphosphine oxides. The corresponding sulfides, selenides and tellurides[47] also demonstrated satisfactory agreement with spectroscopic data. For the phosphine oxides under consideration, calculations adequately interpreted the abundant experimental data (dipole moments, Kerr constants, vibrational spectra of compounds in different aggregation states and solvents at different temperatures) and predicted a noncontradictory set of stable conformations. In particular, the population of the conformation with P=O and C–X bonds in a *trans* orientation was found to decrease as the volumes of the substituents at the phosphorus atom and the methylene group increased.

Data on dialkyl and alkylaryl derivatives $R^1R^2P(O)CH_2X$ containing the above-mentioned substituents retrieved from the Cambridge Structural Database are scarce. Nevertheless, it was noted[45,46] that the conformations of P^{IV}–C(sp^3) with the C–X bond in the *gauche* orientation with respect to the phosphoryl P=O group and the X–C–P–O angles varying from 30° to 60° are statistically most probable taking into account the known crystal structures. The histograms of the torsion angles in phosphine oxides containing the $CP(Ph)(O)CH_2X$ fragment (Fig. 1) show that, in the crystalline compounds, the orientation of the plane of the arene ring relative to the P=O bond (characterised by the τ_2 angle) is close to an eclipsed conformation. According to the results of gas electron diffraction, an analogous situation is observed for mono- and diaryl-substituted phosphine oxides in the gas phase.[48]

Experimental (X-ray diffraction study, IR spectroscopy, dipole moments) and theoretical (PM3) conformational analysis of the bis(methoxycarbonylmethyl)phenylphosphine oxide molecule $PhP(O)(CH_2CO_2Me)_2$ demonstrated that the synclinal (*gauche*) orientation of the substituents relative to the P–C(sp^3) and C(sp^3)–C(sp^2) bonds prevails in both the crystal and solution states.[49] *Ab initio* calculations (HF, DFT, MP2) of the molecular geometry of related phosphonates $(RO)_2P(O)CH_2C(O)X$, where X = Me, EtS, Ph or Et_2N, also predicted the staggered *gauche* orientation of the CH_2–P bond relative to the carbonyl group.[50]

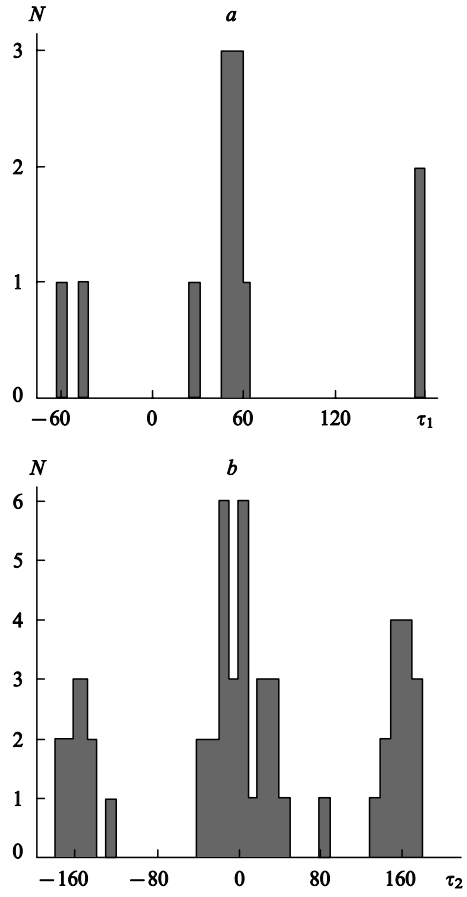


Figure 1. Histograms of the torsion angles in phosphine oxide molecules containing the CP(Ar)(O)CH_2X fragment; the data were retrieved from the Cambridge Structural Database;
(*a*) is the OPCX angle (τ_1), (*b*) is the ArPO (τ_2) angle (see the text).

As mentioned above, a comparison of the calculated data with the experimental results (IR, microwave and Raman spectroscopy, gas electron diffraction, X-ray diffraction analysis, dipole moments) of conformational analysis for a wide range of OPCs containing one $P^{III}-C$ bond,[51–59] one $P^{IV}-C$ bond,[60–68] two $P^{IV}-C$ bonds [69] or three $P^{IV}-C$ bonds [70,71] led to the conclusion that these compounds adopt staggered *gauche* and *trans* conformations regardless of the valence state of the phosphorus atom, the number of internal rotation axes and the aggregation state. For example, *ab initio* calculations for the $EtPCl_2$ molecule (HF/6-31G**) predicted the classical *gauche* conformation with a torsion angle $\varphi = 60^\circ$; the *trans* conformation being 2.09 kcal mol^{-1} less stable. In molecules of other compounds, the *gauche* or *trans* conformation can be stabilised in accordance with the steric and electronic effects of their substituents.

In recent years, interesting conformational analysis results were obtained for OPCs containing the bulky fullerene substituent.[72–77] In the study,[77] the electronic and spatial structure of a new fullerene derivative, phosphorylated methanofullerene $C_{60}C(CO_2Me)[P(O)(OMe)_2]$, was calculated by density functional theory (DFT/PBE/TZ2P) using the exchange-correlation Perdew–Burke–Ernzerhof (PBE) functional [78] and the three-exponent basis set including two polarisation functions (TZ2P) implemented in the PRIRODA program.[79] The calculations demonstrated that the most stable conformations of phosphorylated methanofullerene are characterised by the Coulombic interaction between the phosphoryl oxygen atom and one carbon atom of fullerene and by polarisation of this fragment, resulting in asymmetry of the bond lengths and atomic charges in the C_{60} cluster. The C–C bond lengths in the cisoid polyene fragments

Table 3. Total energies [E (a.u.)], enthalpies of formation (ΔH / kcal mol^{-1}), relative energies (ΔE /kcal mol^{-1}) and torsion angles of selected stable conformations of methanofullerene $C_{60}C(CO_2Me).[P(O)(OMe)_2]$.[77]

Conformation [a]	E or ΔH (see [b])	ΔE	Torsion angles /deg			
			OCCP	CCP(O)	(O)POC	(O)POC
DFT/PBE/TZ2P method						
$-ac$	−3197.217965	0.00	93	−144	35	50
ac	−3197.216779	0.74	91	148	−55	−29
sp	−3197.214680	2.06	88	23	26	47
PM3 method						
$-ac$	582.20	0.00	91	−131	−42	48
ac	582.19	0.00	88	141	−47	45
sp	582.30	0.10	87	20	−47	42

[a] $-ac$ is (−)-anticlinal, ac is (+)-anticlinal, sp is synperiplanar. [b] E in the DFT/PBE/TZ2P method, ΔH in the PM3 method.

adjacent to the *exo*-coordinated C–C bond of the fullerene cage were found to alternate and the differences in the bond lengths decreased with increasing distance from the *exo*-coordinated carbon atoms. The internal rotation of the $P(O)(OMe)_2$ group about the $C_{60}C-P$ bond leads to the three most stable conformations (Table 3), two of which are anticlinal ($-ac$ and ac) with C–C–P = O torsion angles of -144° and 148°, respectively. These conformations are more stable ($\Delta E = 0$ and 0.74 kcal mol^{-1}).§ In the third, less stable, synperiplanar (*sp*) conformation ($\Delta E = 2.06$ kcal mol^{-1}), the orientation of the C–C and P–O bonds corresponds to a distorted (toward the *cis* orientation) *gauche* conformation (the C–C–P = O torsion angle is 23°).

The theoretical study [75] of internal rotation about the P–C bonds in $C_{60}C[P(O)(OMe)_2]_2$ virtually reproduced the situation observed in the previous study [77] for phosphorus-containing fullerene $C_{60}C(CO_2Me)[P(O)(OMe)_2]$. In this case, two anticlinal conformations were also found to be most stable, whereas the third most stable conformation was the *gauche* form distorted toward the *cis* orientation (the C–C–P = O torsion angle is 23°) (Fig. 2). The difference in the results [75] obtained by the DFT/PBE/TZ2P and PM3 methods is attributable to the fact that the stabilising through-space interaction between the phosphoryl group and the C_{60} cage, which is reproduced at the DFT/PBE/TZ2P level of theory, is weakly pronounced in calculations by the semiempirical PM3 method. For the $MeP(O)(OMe)_2$ compound, the *gg* and $-g-g$ conformers are equivalent, whereas the *ac* and $-ac$ (*gg* and $-g-g$) conformers of the $C_{60}C(CO_2Me).[P(O)(OMe)_2]$ molecule differ substantially in energy due to the asymmetrically oriented CO_2Me group. In the stable conformations of the $C_{60}CPhY$ [76] and $C_{60}CY_2$ compounds [75] and the $C_{60}(CY_2)_2$ bis-adducts,[74] where $Y = P(O)(OR)_2$, an additional

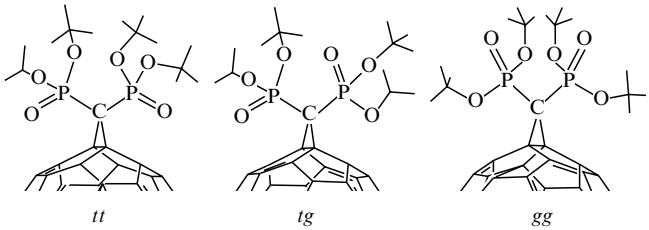


Figure 2. Stable conformations of phosphorylated methanofullerene $C_{60}C[P(O)(OMe)_2]_2$ calculated by the DFT/PBE/TZ2P method.[75]

§ Hereafter, ΔE is the energy difference between the molecular conformation under consideration and the most stable conformer.

intramolecular coordination of the phosphoryl group to the fullerene cage is observed.

As mentioned above, analogous favourable conformations are also typical of other OPCs. Therefore, the addition of even such a bulky substituent as the fullerene fragment to the phosphorus atom has only a slight effect on the relative stabilities of different conformations of these compounds. For rotation about the P–C(sp^3) bonds, staggered (or slightly distorted) conformations remain energetically most favourable for a wide range of compounds.

