Nature of weak inter- and intramolecular interactions in crystals
3.* Intermolecular P=O...C=O contact in crystals of phenyl methylisopropoxyphosphorylformate

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Phenyl methylisopropoxyphosphorylformate was studied by high-resolution X-ray diffraction. The chemical bonding in the vicinity of the phosphoryl group was studied by analyzing the deformation electron density, the Laplacian of the electron density, and the electron localization function. A P=O...C=O intermolecular contact was revealed and its nature was analyzed.

Key words: phosphorylformic acid derivatives, P=O...C=O contacts, nature of P—O chemical bonding, electron density distribution, topological theory of Atoms in Molecules, X-ray diffraction data.

Phosphonoformic acid derivatives belong to widely known biologically active compounds. For example, its esters, salts, and amides are characterized by a wide spectrum of growth-controlling activity. In particular, the arboricide Krenite, *viz.*, ammonium carbamoyl-*o*-ethylphosphonate $(EtO)(NH_4O)P(O)CONH_2$, is produced on an industrial scale.[2] Of special note is antiviral activity of phosphonoformic acid, which inhibits viral DNA polymerase and is used in clinical practice for the treatment for herpes (*Herpes simplex*) as the trisodium salt (foscarnet).[3,4] The structures of this compound and chelate salts of phosphonoformic acid with $Pt(NH_3)_2$ have been established[5] by X-ray diffraction analysis.

With the aim of finding new biologically active compounds and examining the influence of the structural factors on the physiological activity, we synthesized a series of methylphosphorylformic acid derivatives.**

X-ray diffraction study of one of the compounds synthesized in the present study, *viz.*, phenyl methylisopropoxyphosphorylformate $(Me(Pr^iO)P(O)C(O)OPh)$ (**1**), revealed the presence of unusual intermolecular contacts involving the P=O group in the crystal. To elucidate whether these contacts correspond to specific intermolecular interactions, we performed the topological analysis of the electron density distribution function ρ(**r**) in terms of Bader's theory of Atoms in Molecules[6] using high-resolution X-ray diffraction data for compound **1** at 110 K.

Molecular and crystal structure

The principal geometric parameters of molecule **1** are close to the expected values (Fig. 1, Table 1). However, since ester **1** is the first structurally characterized compound containing the P(O)C(O)OR group, it was impossible to directly compare some geometric parameters of **1** with the data published in the literature. Earlier,[5] only salts of phosphonoformic acids, in which the *s-cis* conformation of the C=O and P=O groups was fixed due to coordination to the platinum atom, have been characterized. However, the mutual arrangement of the C=O and P=O groups in molecule **1** is also nearly synperiplanar with the O(1)P(1)C(5)O(3) torsion angle of 31.4°. Apparently, this conformation is rather stable for the P(O)C(O)OR fragment, although the synperiplanar conformation has

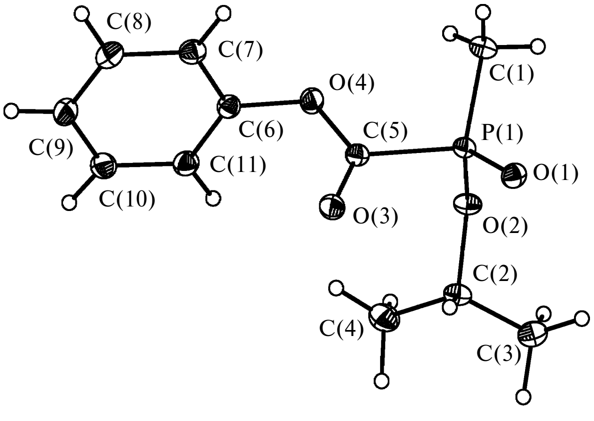

Fig. 1. Overall view of compound **1** with displacement ellipsoids drawn at the 50% probability level.

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* For Part 2, see Ref. 1.