2. Internal rotation about the P – C(sp^2)(alkene) bond

Most organophosphorus compounds containing a bond between the P atom and alkene fragments are liquids with high boiling points. Hence, methods providing information on their molecular structures in solution are of particular importance. Experimental conformational analysis of OPCs with the P–C(sp^2)(alkene) bond has been carried out by gas electron diffraction, the Kerr effect method, the dipole moment method, vibrational spectroscopy and NMR spectroscopy. In solutions and in the gas phase, favourable conformations of vinylphosphonic acid dichloride $CH_2=CH-P(O)Cl_2$, divinylphosphinic acid dichloride $(CH_2=CH)_2-P(O)Cl$ and vinylphosphonic acid difluoride $CH_2=CH-P(O)F_2$ are those which contain C=C and P=O bonds in the *s-cis* orientation or similar conformations, in which these bonds are virtually coplanar.[5] The cisoid structure of the $CH_2=CH-P(O)XY$ fragment is attributable to steric repulsions between the substituents at the P^{IV} atom and the methylene group, not involving electron conjugation. In contrast, the *s-trans* conformation is observed in styrenephosphonic acid difluoride $PhCH_2=CH-P(O)F_2$. Apparently, there is conjugation in this compound due to which the *trans* conformation becomes the most favourable.[5]

In more recent experimental studies,[80–87] the energetically favourable conformations of P^{III} derivatives were found to contain the alkene fragments in the *cis* orientation with respect to the lone electron pair of the phosphorus atom. In these systems, the *trans* conformation can be present as the minor component. In α-cyanostyrenephosphonates, α- and β-substituted vinylphosphonates and other derivatives of alkenylphosphonic acids (results obtained by the dipole moment method, IR and NMR spectroscopy using lanthanide-shift reagents), the favourability of either *s-cis* or *s-trans* conformations is controlled by electrostatic factors. In all cases, structures with interacting dipoles in an antiparallel orientation are more stable.[5]

Semiempirical calculations (CNDO/2) for the $CH_2=CH-P(O)Cl_2$ molecule[88] demonstrated that the dependence of the total energy of this compound on the angle between the $O-P^{IV}-C$ and $P^{IV}-C-C$ planes has a deep minimum corresponding to the *s-cis* conformation ($\varphi = 0^\circ$) and a shallow minimum at $\varphi = 180^\circ$ (*s-trans* conformation). In polar solvents, the *s-trans* conformation may become more stable, whereas the molecule adopts the *s-cis* conformation in the gas phase. More recent *ab initio* calculations for phosphorylated ethylenes $CH_2=CH-P(O)Cl_2$, $CH_2=CH-P(S)Cl_2$, $CH_2=CH-P(O)F_2$, $CH_2=CH-P(O)FMe$, $CH_2=CH-P(O)Me_2$ and $CH_2=CH-PCl_2$ using the 4-31G basis set[89,90] confirmed the earlier conclusion that the *s-cis* conformation is favourable for these compounds. This conformation is also supported by the calculated dependences of the total energy (Fig. 3) and the parameters of the regression relation between the experimental and calculated ionisation potentials (IP) on the angle of internal rotation about the P–C bond. By contrast, calculations for dichlorovinylphosphonate and vinylphosphonic acid using the 6-31G* basis set[91] and for some other derivatives of phosphonic acids (vinyl-, propenyl-, bromoalkenyl- and cyanoalkenylphosphonic acids and their diethyl esters) using the STO-3G basis set[92] gave two minima on the potential energy surface corresponding to the *s-cis* conformation, a distorted *s-trans-gauche* conformation

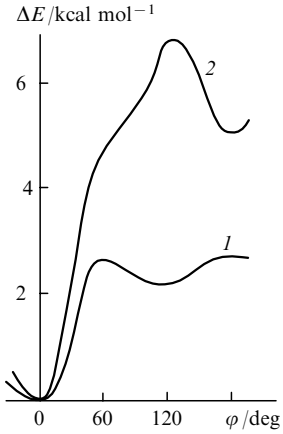


Figure 3. Dependence of the energies of the $CH_2=CHPCl_2$ (*1*) and $CH_2=CHP(O)Cl$ (*2*) molecules on the torsion angle about the P–C bond.[90]

and two transition states with low barriers to rotation about the P–C(sp^2) bond.

In the study,[92] the P=O bond in these compounds was demonstrated to be polarised and characterised by weak π-conjugation between the C=C and P=O groups. In the cited study, alkenylphosphonic acid derivatives were investigated by UV, IR, Raman and NMR (^1H, ^{31}P, ^{13}C) spectroscopy, and it was concluded that the conformational equilibria were shifted toward the *s-cis* conformation [from 87% in the $CH_2=CH-P(O)(OH)_2$ molecule to 99% in the $MeCH=CH-P(O)Cl_2$ molecule]. A distorted *s-trans-gauche* conformation was considered as the second most probable conformer. The energy difference between the conformers varied from 0.22 kcal mol^{-1} in the *E* isomer of $NC-CH=CH-P(O)(OMe)_2$ to 2.81 kcal mol^{-1} in the $MeCH=CH-P(O)Cl_2$ molecule.

The results of *ab initio* calculations for the $CH_2=CHPH_2$,[88] $CH_2=CHPF_2$ (see Ref. 93) and $CH_2=CHPCl_2$ molecules[91,93] are in complete agreement with experiment[94] (rotational spectra, the molecular constants and the dipole moment of vinylphosphine $CH_2=CHPH_2$) and indicate that these compounds adopt *s-cis* conformations. In these conformations, the lone electron pair of the phosphorus atom is parallel to the plane of the π system, hindering conjugation between these fragments. In the studies,[91,93] the form containing eclipsed C=C and P–Cl bonds was found as the minor conformation.

According to orbital models of donor-acceptor interactions (Fig. 4), the favourable conformation of vinyl derivatives of P^{III} is determined by competition between the $n(P)-\pi^*(PX_2)$ and $\pi(C=C)-\pi^*(PX_2)$ interactions. The former interaction stabilises the conjugated *gauche* conformation, whereas the latter stabilises the *cis* and *trans* conformations. In molecules containing electron-withdrawing substituents X at the P atom, the $\pi(C=C)-\pi^*(PX_2)$ donor–acceptor interaction plays the major role, stabilises the *cis* conformation and is responsible for the π-acceptor character of the PX_2 fragment.[93,95–97]

A comparison of the vertical ionisation potentials of the $EtPCl_2$ [$IP_{n(P)} = 9.70$, $IP_{n(Cl)} = 11.57$ eV] and $CH_2=CHPCl_2$ [$IP_{n(P)} = 9.84$, $IP_{\pi(C=C)} = 10.86$ and $IP_{n(Cl)} = 11.53$ eV] molecules, which were determined from the photoelectron spectra,[95] also provides evidence that dichlorovinylphosphine adopts predominantly the *s-cis* conformation, in which there is no conjugation between the lone electron pair of the P atom and the π system of the C=C bond. In the electron-conjugated *s-trans* conformation, the first ionisation potential would be expected to decrease due to mixing of the n and π orbitals; however, an opposite situation is observed. Interestingly, theoretical conformational analysis of the related $CH_2=CHXMe$ molecules (X = O, S or Se) by *ab initio* methods including correlation energy at the MP2/

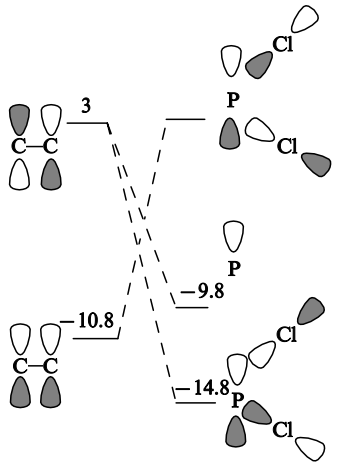


Figure 4. The key orbitals of dichlorovinylphosphine and their interactions in the *cis* conformation.[95]
The calculated energies (eV) are given.

6-31G* and MP2/6-311G** levels of theory,[98] also predicted the *s-cis* conformation as the major one, characterised by a deep minimum in the energy curve.

The results of modern *ab initio* calculations (DFT/B3LYP/6-311++G**)[99] for the molecules $CH_2=CHP(O)Cl_2$ and $CH_2=CHP(O)F_2$ are virtually identical to the results of gas electron diffraction.[88,93,99] The calculations demonstrated that the *s-cis* conformation, in which the phosphoryl group eclipses the vinyl group, is stable at room temperature. It should be noted that the *gauche* rather than *s-trans* conformation (which was evident from the experimental data) was proposed[99] as the second possible form in the conformational equilibrium.

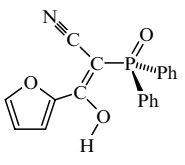
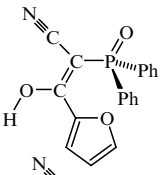
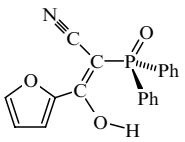
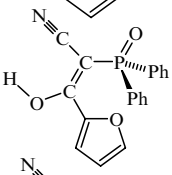
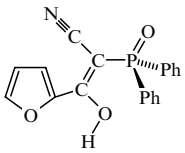
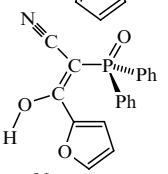
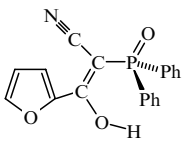
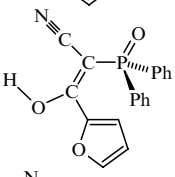
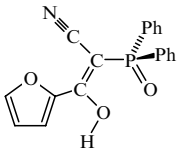
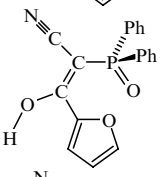
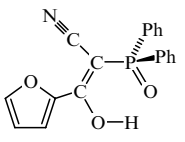
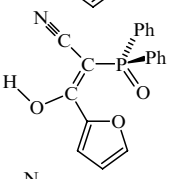
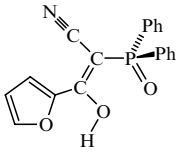
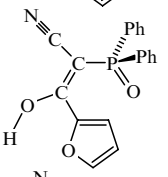
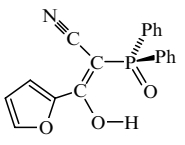
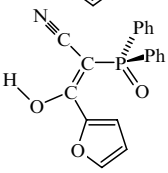
The mechanisms of electron conjugation between the vinyl and PCl_2 fragments were considered in a study,[90] where the photoelectron spectra of phosphorylated ethylenes $Cl_2PCH=CH_2$, $Cl_2P(O)CH=CH_2$ and $Cl_2P(S)CH=CH_2$ were analysed and *ab initio* calculations using the 4-31G basis set were carried out (see above). It was concluded that the *cis* and *trans* conformations of these compounds are stabilised by the $\pi(C=C)-\pi^*(PCl_2)$ and $\pi^*(C=C)-\pi(PCl_2)$ interactions involving the π system of the C=C double bond and the pseudo-π orbitals of the PCl_2 fragment. As a result of this interaction, the energies of the π and π* orbitals of the vinyl fragment, unlike the energy of the $\pi(PCl_2)$ orbital, depend only slightly on the angle of internal rotation about the P–C bond.

In another study,[100] the photoelectron spectroscopic data were compared with the results of calculations for phosphorylated allenes and ethylenes $(Me_2N)_2P(O)CH=C=CH_2$, $Cl_2P(O)CH=C=CH_2$, $Cl_2P(O)CH=C=CMe_2$, $(MeO)_2P(O).CH=C=CH_2$, $(MeO)_2P(O)CH=C=CMe_2$, $Me_2P(O).CH=C=CMe_2$, $Cl_2P(O)CH=CH_2$ and $Cl_2P(S)CH=CH_2$, which were performed using the 3G, 3G*, 4-31G and 4-31G* basis sets. It was demonstrated that at least the 4-31G split-valence basis set is required to achieve the proportionality of the calculated orbital energies ε_m to the experimental ionisation potentials IP_m in phosphorylated allenes and alkenes. An increase in the energy of the $\pi(C=C)$ orbital in the molecules under consideration, compared to the energy of the same orbital in the ethylene molecule, is associated predominantly with the inductive effect of the $P(O)Cl_2$ and $P(S)Cl_2$ groups.

In polyfunctional alka-1,3-diene-2-phosphonates, coplanarity and consequently conjugation in the alka-1,3-diene fragment are disrupted.[101] This is evident from both experimental studies (IR and ^1H and ^{31}P NMR spectroscopy) of these compounds and semiempirical CNDO/2 calculations. The energetically most favourable conformation was found to correspond to rotation about the central C–C bond in the 1,3-diene fragment of the chain by a torsion angle of $\varphi = 75°$ (in fact, the *gauche* conformation). Hence, alkadienephosphonates containing a branched carbon skeleton should be considered as molecules with two isolated fragments, *viz*., the chlorovinyl and vinylphosphonate groups. By contrast, 3-chlorobuta-1,3-dienephosphonates are electron-conjugated systems.