** The synthesis and properties of the compounds will be described elsewhere.

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Table 1. Selected bond lengths (*d*) and bond angles (ω) in the crystal of **1**

Parameter	Value	Parameter	Value
Bond	*d*/Å	Bond	*d*/Å
P(1)—O(1)	1.4765(5)	C(2)—C(3)	1.505(1)
P(1)—O(2)	1.5852(4)	C(2)—C(4)	1.510(1)
P(1)—C(1)	1.7781(6)	O(3)—C(5)	1.2054(7)
P(1)—C(5)	1.8593(6)	O(4)—C(5)	1.3511(7)
O(2)—C(2)	1.4725(7)	O(4)—C(6)	1.4111(8)
Angle	ω/deg	Angle	ω/deg
O(1)—P(1)—O(2)	115.68(3)	C(2)—O(2)—P(1)	120.36(4)
O(1)—P(1)—C(1)	117.84(3)	C(5)—O(4)—C(6)	116.34(5)
O(2)—P(1)—C(1)	101.88(3)	O(3)—C(5)—O(4)	124.90(6)
O(1)—P(1)—C(5)	109.70(3)	O(3)—C(5)—P(1)	122.64(5)
O(2)—P(1)—C(5)	101.39(2)	O(4)—C(5)—P(1)	112.23(4)
C(1)—P(1)—C(5)	108.88(3)		

not been observed in α-phosphorylated ketones, which have been studied in more detail and the data for which are available in the Cambridge Structural Database (CSD).[7] To the contrary, the anticlinal or antiperiplanar conformation of the O=P—C=O fragment is more favorable.

The P(1)—C(5) bond length (1.8593(6) Å) is close to the corresponding values in the above-described salts of phosphonoformic acid (1.846 Å).[5] The phosphorus atom is characterized by a distorted tetrahedral coordination. The bond angles at the phosphorus atom vary in the range of 101.39(2)—117.84(3)°.

Analysis of the crystal packing of **1** revealed weak intermolecular C—H...O contacts (H....O, 2.47—2.56 Å) along with unusual O(1)=P(1)...O(1A)=P(1A) contacts ($(-x, 1-y, 1-z)$), through which the molecules are linked to form centrosymmetric dimers (Fig. 2).

Although nonbonded interactions involving the phosphorus atom are atypical, the analysis of the geometry suggested that these contacts belong to specific intermolecular interactions. Actually, the phosphoryl groups of the adjacent molecules in the crystal are characterized by the parallel arrangement, and the P(1)...O(1A) distance (3.136(1) Å) is substantially smaller than the sum of the van der Waals radii (3.32 Å).[8] Similar intermolecular contacts of the C=O groups with a parallel arrangement of the bonds occur very often in crystals.[9] For example, the analysis of the electron density distribution ρ(**r**) in the crystals of 3-acetyl-4-hydroxycoumarin showed that the C=O...C=O interactions between the carbonyl groups (C...O 3.190—3.218 Å) correspond to chemical bonding with an energy of 0.8 kcal mol^{-1}.[10]

Analysis of CSD data[7] demonstrated that O=P....O=P contacts, unlike C=O...C=O contacts, have not been observed earlier. In the case of carbonyl groups, these interactions are associated with overlap of the π orbitals centered on the oxygen and carbon atoms,[9] whereas the character of chemical bonding for the phosphoryl bonds, in which the contribution of the π component is virtually absent (see Ref. 11 and references therein), argues against the occurrence of an analogous charge transfer.