Experimental and theoretical conformational analysis of 2-phosphorus-substituted acrylonitriles by various methods (X-ray diffraction analysis, IR spectroscopy, dipole moments, quantum-chemical calculations) provides a detailed and non-

Table 4. Results of quantum-chemical calculations [DFT/B3LYP/6-31G(d)] of the relative energies and dipole moments of the possible conformers of α-cyano-β-furyl-β-hydroxyvinyldiphenylphosphine oxide.[102]

Z Isomer			*E* Isomer		
conformers	ΔE (see [a])	μ/D	conformers	ΔE (see [a])	μ/D
	19.05	9.30		22.60	10.87
	15.91	8.32		16.91	8.76
	14.59	8.76		22.78	11.51
	15.54	7.39		20.08	8.88
	17.37	6.53		17.30	4.58
	0.0	0.48		12.75	4.12
	12.72	5.56		12.87	4.26
	0.72	1.08		11.81	4.24

[a] In kcal mol^{-1}.

contradictory description of their structures in the individual state and solution.[102] Calculations using B3LYP/6-31G(d) hybrid density functional theory justified the favourability of the *Z-s-cis* arrangement of the hydroxy and diphenylenephosphine oxide substituents relative to the C=C bond in the molecules under consideration, the conformation being stabilised by intramolecular hydrogen bonding. Table 4 gives the relative energies and polarities of the possible conformers of α-cyano-β-furyl-β-hydroxyvinyldiphenylphosphine oxide. Analysis of the relative energies of the geometric isomers provides unambiguous evidence that the *Z* configuration is favourable; the conformers with the C=C bond in the *s-cis* orientation with respect to the P = O (or P=S) bond correspond to the global energy minimum.

Quantum-chemical calculations of the polarities were carried out for phosphorus-containing acrylonitriles[102] $(EtO)_2P(O).C(CN)=C(OH)(2\text{-Fu})$, $Me(EtO)P(O)C(CN)=C(OH)(2\text{-Fu})$, $Ph_2P(O)C(CN)=C(OH)(2\text{-Fu})$ (where 2-Fu is the 2-furyl substituent) and also for $Ph_2P(O)C(CN)=C(OH)Me$ and $Ph_2P(S)C(CN)=C(OH)Me$ in benzene as the solvent used to determine the dipole moments of these compounds. In these calculations, the influence of the solvent was taken into account using the isodensity polarised continuum model (IPCM).[103] The calculated dipole moments do not differ significantly from their values in the gas phase and are in good agreement with the experimental values measured in solution. These results along with the spectroscopic data indicate that there are no strong interactions between the above compounds and benzene.

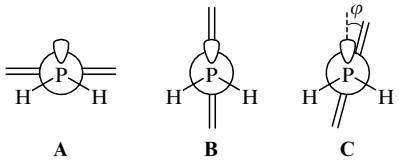
3. Internal rotation about the P – C(sp²)(carbonyl) bond

Data on rotations about the P–C(sp²)(carbonyl) bond are scarce in the literature. Experimental data on the structures of acylphosphine oxides and the corresponding phosphonates and aroylphosphines (dipole moments, ^{13}C NMR spectra) are indicative of a virtually anancomeric equilibrium (*i.e.*, an equilibrium, in which one conformer is predominant) between the *s-cis* and *s-trans* conformations, the percentage of the latter form being as high as 90%–95%.[5] For other OPCs containing a P–C(sp²)(carbonyl) bond (triacylphosphines), *ab initio* and semiempirical calculations of the barriers to rotation about the P–C bond give similar estimates (~5 kcal mol^{-1}).[104] The authors of the cited study believed that semiempirical calculations (CNDO/2) of the barriers to pyramidal inversion of the P^{III} atom in these compounds gave a more reasonable estimate (14.4 kcal mol^{-1}) than *ab initio* calculations with the minimum STO 3G basis set (28.9 kcal mol^{-1}).

4. Internal rotation about the P – C(sp²)(phenyl) bond

The conformational state of OPCs containing P–Ph bonds have received the most attention. A review[5] has summarised considerable experimental data on the conformations of these compounds obtained by the above-mentioned physical methods. Simultaneously, researchers examined the possibility of conjugation between unsaturated fragments at the phosphorus atom and the lone electron pair of $P^{III}(3+)$ atoms or the P=Y bond (Y = O, S) of $P^{IV}(5+)$ compounds (the formal oxidation states of phosphorus are given in parentheses). Since questions about the relative orientations of the benzene ring and lone electron pair of the P atom, and of the benzene ring and P=Y bond are interrelated, they are generally considered simultaneously.

The structure of phenylphosphine $PhPH_2$ was studied[105] by gas electron diffraction and quantum chemistry (*ab initio* HF/6-31G* and B3LYP/6-31G* calculations). Calculations at the HF/6-31G* level of theory predicted the bisecting conformation (**B**) for the $PhPH_2$ molecule characterised by the LEP–P–C–C torsion angle $\varphi = 0^\circ$, whereas calculations at the B3LYP/6-31G* level predicted the skewed conformation (**C**) with the asymmetrically arranged phenyl substituent and angle $\varphi = 20^\circ$. Electron diffraction data were interpreted using the results of calculations by the HF/6-31G* method, and some geometric parameters of the molecule were taken from the quantum-chemical data.

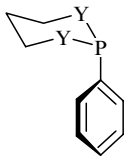


A **B** **C**

The results of numerous studies of phenylphosphine and its derivatives PhPXY by photoelectron spectroscopy using the data from semiempirical calculations were summarised in a monograph.[106] Photoelectron spectroscopy demonstrated that the lone electron pair of the phosphorus atom in the $PhPCl_2$ molecule lies in the plane of the phenyl group, *i.e.*, it is orthogonal to the orbitals of the benzene π system. Due to the absence of the n–π interaction, the photoelectron spectrum showed no splitting of the π levels of the arene fragment. However, this splitting was observed in the photoelectron spectrum of $PhPH_2$, indicative of a considerable contribution of conformation **A**. It should be noted that if the spectra were interpretated in terms of the free internal rotation model about the P–C bond instead of the model of discrete conformers (which is conventionally used in the conformational analysis of OPCs), the theoretical spectrum and band splitting would also be consistent with experimental data.

By contrast, calculations using the Hartree–Fock method (HF/6-31G*, HF/6-31G** and HF/6-311G**) for the $PhPH_2$ molecule gave the total energy minimum for the bisecting conformation **B** and the saddle point for structure **A** (the rotation barriers are 1.25, 1.06 and 1.06 kcal mol^{-1}, respectively). Calculations including correlation energy at the B3LYP/6-31G* and DFT/PBE/TZ2P levels of theory predicted the skewed structures **C** with φ angles of 20° and 45°, respectively, as the favourable conformations. Structures **A** and **B** correspond to saddle points on the potential energy surface with imaginary frequencies of 82 and 73 cm^{-1}, respectively. The barriers to internal rotation are low and similar in height (~0.2 kcal mol^{-1}). On the whole, aromatic derivatives of elements of row three of the Periodic Table (such as $PhPH_2$ or PhSH) are characterised by low barriers to internal rotation and high conformational flexibility. It is this factor that accounts in part for the contradictory experimental data.

In the above-cited review,[7] intramolecular electronic interactions in tri- and tetracoordinate phosphorus compounds were analysed on the basis of available structural data, and an example of the forced coplanar orientation of the lone electron pair of the P atom and the π orbitals of the phenyl group was given. In compounds containing 1,3,2-dioxa- (Y = O) or 1,3,2-dithiaphosphine (Y = S) rings, strong 1,3-*syn*-axial interactions between the H atoms at positions 4 and 6 of the heterocycle and the *ortho*-H atoms of the axial phenyl group are responsible for the rotation of the arene ring by an angle of 90° with respect to the symmetry plane of the molecule in which the lone electron pair of the P atom lies. In this conformation, n,π conjugation is theoretically possible, but weak.



A systematic consideration of the steric and electronic characteristics of bonds involving P^{III} and P^{IV} demonstrated that specific orbital interactions between the arene fragment and the low-lying unoccupied π* and σ* orbitals of the bonds with phosphorus are of great importance. In a study,[7] an appropriate classification, in our opinion, of the structural features of OPCs was proposed in the context of the perturbation theory. The nature of the orbital effects discussed in this study is closely related to the conformational characteristics of the interacting orbitals. For example, n,σ* hyperconjugation plays the major role in the case of a *trans* orientation of the lone electron pair and

polarised σ bond, the acceptor properties of which are most pronounced in the presence of destabilising n,n repulsion between the lone electron pairs of the adjacent heteroatoms involved (α effect). In the case of a parallel orientation of the π orbitals of the benzene ring and pseudo-π* orbitals of the PX_2 fragment, the n,σ* interaction in arylphosphines $ArPX_2$ plays the major role and stabilises the bisecting conformation. The same structural features are observed in molecules containing P–O–Ar fragments.

A recent study [107] of the molecular structure of triphenylphosphine by gas electron diffraction and *ab initio* calculations at the HF/6-31G* level of theory demonstrated that the Ph_3P molecule has C_3 symmetry with a torsion angle φ of 32(3)°. The structure of the diphenylphosphine molecule Ph_2PH determined by gas electron diffraction and *ab initio* calculations at the same level of theory [108] is asymmetrical, the torsion angles at the P–C bonds being 65(7)° and 154(7)°.

It should be noted that the favourable structural factors are necessary but insufficient to account for the occurrence of p,π interactions alone. Apparently, the assumption of the presence of these interactions with the P^{III} atoms in OPCs should be considered with caution taking into account the reasons stated in the debated papers [109–111] and analysis of this problem in the reviews.[5,7] In particular, the authors of the study [112] reasoned that UV spectroscopy is sometimes unsuitable for the detection of p,π conjugation. Nevertheless, several examples [7,113] show that, in favourable molecular conformations, this conjugation can be revealed by quantum-chemical methods.

For example, *ab initio* calculations [113] at the HF/6-31G(d,p) level of theory of the geometry and electronic structures of triphenylphosphine, phenylphosphabicyclo[3.3.1]nonane and the [4.2.1]-isomer of the latter demonstrated that steric repulsion of the bicyclononane fragment causes the phenyl substituent at phosphorus to be located perpendicular to the lone electron pair (Fig. 5). This orientation is favourable for n,π conjugation, which, in the authors' opinion, is responsible for high catalytic activity of both of the phosphorus-containing bicyclononanes. The sterically unhindered $PhPH_2$ and Me_2PPh molecules do not adopt this conformation and, correspondingly, their catalytic activity is low.[113] The calculated geometric parameters of the molecules agree well with X-ray diffraction data.

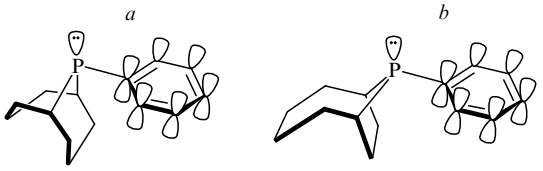


Figure 5. Stable conformations of phenylphosphabicyclo[3.3.1]nonane (*a*) and phenylphosphabicyclo[4.2.1]nonane (*b*).[113]

Semiempirical calculations,[114] where the angle of rotation of the PX_2 group relative to the plane of the benzene ring was varied, also predicted the bisecting conformation as being the major one for the $PhPF_2$, $PhPCl_2$ and $PhP(CN)_2$ molecules. However, the authors of this study suggested that there is an equilibrium between two of the conformations of $PhPH_2$ and $PhPMe_2$, and an n,π interaction can occur in one of these.