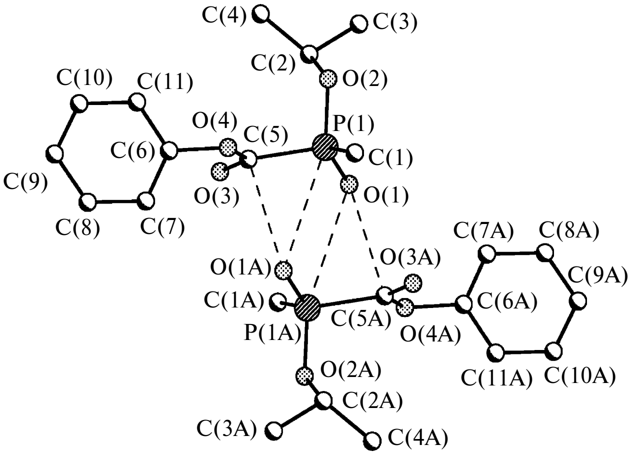

Fig. 2. Centrosymmetric dimer in the crystal of **1**.

Earlier theoretical and experimental studies of various compounds XYZP=O demonstrated that it is most correct to consider the P—O bond as a single exchange-type chemical bond ($\mathrm{XYZP^{+}—O^{-}}$), due to which there are three lone electron pairs on the oxygen atom located antiperiplanar to the substituents at the phosphorus atom.[11—13] This arrangement of the lone pairs makes possible the charge transfer from the lone pairs of the oxygen atom to the corresponding σ-antibonding orbitals of the P—X, P—Y, and P—Z bonds, which was demonstrated by analysis of the electron localization function (ELF) in the crystals of diphenylphosphonic acid.[11]

In addition to the above-described contact between the PO groups in the dimers in crystal **1**, there are also P(1)—O(1)...C(5A)=O(3A) intermolecular contacts ($(-x, 1-y, 1-z)$), which can also be assigned to specific interactions between these atoms. Actually, the O(1)...C(5A)O(3A) angle (100.6°) and the O(1)...C(5A) distance (2.807(1) Å) are characteristic of O...C=O interactions. The presence of such inter- and intramolecular O...C=O contacts, which are generally related to the charge transfer from the lone electron pair of the O atom to the antibonding π-orbital of the C=O bond, served as the basis for modeling the nucleophilic substitution in terms of the structural correlation method.[14—16] In particular, these contacts are observed in *peri*-substituted naphthalenes. The statistical processing of the CSD data on these compounds demonstrated that shortening of the O...C=O distance leads to an increase in the degree of pyramidalization of the carbon atom in the carbonyl group in the direction away from the attacking group.[14,15] Although the P=O...C=O contact causes a slight pyramidalization of the C(5) atom (deviation of the C(5) atom from the plane through the O(3), O(4), and P(1) atoms is 0.04 Å), the latter in molecule **1** deviates in the same direction as the attacking O(1) atom.

We expected that the formation of a contact involving the phosphoryl group would be reflected in the spectroscopic characteristics of this compound, primarily, in the shift of the P=O absorption band (ν(P=O)) in the IR spectra of crystalline samples compared to its position in the spectra of solutions, where this contact cannot, apparently, occur. Taking into account the literature data,[17] an intense absorption band with the maximum at 1248 cm^{-1} and a shoulder at 1240 cm^{-1} was assigned to the P=O vibration. In the spectra of solutions of compound **1** in $CDCl_3$, CH_3CN, and CH_3OH at different concentrations, the ν(P=O) band is observed at 1245 cm^{-1}, *i.e.*, its position remains virtually identical both in the crystalline state and solution and is independent of the solvent.

Therefore, the analysis of the geometric parameters and IR spectroscopic data did not allow us to reach an unambiguous conclusion about the presence and nature of interactions through which molecules **1** are linked in dimers. Taking into account that the theory "Atoms in Molecules"[6] enables one to directly solve such problems for studying the character of intermolecular contacts, we performed the multipole refinement of X-ray diffraction data followed by the topological analysis of the electron density distribution in the crystals of **1** determined in the analytical form. In addition, it was also of interest to elucidate the character of bonding in the vicinity of the P—O bond and compare this bond with the data obtained earlier for diphenylphosphonic acid.

Electron density distribution

Let us consider the character of P=O and C=O chemical bonds in molecule **1**. Analysis of deformation electron density (DED) maps showed that the character of electron density distribution in the vicinity of the P(1)C(5)O(3)O(4) fragment is typical of this functional group, *viz.*, electron accumulation is observed at the P—C and C—O bonds, and two lone electron pairs are localized in the vicinity of the O(3) atom (Fig. 3). The deformation electron density about the oxygen atom of the P(1)—C(1) phosphoryl group differs from that observed for the C(5)—O(3) carbonyl group. It can be seen that the difference electron density in the O(1)P(1)C(1) plane differs substantially from that in the O(1)P(1)C(5) plane. Two peaks of different heights are observed in the O(1)P(1)C(5) plane about the O(1) atom, whereas only one maximum is located on the extension of the P(1)—O(1) bond line in the O(1)P(1)C(1) plane (Fig. 4).

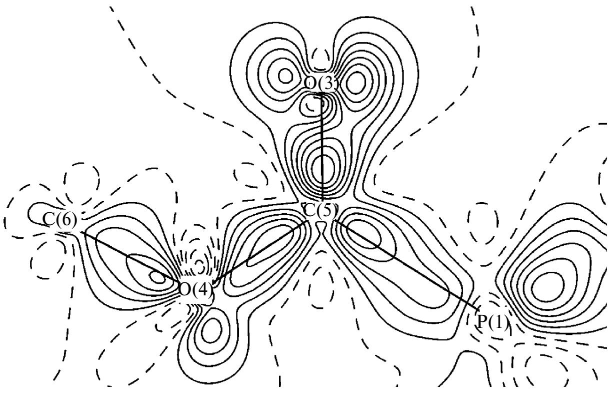

Fig. 3. The DED sections through the O(3)C(5)O(4) plane. The maps are contoured at 0.01 e $Å^{-3}$ intervals. The zero and negative contours are dashed.

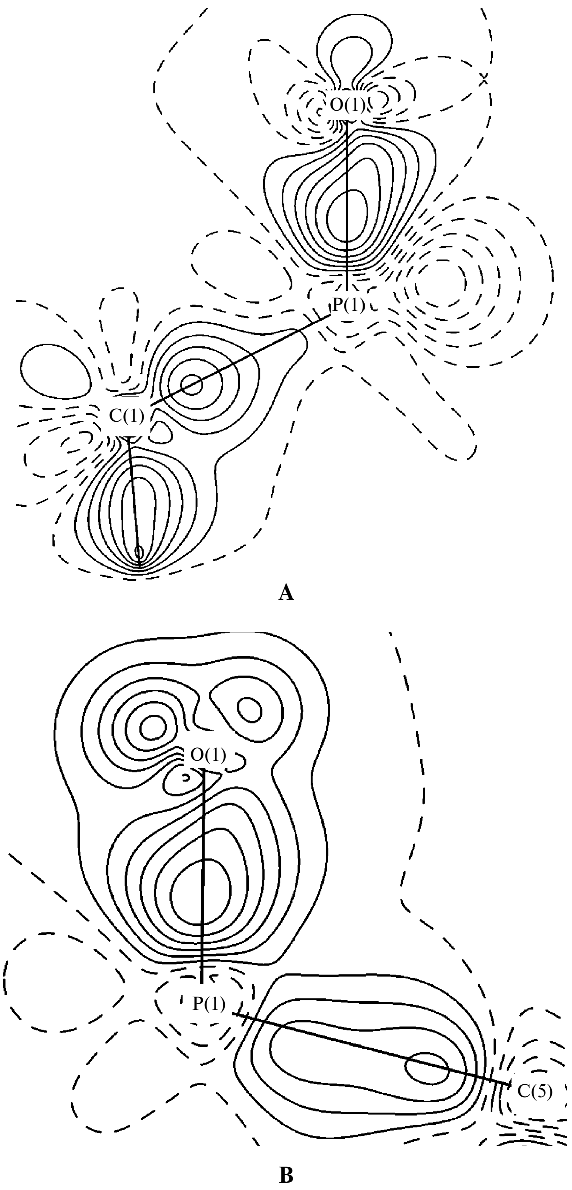

Fig. 4. The DED sections through the C(1)P(1)O(1) (**A**) and C(5)P(1)O(1) (**B**) planes. The maps are contoured at 0.01 e $Å^{-3}$ intervals. The zero and negative contours are dashed.