In an earlier study,[115] theoretical conformational analysis of the R_2PPh (R = H, F, Cl, Br, I, Me, Et, Pr^i, Bu^t) and MeXPPh (X = H, F, Cl, Br) molecules by the atom–atom potential method revealed flat minima in all conformational energy curves corresponding to the bisecting conformer. This provides evidence that the orientation of the Ph groups can be varied about the bisecting R_2P (or MePX) plane within ±20°, even in the case of di-*tert*-butylphenylphosphine. Therefore, the conformations of the above phenylphosphines do not rule out an insignificant p,π interaction in these systems. Nevertheless, the conformations of aryl-substituted OPCs favourable for p,π interactions (and, correspondingly, for the manifestation of these interactions in the spectra and properties) in this class of compounds are exceptions to this rule.

Semiempirical (CNDO/2, INDO, MINDO/3) calculations for the structures of diphenyl- and triphenylphosphines predicted the conformations that are unfavourable for conjugation between the lone electron pair of the phosphorus atom and the π system of the benzene ring.[116] Analysis of the results of semiempirical quantum-chemical calculations and spectroscopic characteristics (UV, IR, Raman) of *p*-carboxyphenyl-substituted dialkylphosphines and dialkylamines *p*-$HOOCC_6H_4EMe_2$ (E = P, N) showed that in the orthogonal conformation, the p,π conjugation with the Ph fragment for a Me_2P group is half as strong as that observed for a Me_2N group, and, if the conformational equilibrium is not considered, this conjugation is weaker by a factor of 3–4.[117] Semiempirical (MNDO) and *ab initio* (HF, MP2) calculations for the $RPCl_2$ (R = Me, $ClCH_2$, CF_3, CCl_3) and $ArPCl_2$ molecules and investigations of these compounds by ^{35}Cl NQR spectroscopy led the authors of the study [118] to conclude that enhancement of steric interactions between the R and Cl substituents (the PCl_2 group) and between the Ar and Cl at the P^{III} atom results in an increase in the s character of the lone electron pair of the chlorine atom. In a recent study,[119] the influence of the substituents on the structure of aromatic phosphines was investigated by the *ab initio* [MP2/6-311++G/(U)B3LYP/6-31G(d)] method, and the P–X bond dissociation energies of *para*- and *meta*-substituted phenylphosphines *p*-YC_6H_4PHX and *m*-YC_6H_4PHX (X = H, F, Cl; Y = H, Me, NH_2, NMe_2, OMe, OH, SMe, *etc*.) were evaluated.

Cyano derivatives of tri- and tetracoordinate phosphorus with one or two Ph substituents [$PhP(CN)_2$, Ph_2PCN, Ph(Et)PCN, $Ph_2P(O)CN$] were studied by the Kerr effect and dipole moment methods. These studies revealed structures in which the planes of the benzene rings virtually eclipse the lone electron pair of the phosphorus atom [$PhP(CN)_2$, φ = 70°] or the phosphoryl group [$Ph_2P(O)CN$, φ = 60°]. This excludes the possibility of efficient overlapping of the lone electron pair of the P atom with the π system of the benzene ring.[120] Therefore, it was experimentally demonstrated that the introduction of a strongly electron-withdrawing and small nitrile group directly at the phosphorus atom had no effect on the conformational behaviour of the phenyl fragments at the P^{III} and P^{IV} atoms and is not manifested in intramolecular electronic interactions involving these atoms. More recent [121] semiempirical (PM3) and *ab initio* (RHF/6-31G**) calculations for the above-mentioned molecules also provided evidence that nearly-bisecting conformations are energetically favourable (Fig. 6).

The possibility of conjugation between the π-electron system and the lone electron pairs of P^{III} and P^{IV} atoms was actively discussed in the 1970s and 1980s. More recent studies did not confirm the initial assumption (which was made by many researchers) that trivalent phosphorus compounds, like nitrogen compounds, should be stabilised by p,π conjugation. Tsvetkov and Kabachnik [122] analysed considerable experimental data and concluded that this conjugation in arylphosphines was inhibited. Later on,[123] dimethylphenylphosphine was studied by gas electron diffraction and IR and Raman spectroscopy. The authors of the cited study assumed the presence (along with that of an orthogonal conformer) of up to 30% of a conformer in which the mutual arrangement of the Ph group and the lone electron pair

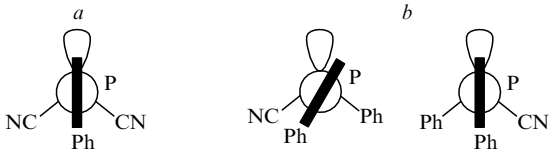


Figure 6. Newman projections of the stable conformers of dicyanophenylphosphine (*a*) and cyanodiphenylphosphine (*b*).[121]

of the P^{III} atom was favourable for conjugation. It was noted that the energy difference between these conformers was as small as 0.40 – 0.63 kcal mol^{-1}, and the shape of the internal rotation potential was determined primarily by steric interactions. Compared to these interactions, p,π conjugation is substantially weaker, if existent at all. The same conclusion was reached in a study [124] based on the results of IR, X-ray fluorescence and Raman spectroscopy. Therefore, the following conclusion can be drawn from all the available data: both experimental methods and calculations demonstrate that conformations favourable for most P^{III} compounds containing one aryl substituent are those in which the aromatic ring is coplanar with the lone electron pair of the phosphorus atom, hindering p,π conjugation.

In monoaryl derivatives of $P^{IV}(5+)$, the arene ring is coplanar with the P=O and P=S bonds, which is favourable for its conjugation to the phosphorus-containing group. In contrast, steric interactions play a decisive role in diaryl- and triaryl-containing OPCs (regardless of the valence state of the phosphorus atom) and the least hindered conformations become favourable. This is evident from both experimental data and the results of *ab initio* calculations. Recall that calculations by the atom – atom potential method performed by Baranov, Dashevskii, Medved' and Kabachnik more than 20 years ago [125, 126] predicted, on the whole, the same conformational pattern.

Without discussing the role of d orbitals in the formation of bonds involving phosphorus in detail, we shall give several examples. Estimations of the contribution of d-orbital interactions in the $Ph_2P(Y)C_6H_4OH$-*o* molecules (Y = O, S or Se) by semiempirical methods (CNDO/2, CNDO/C) [127] showed that the d(P) ← s,p(O,S,Se) charge transfers calculated from the overlap populations of phosphorus, sulfur and selenium AOs are substantially larger than the s,p(P) → d(S,Se) back bonding. The occurrence of strong electronic interactions between the PY groups and aromatic fragments in these molecules was also confirmed by CNDO/C calculations of the electronic spectra of these compounds. However, in an earlier study,[128] where the electronic structures of selected OPCs containing phosphoryl groups were analysed by similar methods (CNDO/2 and INDO) and these data were compared with the results of *ab initio* calculations, it was inferred that the d orbitals played a negligible role in binding. Therefore, estimations of the contribution of d-AOs of P atoms to OPC bond systems by semiempirical methods often give contradictory results.

5. Internal rotation about P – O and P – S bonds

Experimental studies [5, 129 – 152] have demonstrated that internal rotation about P – O, P – S and P – Se single bonds in tri- and tetracoordinate phosphorus compounds (scarce data) is, in principle, similar to internal rotation about P – C(sp^3) bonds. However, there are substantial differences in their conformational behaviour due to anomeric n – σ* interactions between the lone pairs of the heteroatoms (O, S, Se) and the antibonding orbitals of the adjacent P – X bonds involving the phosphorus atom.

By the mid-1980s, semiempirical quantum-chemical calculations had been carried out for a series of OPCs containing P – O and P – S bonds. A few publications on *ab initio* calculations were also reported (these studies are considered in other reviews [5, 7]). In most cases, the staggered *gauche* or *trans* conformations are favourable for acyclic OPCs regardless of the coordination of the phosphorus atom (P^{III} or P^{IV}), the nature of the heteroatom bound to phosphorus and the number of internal rotation axes.[5] In the case of internal rotation about exocyclic P – X bonds (X = O, S, Se), the staggered conformations of 1,3,2-dioxaphosphorinanes are also more stable, regardless of the nature of the heteroatom adjacent to the phosphorus.[5, 27] In solutions of 1,3,2-dioxaphospholanes, the general characteristic features are responsible for a *cis* orientation of irregular (*i.e.*, those having additional degrees of freedom associated with their own internal rotation) exocyclic substituents with respect to the lone electron pair of phosphorus atom or the P=O and P=S bonds.[5]

Exceptions to these rules are attributable to additional intramolecular interactions (hydrogen bonds, high dipole moments at the adjacent atoms, *etc.*).[5] In one review,[153] it was noted that P^{III} derivatives are characterised by stabilisation of one conformer, whereas an equilibrium between several rotamers is often observed for P^{IV} compounds. The differences in conformations of the molecules in the gas phase, liquid state (solution) and in crystals can be associated with crystal packing forces. In most examples, the conformation observed in crystal form is also present as one of the components of the conformational equilibrium in the liquid state and solution. However, this is not always the case, and the major conformers in solution can differ from the molecular conformation found in crystals.

a. Molecules with one internal rotation axis

Semiempirical quantum-chemical methods predict that the staggered *gauche* and (or) *trans* conformations of $MeOPF_2$ and $MeOPCl_2$ molecules are favourable,[154 – 156] which is in agreement with the gas electron diffraction data and dipole moment measurements. The geometric parameters of difluoromethoxyphosphine calculated by *ab initio* methods [157] agree well with the corresponding experimental parameters. Semiempirical calculations (CNDO/2) for thio derivatives of trivalent phosphorus acids, such as Cl_2PSMe, Et_2PSMe, $MeP(SMe)_2$ and $P(SEt)_3$, revealed a conformational equilibrium between the staggered synclinal and antiperiplanar conformations resulting from rotation about the P – S bond.[156, 158] This is consistent with the experimental dipole moment and Kerr constant data as well as with the vibrational spectra of these compounds.[5]

At least four staggered *gauche* and *trans* conformations were found for dichloropropyl and dichloroisopropyl thiophosphites $Pr^n-S-PCl_2$ and $Pr^i-S-PCl_2$ by Raman spectroscopy and quantum-chemical calculations.[159] In this case, as in the case of rotation about the P – C(sp^3) bonds (see Section II.1), only one conformer with the lone pair of the P atom in the *trans* orientation with respect to the C – S bond is present in crystals, whereas in the liquid state and solution, rotation about the P – S, S – C and C – C bonds leads to dynamic equilibrium between synclinal and antiperiplanar conformations. It was also noted that variation in length and branching of the alkyl substituent at sulfur in a series of thiophosphites $RS-PCl_2$ (R is alkyl) does not lead to a qualitative change in barriers to internal rotation about the P – S bond, *i.e.*, the conformation with a *trans*-R – S bond relative to the lone pair of the P atom remains energetically favourable for all members of the series.

Several studies have been devoted to *ab initio* calculations of the structures of fluorophosphinates R′(F)P(O)OR, where R = Me, Pr^i, CH(Me)Bu^t, cyclo-C_6H_{11} and R′ = Me, Et.[160, 161] Calculations at all the levels of theory used in these studies [RHF/6-31G(d), MP2/6-31G(d), B3LYP/6-31(d), 3-21G*] revealed one stable staggered conformer in which the O – C(R) bond is perpendicular to the P – F bond due to the anomeric effect. Figure 7 shows the potential energy curve for internal rotation about the P – O(R) bond in these molecules. The ^{31}P and ^{13}C NMR spectra of Me(F)P(O)OMe are also indicative of the occurrence of one stable conformer.[160] (In the cited study, the earlier interpretation of electron diffraction data was corrected.)