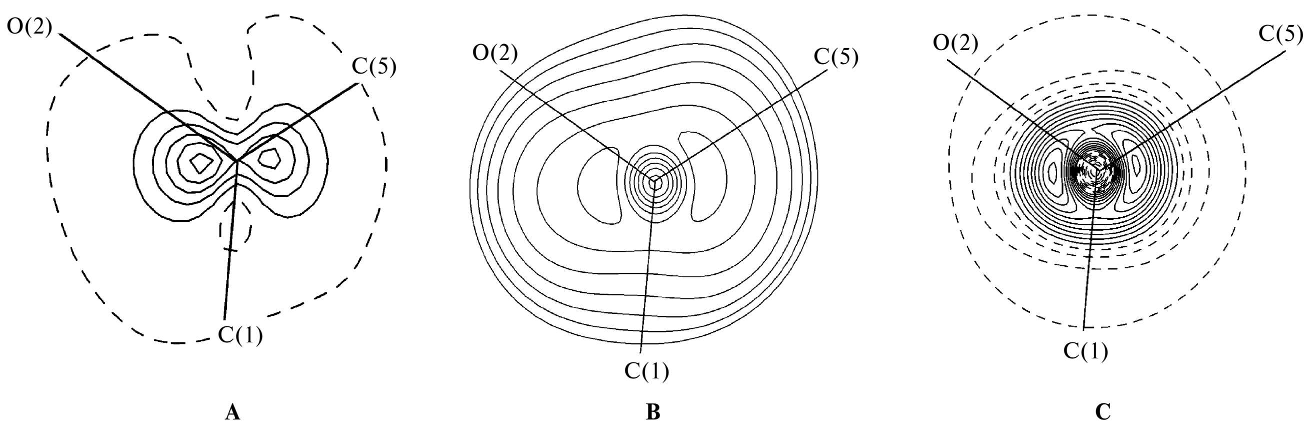

Fig. 5. Deformation electron density maps (**A**), ELF (**B**), and $\nabla^2\rho(\mathbf{r})$ (**C**) in the plane perpendicular to the P(1)—O(1) bond line at a distance of 0.25 Å from the O(1) atom: **A**, maps are contoured at 0.1 e Å^{-3} intervals, the zero and negative contours are dashed; **B**, maps are contoured at 0.5 intervals (contours with ELF <0.5 are omitted); **C**, maps are contoured at 10 e Å^{-5} intervals, the positive contours are dashed.

To determine the number of lone electron pairs of the O(1) atom and their arrangement with respect to the substituents at the P(1) atom, we analyzed the DED sections in the plane perpendicular to the P(1)—O(1) bond line at a distance of 0.25 Å from the O(1) atom (Fig. 5). In addition to the deformation electron density, we also analyzed the electron localization function (ELF) and the Laplacian of the electron density in this section. Unlike the deformation electron density, the latter two functions are independent of the reference function.

It can be seen that the same situation is observed in these sections for all three functions. Two lone pairs are located on the O(1) atom. The peaks corresponding to lone electron pairs are located on the line perpendicular to the projection of the P(1)—C(1) bond anticlinal to the P(1)—O(2) and P(1)—C(5) bonds (see Fig. 5). Therefore, the situation in molecule **1** differs from that observed for diphenylphosphonic acid, in which three lone pairs were revealed on the oxygen atom of the phosphoryl group.