It should be noted that *ab initio* calculations of the molecular structures of methyl hypophosphite $H_2P(O)OMe$, dimethyl phosphite $HP(O)(OMe)_2$ and trimethyl phosphate using different basis sets (STO-3G*, 3-21G* and 4-31G*) gave different results.[162] The relative energies of stable conformers resulting from internal rotation about the P – O bond and the changes in the dipole moments of the methyl hypophosphite and dimethyl phosphite molecules depending on the O=P – O – Me torsion angle were calculated using the STO-3G* basis set. These calculations showed that there was a conformational equilibrium between two forms, with the *cis* conformation predominating. Calculations using alternative basis sets predicted that the *trans* conformation was more stable. It was noted that the energy difference

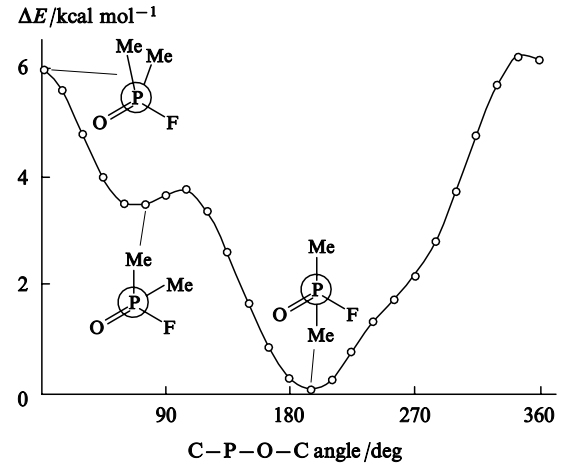


Figure 7. The curve of the potential energy of rotation about the P—O bond (directed perpendicular to the plane of the page) for the MeOP(O)FMe compound.[160]
The geometric parameters were fully optimised at the B3LYP/6-31G* level of theory, except for the C—P—O—C torsion angle.

ΔE between the conformers was insignificant (0.08 kcal mol^{-1} for methyl hypophosphite and dimethyl phosphite and 0.9 kcal mol^{-1} for trimethyl phosphate). *Ab initio* calculations (RHF/6-31G*) for the $MeOP(CN)_2$ and $MeP(O)(CN)_2$ molecules, which were carried out [163] to study the tautomeric and conformational stability of these compounds, revealed a deep minimum for the *trans* configuration of Me—O—P—LEP in dicyanomethoxyphosphine (Fig. 8). In contrast, three minima corresponding to the staggered *gauche* and *trans* conformations of dicyanomethylphosphine oxide are observed in the potential curve.

Analogous results were obtained for dicyanomethoxyphosphine in the study,[121] where the *trans*-Me—O—P—LEP structure was demonstrated to be the favourable conformation with the lowest energy, regardless of the method used for calculation (PM3, RHF/6-31G**). This conclusion is in complete agreement

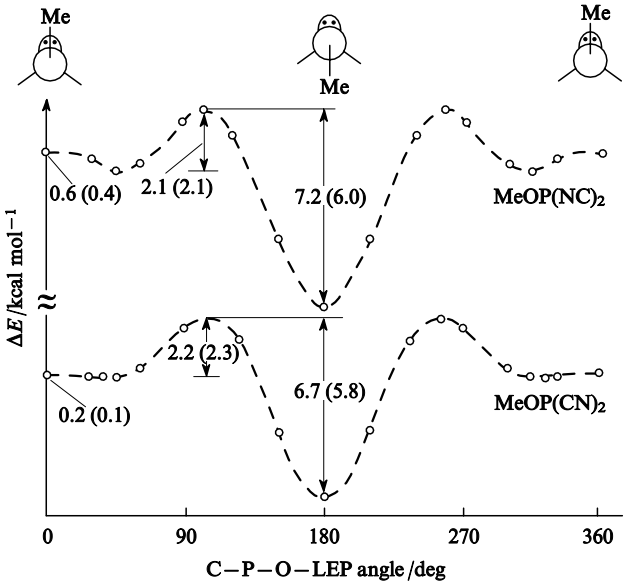


Figure 8. Potential curves of the internal rotation about the P—O bond and barriers to transition for the $MeOP(CN)_2$ and $MeOP(NC)_2$ molecules calculated by the MP2/6-31G* method.
The potential barriers calculated at the RHF/6-31G* level [164] are given in parentheses.

with experimental data [165] and with the results of other *ab initio* calculations,[164] including electron correlation (MP2 = FULL/6-31G*). In the latter case, a deep minimum was found in the potential curve of internal rotation, corresponding to the *trans* arrangement of the MeO group with respect to the lone pair of the P atom.

It should be emphasised that the *trans* conformer appeared to be favourable for $MeOP(CN)_2$ regardless of the quantum-chemical method used [PM3 and 6-31G**,[121] 6-31G* and MP2 = FULL/6-31G* (see Ref. 164)]. Stabilisation of the *trans* conformation of this compound is, apparently, associated with two factors acting in the same direction, *viz*., Coulombic attraction between the oppositely directed P → CN and Me → O dipoles and the *gauche* effect. Apparently, due to the presence of the polar P—CN fragment with a large charge separation, interactions between the polar bonds play a major role in the stabilisation of conformations. The staggered *gauche* and *trans* conformations also result from rotation about the P—O bonds in phosphonite $(MeO)_2PCN$ and phosphonate $(MeO)_2P(O)CN$.[121] Therefore, in some cases the favourable conformations with respect to the P—O bond can be transferred to related OPC molecules containing two or three identical internal rotation axes.

Somewhat unexpected results were obtained [166] in *ab initio* calculations of the molecular structure, conformational stability, vibrational frequencies and intensities of the absorption bands in the IR and Raman spectra of methyl dimethylphosphinite Me_2POMe. Internal rotation about the P—O bond gives rise to two favourable conformers with the lone electron pair of the P atom in 'nearly *cis*' and 'nearly *trans*' orientations relative to the methyl group, the cisoid structure being more stable by more than 1.5 kcal mol^{-1}. Similar results were obtained in photoelectron spectroscopy and semiempirical quantum-chemical calculations (MNDO and INDO) for the $Me_2P—XMe$ compounds, where X = S or Se (and their arsenic analogues).[167] For these compounds, intermediate conformations with the φ angle varying between 0° and 180° rather than the ideal *cis* or *trans* conformations are stabilised. A study of the molecular structures of Me_2PSMe and Ph_2PSEt by photoelectron spectroscopy in combination with quantum chemistry (CNDO/2 and *ab initio* calculations using various basis sets from 3G to 6-31G) [168] also led the authors to conclude that dimethyl methylthiophosphinite adopts a distorted (toward *cis*) *gauche* conformation with a torsion angle of 32°.

Semiempirical calculations demonstrated that methyl di(thiomethyl) phosphonite $MeP(SMe)_2$ with two internal rotation axes also adopts an 'intermediate' favourable conformation, in which the Me—P—S—Me torsion angles have similar values (17° and 14°).[168] If the photoelectron spectrum of this compound is modelled by an equilibrium between two conformations, the *gt* conformation with torsion angles of −45° and 180°, should be included. This is in complete agreement with the results of calculations using the HF/6-31G** and DFT methods at the B3LYP/6-31G** and PBE/TZ2P levels of theory (Table 5). The conformational equilibrium of phenyl di(thioethyl) phosphonite, which also has two internal rotation axes about the P—S bond, always includes the g_1g_2 conformation, in agreement with the earlier experimental data.[168]

The existence of distorted conformations of OPCs in the case of a flat potential energy curve for the internal rotation about the P—O bond was demonstrated in principle by semiempirical quantum-chemical calculations performed by Gorenstein *et al*.[169] in the 1970s.

Ab initio calculations for the methyl phosphinate $Me_2P(O)OMe$, dimethyl phosphite $HP(O)(OMe)_2$ and dimethyl phosphonates $MeP(O)(OMe)_2$, $(MeO)_2P(O)CH_2OH$ and $(MeO)_2P(O)CH(OH)CMe_2CH_2NMe_2$ (HF/6-31G**, B3LYP/6-31G* and DFT/PBE/TZ2P), performed by one of the authors of this review, showed that, regardless of the number of P—O bonds (one or two) in these compounds and the basis set used in calculations, *gauche* (one internal rotation axis) or *gauche*,*gauche*

Table 5. Relative energies (ΔE/kcal mol^{-1}) of the stable conformers of the $P(OMe)_3$, Me_2PSMe, $MeP(SMe)_2$ and $P(SMe)_3$ molecules (HF/6-31G** and DFT methods at the B3LYP/6-31G** and PBE/TZ2P levels of theory).[a]

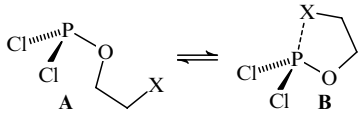
Conformer	Calculation method		
	HF	B3LYP	PBE
$P(OMe)_3$			
ggt	0.00	0.00	0.00
gtt	1.38	1.39	1.77
ttt	5.75	5.75	5.29
Me_2PSMe			
c	0.00	0.00	0.00
t	0.93	0.84	1.12
$MeP(SMe)_2$			
gt	0.00	0.00	0.00
gg	1.09	0.84	0.56
tt	4.68	4.06	4.42
$P(SMe)_3$			
$-ggt$	0.02	0.00	0.00
ggt	0.00	0.32	0.51
ggg	0.59	1.09	0.99
gtt	2.89	2.38	1.53

[a] V V Zverev, unpublished data.

(two internal rotation axes) conformations are the most favourable rotamers. These conformations are characterised by energy minima in the potential curves, in complete agreement with the experimental data.

In contrast, *ab initio* HF/6-31G** calculations [170] and calculations including electron correlation (see Tables 1 and 2) for phosphorus acids H_2POH, $H_2P(O)OH$ and $H_2P(S)OH$ led to three different situations. The eclipsed *cis* and *trans* conformations were found for H_2POH, the staggered *gauche* and *trans* conformations were revealed for $H_2P(O)SH$, whereas the energy difference between the *cis* and *gauche* conformations of $H_2P(S)OH$ is negligibly small. In the vicinity of *cis*–*gauche* conformations, the potential energy surface resembles a plateau. Unlike the neutral H_2POH molecule, the most favourable conformation of the radical cation of this compound is *gauche*. The inclusion of the solvent effect in calculations using the SCRF HF/6-31G** method was demonstrated to lead to the elongation of the P=O bond and slight changes in the geometric parameters.[170] The calculated energies of the rearrangement of the molecule and solvation shell upon ionisation are slightly higher than the experimental values.

An analysis of normal vibrations in the IR and Raman spectra of phosphorodichloridates $R(CH_2)_2O-PCl_2$ (R = Et, OMe, Cl, SCN) and molecular mechanics calculations [171–173] demonstrated that the *anti* (*trans*) and *gauche* conformers with respect to the P–O and C–O bonds are favourable for alkoxy groups. The energy differences between these conformations are small (0.9 kcal mol^{-1} for the P–O bond and 0.8 kcal mol^{-1} for the C–O bond). In the liquid state, *gauche* conformations are favourable. At low temperatures, for R = Cl, these conformations are frozen out and the *trans* conformer becomes the most stable. In the liquid state, all compounds are characterised by a conformational equilibrium between the *gauche* conformation (**A**) and 'bent' conformation (**B**). In various studies,[171–173] it has been suggested that there is an additional intramolecular interaction between the phosphorus and oxigen (sulfur, chlorine) atoms in the latter conformer.



b. Molecules with two and three internal rotation axes

Semiempirical [MNDO and CNDO/2(s,p,d)] calculations of dialkyl phosphites $(RO)_2P(O)H$ (R = Me, Et, Pr, Bu, C_5H_{11}, C_6H_{13}) substantiated the fact that the staggered *gauche* and *trans* conformations are energetically favourable, regardless of the method used.[174] Interestingly, a very small energy difference between the major conformer and the second most energetically favourable conformer (0.06 eV) was obtained in all approximations. An analogous conclusion about stability of the staggered *gauche*,*gauche* (*gg*) and *trans*,*gauche* (*tg*) conformations was drawn in an earlier experimental study of dimethyl phosphite and its deuterated analogue.[175] These conformations were evident from vibrational spectra measured at different temperatures, in different aggregation states and in solvents of different polarity and concentration, and were supported by force constant calculations.