The observed differences can reflect the radical differences in the nature of chemical bonding in the vicinity of the PO group in compound **1** compared to that observed in diphenylphosphonic acid and phosphine oxides. At the same time, the absence of the third lone electron pair may be associated with a considerable charge transfer from this electron pair to the antibonding orbital of the P(1)—C(1) bond. In this case, it is unlikely that the lone electron pair located antiperiplanar to the P(1)—C(1) bond is "drawn in" the oxygen atom and is localized in the vicinity of the O(1) atom. The influence of the C=O group, which can be partially conjugated with the antiperiplanar P(1)—O(1) bond (see above), also cannot be ruled out.

In turn, a change in the mutual arrangement of the lone electron pair with respect to the P(1)—O(2) and P(1)—C(5) bonds can be partially associated with a decrease in the C(1)—P(1)—O(2) and C(5)—P(1)—O(2) bond angles to 101.39(2)—101.88(3)°.

Therefore, the data on the character of electron density distribution in the vicinity of the P—O bond in molecule **1** and a comparison of these data with the corresponding data for the diphenylphosphonic acid molecule provide no unambiguous evidence for the type of chemical bonding about the P(1)—O(1) group in compound **1**. Further studies of phosphorus compounds containing the phosphoryl group with various substituents will allow one to elucidate whether the character of chemical bonding found for phosphine oxides[12,13] and diphenylphosphonic acid[11] has a general character.

In spite of the above-described differences in the number and mutual arrangement of the lone electron pairs of the O(1) atom, the topological characteristics of $\rho(\mathbf{r})$ at the critical points (3,–1) (CP (3,–1)) of the bonds involving the phosphorus atom are close to the expected values. The P(1)—O(1) and P(1)—O(2) bonds belong to the intermediate type of interactions, $\nabla^2\rho(\mathrm{r})$ have positive values (6.38 and 4.30 e Å^{-5}), whereas the local energy densities ($h_e(\mathbf{r})$) are negative (–0.362 and –0.171 a.u.). To the contrary, the P(1)—C(1) and P(1)—C(5) bonds, like all other bonds in molecule **1**, correspond to shared interactions ($\nabla^2\rho(\mathrm{r})$ have negative values).

Analysis of the critical points in the vicinity of the intermolecular contacts showed that only CP (3,+1) corresponding to the formation of the cyclic structure is located in the center of the O(1)=P(1)...O(1A)=P(1A) fragment, whereas the bond paths and CPs (3,–1) on the P(1)...O(1A) and P(1A)...O(1) lines are not observed. To the contrary, CPs (3,–1) were revealed in the region of the O(1)...C(5A) and O(1A)...C(5) contacts. These CPs are responsible for the six-membered ring closure and, as a consequence, the appearance of the above-described CPs (3,+1). Therefore, the topological analysis of $\rho(\mathbf{r})$

provided evidence that the formation of dimers in the crystal of **1** is associated with interactions between the phosphoryl and carbonyl groups rather than with interactions between the phosphoryl groups.

This effect is related to closed-shell interactions ($\nabla^2\rho(\mathbf{r})$ = 1.08 e Å^{-5}, $h_e(\mathbf{r})$ = 0.001725 a.u.), the value of $\rho(\mathbf{r})$ at CP (3,–1) for the O(1)...C(5A) contact (0.086 e Å^{-3}) being comparable with the corresponding value (0.110 e Å^{-3}) for the $Me_2N...C=O$ intramolecular contact (N...C=O 2.700(1) Å) in 8-dimethylamino-*N*′,*N*′-dimethylnaphthalene-1-carboxamide.[16] Taking into account that the latter contact (as follows from the analysis of the electron density distribution in the crystals) is associated with the charge transfer from the lone electron pair of the nitrogen atom to the antibonding orbital of the C=O bond, one would expect that the interatomic interaction in the case of the O(1)...C(5A)=O(3A) contact is of similar nature.