Similar results were obtained by semiempirical calculations for trialkyl phosphate molecules [176, 177] (an equilibrium mixture of C_3 and C_1 rotamers). The conformational equilibrium was also evident from photoelectron spectra. In the cited study, a new assignment of the bands in the spectra was made and the ionisation potentials were refined. In continuation of these studies, the first five ionisation potentials were determined by mathematical processing, and the conformational inhomogeneity of samples was found to influence the photoelectron spectra of trimethyl and triethyl phosphates.[178] In the spectra of more complex phosphates, the contributions of different conformers became indistinguishable because of overlapping of the bands corresponding to the n_σ and σ orbitals of similar energies.

The conformational equilibrium between rotamers of trimethyl phosphate with C_3, C_1 and C_s symmetry corresponding to three minima on the potential energy surface (PES) was found in the study [179] with the use of *ab initio* methods (6-31G* and 6-31G** basis sets). The energy of the conformer with C_1 symmetry is higher than that with C_3 symmetry by 0.56 kcal mol^{-1}, and the energy of the C_s conformer is higher than that of the C_3 conformer by 1.43 kcal mol^{-1}. The study of triethyl phosphate [180] by the semiempirical AM1 method and IR spectroscopy revealed two conformers with C_1 symmetry.

Theoretical conformational analysis was carried out for a wide range of tetravalent phosphorus compounds containing one, two or three P–O rotation axes: $H_2P(O)OH$, $HP(O)(OH)_2$, $(HO)_3PO$, $MeP(O)(OH)_2$, $HP(O)(OMe)_2$, $Me_2P(O)OMe$, $Me_3P(O)$, $MeP(O)(OMe)_2$ and $(MeO)_3PO$.[181, 182] In the study,[181] the authors used the molecular mechanics method (MM3) and parameters chosen from the results of *ab initio* calculations of the conformations of several phosphates (HF/6-31G**). Figure 9 shows the plots of the relative energies of dimethyl phosphinate and trimethyl phosphate *vs*. the angle of rotation about the P–O bond. The *gauche* and *trans* conformations appeared to be favourable for these esters, whereas the *cis* conformation was favourable for dimethylphosphinic acid.

The possibility of P^{IV} acids adopting eclipsed conformations was also discussed above. It should be noted that the *cis* conformation of dimethylphosphinic acid and analogous compounds was found only in calculations by the Hartree–Fock method, whereas calculations by the MP2, MP4 and DFT methods using the correlation energy density functional predicted that the lowest energy corresponds to the staggered *gauche* structures, and the saddle point on the potential energy surface corresponds to the *cis* conformation (see Table 2). The parametrisation of the MM3 force field on the basis of *ab initio* calculations at the RHF/6-31G* level of theory includes all the errors of the latter method. Here we are dealing with the relative energies of the conformations rather

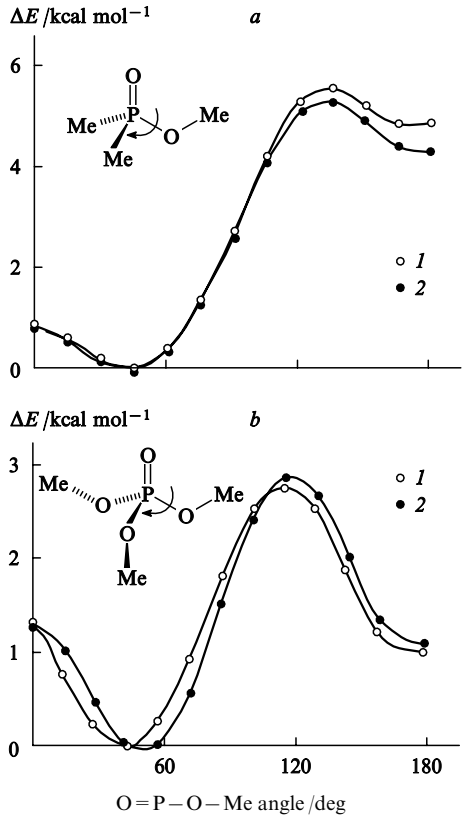


Figure 9. Rotation profiles [HF/6-31G** (*1*) and MM3 parameterised from the results of HF/6-31G** calculations (*2*)] for the O=P−O−Me fragment in methyl dimethylphosphinate (*a*) and trimethyl phosphate (*b*).[181]

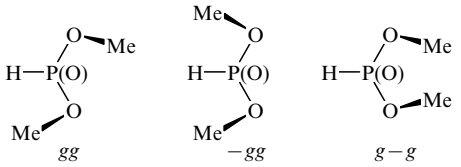
than with a considerable deformation of the overall calculated potential surface.

Ab initio MP2/6-31+G* and MP2/6-31G* calculations for the methyl phosphinate, dimethyl phosphonate, trimethyl phosphate and hypophosphorous, phosphorous and phosphoric acids revealed[182] the global minimum in the energy curve for R−O−P=O torsion angles of 35–58° corresponding to the *gauche* conformation (in some cases, the conformation is slightly distorted towards the *cis* conformation). Analogous results were obtained for P^{IV} compounds at other levels of theory (see Tables 2 and 6). Phosphorous and phosphoric acids are characterised by the presence of a second minimum at 180° (a *trans* conformation). The barrier to rotation about the P−O bond was estimated at 5 kcal mol^{-1}. Calculations using the molecular mechanics method including interactions of the lone electron pairs for dialkyl phosphites $(RO)_2P(O)H$ demonstrated that these molecules can adopt at least two stable conformations of similar energy,[184] one of which is the above-mentioned *gauche* conformation distorted toward the *cis* conformation.

Conformational analysis of dimethyl phosphite in aqueous solution by the DFT method[185] demonstrated that solvent reorganisation plays an important role in the conformational equilibrium between the *gauche*,*gauche* and *gauche*,*trans* conformations favourable for these compounds. In these calculations, the solvent was taken into account by the isodensity polarised continuum model (IPCM). Conformational analysis of this compound in the pure liquid state (dielectric permeability $\varepsilon = 34.3$) and in carbon tetrachloride by the *ab initio* self-consistent reaction field (SCRF) method with a fixed cavity, in which the solute is embedded, at the HF/6-31G** level of theory, also showed that solvent reorganisation plays an important role in the equilibrium between the above-mentioned conformations (Table 6). The molar fractions of the conformers of dimethyl phosphite in polar solvents calculated by the SCRF method are equal to their empirical values and account for the kinetic data of this compound's homolytic reactions.[183]

The results of theoretical studies of the conformations of the $HP(O)(OMe)_2$ molecule by the Hartree–Fock method were compared with the results obtained using density functional theory (see Table 6).[77,183]

Calculations of the conformations of $HP(O)(OMe)_2$, $MeP(O)(OMe)_2$ and $C_{60}C(CO_2Me)[P(O)(OMe)_2]$ using the PM3 method predicted that the $-gg$ orientation of the methoxy groups relative to the P=O bond (which is directed perpendicular to the plane of the figure) corresponds to the most stable conformation.



The $-gt$ and tt conformers are less stable, and their energies are lower than that of the $-gg$ conformation by 2 and 4 kcal mol^{-1}, respectively. However, *ab initio* calculations at HF/6-31G* and MP2/6-31G* levels and by the density functional theory with two different exchange-correlation functionals for $HP(O)(OMe)_2$ demonstrated that the gg rather than $-gg$ conformation is most stable, whereas the energies of the less stable $-gt$ and gt conformers are lower than that of the gg by $\sim$2 kcal mol^{-1}. Analogous results were obtained for $MeP(O)(OMe)_2$. Analysis of the potential energy surfaces for the $(MeO)_2P(O)H$ and $MeP(O)(OMe)_2$ molecules showed[77] that the gg and $-gg$ structures correspond to stationary points, but only one of these points is a local minimum ($-gg$ according to calculations by the PM3 method and gg according to calculations by *ab initio* and DFT methods), whereas the second conformation is characterised by a saddle point (gg and $-gg$ according to calculations by the PM3 and *ab initio* methods, respectively).

Semiempirical calculations (AM1, PM3) for *O*,*O*-di(isopropyl) isoxazolinophosphonate, in combination with the dipole moment method, demonstrated the favourability of the staggered *gauche* and *trans* conformations.[186] These recent results agree well with the experimental and calculated data reported in the preceding review.[5]

Examination of the photoelectron spectra and electronic structures of $(MeO)_3P$, $(MeO)_2PNCO$, $MeOP(NCO)_2$ and $P(NCO)_3$ by *ab initio* methods using the STO-3G basis set[187] showed an increase in the first ionisation potential corresponding to the n(P) orbital and in the second ionisation potential corre-

Table 6. Relative energies (kcal mol^{-1}) and torsion angles OPOC(1) (φ_1) and OPOC(2) (φ_2) (deg) of different conformers of the dimethyl phosphite molecule $HP(O)(OMe)_2$ in the gas phase and in a solution with a dielectric permeability of $\varepsilon = 34.3$.[77,183]

Conformer	HF/6-31G*			HF/6-31G* ε			MP2/6-31G*			B3LYP/6-31G*			PBE/TZ2P		
	ΔE	φ_1	φ_2	ΔE	φ_1	φ_2	ΔE	φ_1	φ_2	ΔE	φ_1	φ_2	ΔE	φ_1	φ_2
gg	0.00	30	51	0.09	30	60	0.00	31	58	0.00	30	55	0.00	31	49
−gt	1.91	−32	179	0.00	−44	178	1.76	−40	177	1.71	−36	−179	1.89	−38	177
gt	2.39	27	173	0.77	45	173	2.68	35	172	2.48	30	176	2.39	42	168

sponding to the n(O) orbital, which is gradually transformed into π(NCO) in a series from trimethyl phosphite to triisocyanatophosphine. The non-additive change in the first ionisation potential in this series of compounds, which was noted by the authors of the cited study, is attributable to the fact that the isocyanate group initially replaces the *gauche*-methoxy group on going from trimethyl phosphite to dimethyl isocyanatophosphonite and then replaces the *trans*-methoxy group on going to methyl diisocyanatophosphinite and triisocyanatophosphine. The results of *ab initio* calculations for the $(MeO)_3P$ and $(MeS)_nPMe_{3-n}$ molecules performed in this study (see Table 5) are consistent with the earlier experimental data (the Kerr effect, dipole moments, vibrational spectroscopy, gas electron diffraction).

Investigation of selenophosphate $(MeO)_3P=Se$ by the DFT method (6-311++G**) and temperature-dependent vibrational spectroscopy revealed an equilibrium between conformations [188] of C_3 and C_1 symmetry. Calculations by the DFT method with the 6-31G* basis set for the dicharged dimethyl diphosphate anion [189] demonstrated that staggered conformations resulting from rotation about its P–O bonds are favourable for this anion, the synclinal (*sc*) conformation being more stable than the antiperiplanar (*ap*) conformation due to the anomeric effect.

Vibrational spectroscopy (IR and Raman) and *ab initio* calculations (HF/6-31G*) revealed [190] the staggered *gauche* and *trans* conformations of the modified oligonucleotide chains $[MeOCH_2-P(O_2)OMe-]_n$; the experimental results were in good agreement with theoretical data. Orbital interactions in the stable and metastable conformations of the dimethyl phosphate anion $(MeO)_2P(O)O^-$ were considered, and the favourability of the staggered *gauche*,*gauche* and *trans*,*gauche* conformations was accounted for by stereoelectronic effects.[191] The key geometric parameters of phosphoric acid derivatives were determined by *ab initio* methods [HF/6-31G**, B3LYP/6-31G(d), EDF1/6-31+G(d), B3LYP/6-31+G(d,p)].[192, 193] For the $(EtO)_2P(O)CH_2C(O)X$ compounds (X = Me, Ph, OEt, NEt_2, SEt), the results of the calculations were compared with experimental spectroscopic data (IR and ^{13}C NMR).

Investigation of the vibrational spectra and conformations of phosphorus dithio acids by the molecular mechanics method [194] showed that the conformational equilibrium is shifted to the *trans* and *gauche* conformations of *O*,*O*-dimethyl dithiophosphate due to rotation about the P–O bonds. For *O*,*O*-diethyl dithiophosphate, only the *gauche* orientation of the C–O bonds (in the ethoxy substituents) relative to the P=S group was found. The crystals of the former compound are composed of two staggered conformers, whereas the latter compound is conformationally homogeneous in the solid state.

Experimental and theoretical conformational analysis of silyl, germyl and stannyl derivatives of *O*,*O*-dialkyl dithiophosphates gave interesting results.[195] Photoelectron spectroscopy and calculations (*ab initio*, MNDO and PM3) for $(RO)_2P(S)S-EMe_3$ (R = Me, Et, Pr^i; E = Si, Ge, Sn) demonstrated that the *gauche* and *trans* conformations of the E–S–P=S fragments are favourable. This conclusion is consistent with the results of the earlier experimental conformational studies of acyclic derivatives of phosphorus dithio acids and *O*,*O*-dialkyl *S*-triethylstannyldithiophosphates (dipole moments, the Kerr effect, vibrational spectra).[196–198]

Therefore, semiempirical methods and most *ab initio* methods provide evidence for a threefold barrier to rotation about the P–O bond in OPCs, which is consistent with experimental data on the staggered synclinal and antiperiplanar conformations. It should be noted that this principal fact is virtually independent of the coordination state of the phosphorus atom, the number of internal rotation axes of the molecule and the nature of the substituents at the P atom. The conformational behaviour of various molecules differs primarily in the presence or absence of a conformational equilibrium between staggered conformations. For some molecules, synclinal conformations (+*sc* or −*sc*) are stabilised, whereas antiperiplanar (*ap*) conformations are stable for other molecules. In the presence of two or more internal rotation axes, the conformational equilibrium between two or several energetically favourable and least sterically hindered staggered conformers is, as a rule, observed.

Intramolecular electronic interactions in OPCs have been studied most thoroughly by theoretical methods for tri- and tetracoordinate phosphorus cyanides. The relative contributions of the interactions between the cyano group, on the one hand, and the lone electron pair of the phosphorus atom and the phosphoryl group, on the other hand, to stabilisation of the conformers of phosphorus cyanides were examined.[121] Unlike the n,π conjugation between the lone pair of the phosphorus atom and the benzene ring, this interaction in the P–C≡N system is sterically unhindered. Figure 10 shows the correlation diagram of the energies of the frontier MOs for favourable conformations of the MeO–P(CN)$_2$ (*t*), Ph–P(CN)$_2$ (*c*), $Ph_2P(O)CN$ (−*gc*) and $(MeO)_2P(O)CN$ (*g*−*g*) molecules and the hydrocyanic acid molecule. In the favourable *trans* conformation of MeO–P(CN)$_2$, the

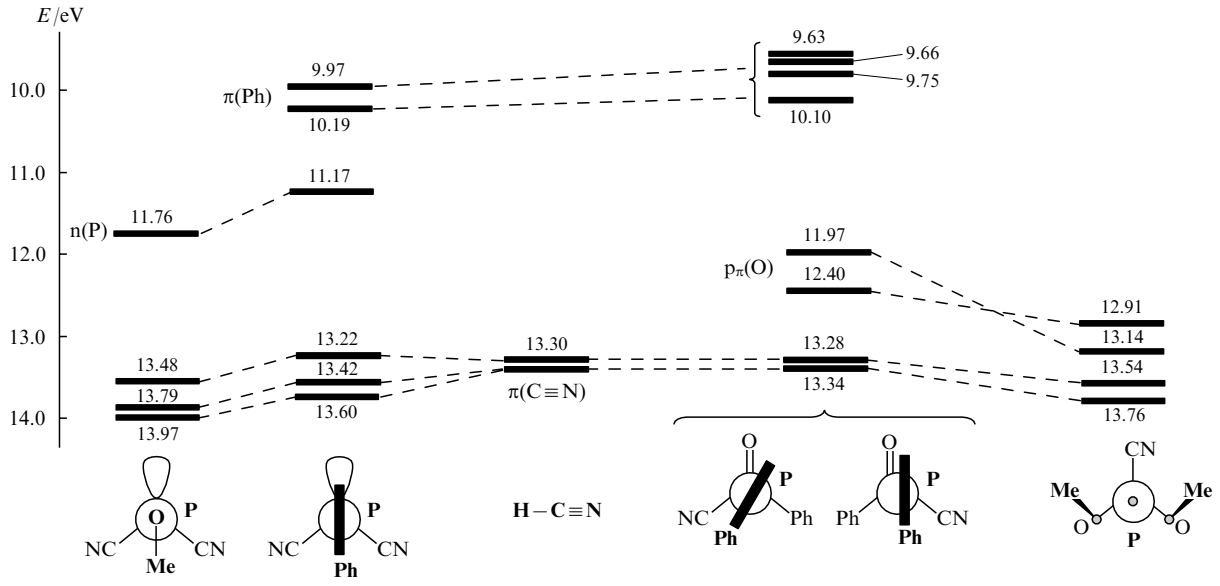


Figure 10. Correlation diagram of the HOMO energies for the stable conformations of phosphorus cyanides and HCN.[121]

highest occupied molecular orbital (HOMO), which is predominantly n(P) in character, is additionally stabilised by the n(P)–σ*(O–C) hyperconjugation interaction, absent in the eclipsed structure of Ph–P(CN)$_2$. This is also evident from a decrease in the effective charge on the phosphorus atom from 1.05 in methoxydicyanophosphine to 0.79 in phenyl dicyanophosphine. Analysis of the energies and compositions of the frontier MOs showed that interactions between the n(P) and π(C≡N) orbitals are absent in MeO–P(CN)$_2$ and Ph–P(CN)$_2$, and the interactions between the p_π(O) and π(C≡N) orbitals are absent in Ph$_2$P(O)CN and (MeO)$_2$P(O)CN. In addition, all of the above-mentioned favourable conformations are characterised by a low population of d_{π^*}-AOs on the phosphorus atom, which indicates that there are no interactions between these orbitals and the orbitals of the substituents with suitable symmetry. Therefore, it can be concluded that interactions between the cyano group and the lone pair of the phosphorus atom, its d orbitals or the phosphoryl group make no contribution to stabilisation of the favourable conformers of phosphorus cyanides. Apparently, the nitrile group in the P–CN fragment behaves predominantly as a σ acceptor and does not exhibit π-acceptor properties.

The relationship between the conformations of OPCs and their reactivity has been studied in detail by photoelectron spectroscopy. At the Arbuzov Institute of Organic and Physical Chemistry (Kazan, Russia), the ionisation potentials of about 170 various organic unicoordinate, dicoordinate and tricoordinate phosphorus compounds (which comprise about one-half of all the data published in the literature) were determined by photoelectron spectroscopy in combination with quantum-chemical calculations.[106] The relationships between the ionisation potentials and the molecular structures, in particular, the bond and torsion angles, were revealed.

The ionisation potentials of the favourable and less stable conformations of selected OPCs are given in Table 7. The dependence of conformation on ionisation potential was found, and the regression relationship between the vertical ionisation potentials and the molecular orbital energies, calculated by varying the geometric parameters, was optimised:[106, 168]

$$IP_m = a\varepsilon_m + b,$$

where ε_m are the energies of the highest occupied orbitals.[90, 97, 168, 187] For the molecules under study, the conformations predicted by optimisation of the total energy of the molecule and the regression relationship were similar, but the latter approach was less sensitive to the calculation method.

In the publication,[168] a procedure was described for theoretical simulation of the photoelectron spectra of systems consisting of two conformers. The molecular orbital energies scaled from the experimental ionisation potentials of favourable conformers and their regression relationships can also be used to estimate the ionisation potentials of unstable conformations. The latter are not detected by photoelectron spectroscopy. However, in specific cases, these values can determine the reactivity of molecules.

Table 7. Ionisation potentials and relative energies of stable conformers of organophosphorus compounds.[90, 97, 168, 187]

Compound	Basis set	Conformer	ΔE (see [a])	IP_1 / eV	r (see [b])
$PhPH_2$	3-21G*	**A** [c]	1.25	8.88	0.999
		B [c]	0.00	9.66	0.987
$F_2P(O)CH=CH_2$	6-31G*	*c*	0.00	11.58	0.977
		t	1.95	11.46	0.902
$Cl_2P(O)CH=CH_2$	4-31G	*c*	0.00	11.24	0.996
		t	4.80	11.12	0.986
Me_2POMe	6-31G**	*g*	0.00	8.78	0.994
		t	1.57	8.97	0.991
Cl_2PMe	6-31G**	*t*	0.00	10.26	0.997
		g	3.81	10.14	0.992
Me_2PSMe	CNDO/2	*g*	0.00	8.60	0.997
	6-31G**	*c*	0.00	8.60	0.992
	6-31G**	*t*	0.93	8.81	0.966
Cl_2PSMe	6-31G**	*t*	0.00	9.75	0.984
		g	1.75	9.32	0.981
$Cl_2PCH=CH_2$	4-31G	*c*	0.00	9.84	0.994
		g	2.03	10.03	0.943
$P(OMe)_3$	3G	*ggt*	0.00	9.18	0.993
	6-31G**	*ggt*	0.00	9.18	0.973
$HP(O)(OMe)_2$	6-31G*	*gg*	0.00	11.10	0.998
		−gt	1.93	11.15	0.995
		gt	1.94	11.08	0.995
$MeP(O)(OMe)_2$	6-31G*	*gg*	0.00	10.53	0.994
		−gt	2.64	10.55	0.986

[a] In kcal mol^{-1}.

[b] r is the correlation coefficient of the regression equation $IP = a\varepsilon + b$, where ε are the energies of the highest occupied molecular orbitals.

[c] **A** and **B** are respectively the conjugated and bisecting conformations of phenylphosphine.

6. Internal rotation about P–N and P–P bonds

Experimental and selected calculated data on the conformations and barriers to internal rotation about P–N bonds published before 1982 were summarised in a review.[5] The results of semi-empirical and *ab initio* calculations for OPCs with P–N bonds were analysed in several studies.[199–207] Apparently, this is in part attributable to the complexity of the systems under consideration because of internal rotation about this bond often being accompanied by a change in the configuration at the nitrogen atom. For example, it was noted [208] that topomerisation in aminophosphines is a complex process involving simultaneous rotation about the P–N bond and possible inversion of configuration at the N atom.

Substituents at the N(sp^3) atom increase the height of the barrier to internal rotation due to destabilising steric repulsions in its pyramidal environment. On the contrary, substituents at the P atom decrease this barrier because they induce the pyramidal configuration of the nitrogen atom. *Ab initio* calculations demonstrated [208] that a change in the torsion angle of the LEP–N–P–LEP fragment from 90° to 180° leads to a change in the configuration at the nitrogen atom from trigonal-planar to pyramidal with close to tetrahedral bond angles. Rotation of the amide group about the P–N bond is hindered, and the barrier height was estimated [202] to be approximately 6.5 kcal mol^{-1}. The complexity of the equilibrium set of configurations results in an ambiguous interpretation of the photoelectron spectra of phosphoramidates.[201]

Ab initio calculations performed in recent years have provided an essential supplement to our knowledge about internal rotation about P–N bonds. For acid amides of Group V elements, E(NMe$_2$)$_3$ (E = As, Sb, P), a comparative study of the structures and favourable conformations was performed by electron diffraction and quantum-chemical methods.[209] The structural parameters are intended for use in compiling electronic databases, calculating the physicochemical properties of molecules and constructing a theory of reactivities for this class of compounds.

The use of the results of *ab initio* quantum-chemical calculations (HF/6-31G*) and spectroscopic data for the interpretation of electron diffraction data made it possible to determine the geometric parameters and force fields for two stable rotamers of the Me$_2$N–PCl$_2$ molecule: *gauche* (C_1 symmetry) and *trans* (C_s symmetry).[210] For the energetically much more favourable *gauche* conformer, the vibrational spectra of undeuterated and completely deuterated isotopomers of Me$_2$N–PCl$_2$ were reliably interpreted for the first time in the cited study. Gas electron diffraction data were analysed and the equilibrium geometric parameters of the molecules evaluated, taking into account the non-linear kinematic effect in first-order perturbation theory, which led to the conclusion that the Me$_2$N group has a non-planar equilibrium configuration.

In the study,[211] the effects of the electronic and steric factors on the structures of mono-, di- and triaminophosphines and dialkylaminophosphines were investigated by *ab initio* methods, providing evidence that the orthogonal conformation of the LEP–P–N–LEP fragment ($\varphi = \pm 90^\circ$) is energetically more favourable. The *anti* conformation ($\varphi = 180^\circ$) can occur as a minor structure. Tris(dimethylamino)phosphine can adopt a *syn* conformation. Therefore, the structures of the aminophosphines considered in the cited study were determined by interactions between the lone electron pairs of the phosphorus and nitrogen atoms, the hybridisation of the nitrogen atom and the steric requirements of the substituents.

It should be noted that the structure of the tris(dimethylamino)phosphine molecule has been debated for three decades and studied many times by gas electron diffraction using semiempirical and *ab initio* calculations.[200, 203, 204] *Ab initio* calculations revealed two stable conformations with C_3 and C_s symmetry, the latter being more stable by 7 kcal mol^{-1}. The electron diffraction study demonstrated that two of the NMe_2 groups in the C_s conformation are oriented so that the lone electron pairs of the nitrogen atoms [N(2) and N(3) in Fig. 11] are approximately perpendicular to the lone electron pair of the P atom, and the lone pair of the third NMe_2 fragment is positioned antiparallel with respect to the lone pair of the P atom. The environment of the N atom in the third fragment is essentially pyramidal (the sum of the bond angles is 337°), whereas two other nitrogen atoms have a flattened configuration (the sum of the bond angles is 353°). In the study,[203] it was hypothesised that the equilibrium C_s-symmetric structure is stabilised due to the anomeric effect, *i.e.*, due to overlapping of the lone electron pairs of the N(2) and N(3) atoms with the antibonding σ* orbital of the P–N(1) bond (Fig. 11). The cited study has summed up the discussion and probably proposed an adequate model for this complicated conformational system.

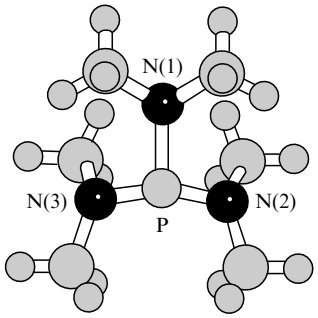


Figure 11. Perspective model of the C_s-symmetric conformation of the $P(NMe_2)_3$ molecule based on the results of gas electron diffraction and *ab initio* calculations.[203]

Data on internal rotation about P–P bonds are scarce. *Ab initio* calculations for the 1,1-difluorophosphine (H_2P-PF_2) molecule revealed[212] the existence of the staggered *trans* and *gauche* conformations, separated by a barrier of 0.9 kcal mol^{-1}. Previously, the *trans* and *gauche* conformers of the Me_2P-PMe_2 molecule had been detected by photoelectron spectroscopy by varying the temperature from 20 to −252 °C.[213]

III. Conclusion

Modern quantum chemistry combined with the results of physicochemical methods of investigation provides a reliable theoretical basis for many general chemical features in terms of orbitals and electronic configurations.[214] Moreover, modern aspects of the theory, such as the structures of metastable intermediate particles, the compositions and geometries of molecular associates, the shapes of potential surfaces, *etc.*, give impetus to experimental investigations and the development of new concepts.¶ However, a search for stable conformers of molecules, analysis of their relative stabilities and examination of the shapes of their barriers to internal rotation are complicated physicochemical problems, which remain, in many respects, unresolved.

In recent years, the molecular structures of OPCs have been reinvestigated more thoroughly by various experimental methods (gas electron diffraction, vibrational and photoelectron spectroscopy, the dipole moment method, *etc.*) and quantum-chemical calculations. The results of calculations using extended basis sets including correlation effects are in some respects similar to the results of high-precision experiments; they also require generalisation and explanation in terms of approximate models and theories. The main aim of each systematic conformational study is to draw generalisations which have predictive capabilities and allow one to exclude steps that give unambiguous and predictable results. An important problem is to reveal the general and specific features in the body of data and determine their place in general chemical theory.

It can be stated that experimental and theoretical results obtained by the conformational analysis of relatively simple OPCs (for example, OPCs containing one internal rotation axis) adequately describe sets of conformers resulting from internal rotation about P–C, P–O and P–S bonds. The data considered in this review demonstrate that the staggered *gauche* and *trans* conformations are favourable for OPCs, which is also true for molecules of classical organic compounds. The occurrence of eclipsed conformations is attributable to the structural features of particular molecules and these require special theoretical analysis.

The structures of more complex compounds with several internal rotation axes (particularly, if these axes belong to different atoms) cannot necessarily be unambiguously determined, even using physical methods combined with calculations. The spatial and electronic structures of polyfunctional OPCs (in which intramolecular interactions can give rise to unusual conformations) and OPCs containing P in low coordination states were poorly studied. Experimental and theoretical data on these compounds are scarce. Quantum-chemical studies of OPCs in solution are few in number. In addition to the above-considered publications on the theoretical conformational analysis of phosphorus-substituted acrylonitriles[102] and studies of a number of the simplest phosphorus compounds and their radical cations by *ab initio* self-consistent reaction field calculations,[170] several investigations also dealt with the conformational composition and reactivity of dimethyl phosphite in the gas phase and solvents of varying polarity[183] and with the conformational composition and spin properties of iminoxyl radicals containing the phosphine oxide substituent.[216, 217]

When using calculated data, it should be remembered that semiempirical quantum-chemical methods, which, on the whole, correctly reproduce the structures and conformations of organic molecules, can give large errors in their estimates of the geometric parameters and relative stabilities of OPCs. With certain exceptions, this is also true for *ab initio* calculations. In Section II.5, it was demonstrated that calculations for the $H_2P(O)OH$ molecule by the Hartree–Fock method using the rather large 6-31G** basis set predicted the eclipsed *cis* conformation; however, this result is reproduced in the single-determinant approximation only for particular basis sets, whereas various modes of inclusion of electron correlation always predict a skewed conformation. On the other hand, transition structures on potential energy surfaces (saddle points with one imaginary frequency), *i.e.*, the peaks of the

¶ In a recent theoretical study,[215] it was stated that the staggered conformation of the ethane molecule, which has been studied many times by various methods is, contrary to popular opinion, determined by superconjugation of the C–H bonds rather than by steric repulsions between hydrogen atoms.

barriers to internal rotation, generally correspond to the C_s-symmetric *cis* conformations for P—O and P—S bonds. Nevertheless, for H_2POH, H_2PSH and some other molecules, conformations with the eclipsed lone electron pair of the phosphorus atom are predicted at several levels of theory.

The relative stabilities of the *gauche* and *trans* conformations of the $X_2PCH=CH_2$ or X_2POMe molecules are, apparently, determined from competition between the $n(P)-\pi^*(PX_2)$ and $\pi(C=C)-\pi^*(PX_2)$ donor–acceptor interactions (see Fig. 4). In molecules containing electron-withdrawing PX_2 groups, the $\pi(C=C)-\pi^*(PX_2)$ donor-acceptor interactions stabilise the *trans* conformation. Compounds H_2POH, $H_2PCH=CH_2$ and H_2PPh belong to an intermediate type, in which competitive interactions are of similar magnitudes and the conformers have similar energies. Calculations by the Hartree–Fock method using the 3-21G*, 6-311G** and 6-311(2d,2p) basis sets demonstrated that the *trans* conformation of these molecules is more stable, whereas calculations with the 6-31G*, 6-31G**, 6-31+G* and 6-31+G** basis sets predicted the *cis* conformation as the more stable. A further extension of the basis set up to 6-311++(3d,3p) results in a zero energy difference between the conformers. Calculations including of electron correlation at different levels of theory predict the *cis* conformation as the favourable one; however, an extension of the basis set decreases the energy difference between the *cis* and *trans* conformers.

These data suggest that investigations of the relative stabilities of conformers with similar energies and the correct treatment of eclipsed conformations requires the use of quantum-chemical methods at the maximum possible levels of theory with inclusion of electron correlations at the MP2, B3LYP or PBE level (see Tables 1, 2 and 6). However, the principal limitations of the model of discrete conformers are manifested in compounds with low barriers to internal rotation. Examples of these limitations encountered in the conformational analysis of the $PhPH_2$ molecule were considered in Section II.4.

The predictive capabilities of quantum chemistry and its role in modern conformational analysis are still debated.[218] In Scerri's opinion,[219] quantum theory often simulates and interprets (although at a very high level) experimental data (for example, spectroscopic characteristics and geometric parameters of the molecules) rather than gives predictions. At the same time, it was noted that the reliability of quantum-chemical predictions increases.[218] For example, a review[220] where the use of various versions of the Gaussian package for describing ion-molecular processes was considered, gave examples of the refinement of experimental data using the results of quantum-chemical calculations, which made it possible to reveal and eliminate errors in the measurements. The direct relationship between the quantum-chemical theory and conformational analysis of OPCs is clearly demonstrated by the evolution of views on the structure of the Cl_2POMe molecule discussed in the study.[221] In the period from 1974 to 1994, the initial views on the *cis* conformation of this molecule were revised first in favour of the *gauche* conformer and then in favour of the *trans* conformer, which is sterically hindered but stabilised by electronic factors, according to calculated data.

On the whole, conformational analysis of organoelement compounds is in its infancy. A general system for determining the conformations of such compounds, which could allow one to reveal the characteristic features of internal rotation about any chemical bond in an arbitrary environment, so far is only qualitatively developed. For many organoelement compounds, conformational data are lacking, often for objective reasons (instability of compounds, the impossibility of preparing their solutions, *etc.*). However, experimental and theoretical studies are opening up new possibilities for the development of conformational analysis as a necessary step in routes to the synthesis of compounds possessing specified physical, chemical and biological properties, to explain of the reactivities of such compounds and to elucidate their reaction mechanisms.

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