The energy of the O(1)...C(5A) interaction was estimated based on a semiquantitative correlation between the energy of the contact (E_{cont}) and the potential energy density.[18] The energy E_{cont} for this interaction is as high as 2.44 kcal mol^{-1}, which is substantially higher than the analogous values for the C—H...O, C—H...F, and C—F...O contacts studied earlier and is typical of weak N—H...O bonds.[19]

Analysis of the DED sections in the O(1)...C(5A)O(3A) plane showed that the interaction under consideration can be described in terms of a peak—hole model (Fig. 6). As can be seen from this section, the maximum is located in the vicinity of the O(1) atom, and the local electron depletion is observed in the vicinity of the C(5A) atom perpendicular to the C(5A)—O(3A) bond. Consequently, the present study demonstrated that the O(1)...C(5A)O(3A) interaction, like the interactions in peri-substituted naphthalenes studied earlier,[16] also corresponds to the charge transfer from the lone electron pair of the O(1) atom to the antibonding orbital of the C—O π-bond.

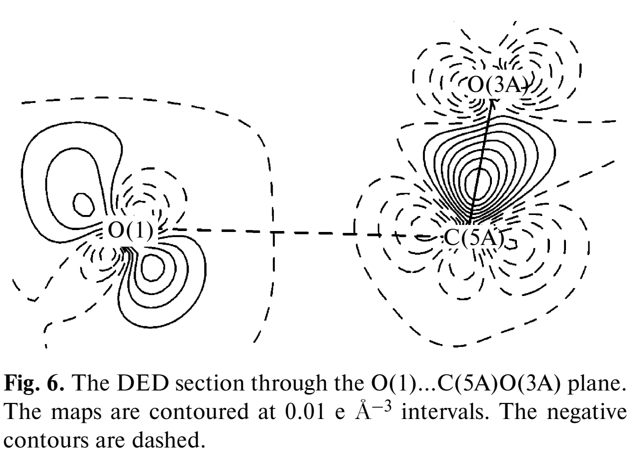

Fig. 6. The DED section through the O(1)...C(5A)O(3A) plane. The maps are contoured at 0.01 e Å^{-3} intervals. The negative contours are dashed.

To summarize, the investigation of the electron density distribution in the crystals of phenyl methylisopropoxyphosphorylformate not only elucidated the nature of the new type of intermolecular contacts and provided an estimate of its energy but also demonstrated that even the presence of geometric directionality (parallel arrangement of the P—O bonds) and a substantial shortening of the distance compared to the sum of the van der Waals radii cannot serve as a sufficient criterion of the presence of specific interatomic interactions.

Experimental

Phenyl methyl(isopropoxy)phosphinylformate. Phenyl chloroformate (2.35 g, 0.15 mol) was added dropwise with stirring to a solution of diisopropyl methylphosphinate (2.46 g, 0.015 mol) in benzene (50 mL) at a rate such that the temperature of the reaction mixture was maintained at 30 °C. After completion of the addition, the mixture was warmed to 65 °C and kept at this temperature for 2 h. Then the benzene was distilled off, and the residue was distilled *in vacuo*. The target compound was obtained in a yield of 2.35 g (73%), b.p. 120 °C (0.1 Torr). The oil that solidified was recrystallized from diethyl ether, m.p. 73 °C. ^{31}P NMR, δ: 26.2 (CCl_4). ^{1}H NMR (CCl_4), δ: 1.40 (d, 6 H, $(C\underline{H}_3)_2CH$, *J* = 7.6 Hz); 1.80 (d, 3 H, CH_3P, *J* = 15.7 Hz); 5.05 (m, 1 H, CH); 6.81—7.40 (m, 5 H, C_5H_5). ^{13}C NMR ($CDCl_3$), δ: 12.92 (d, CH_3P, *J* = 105.3 Hz); 22.25 (d, $\underline{C}H_3CH$, *J* = 5.0 Hz); 24.09 (d, $\underline{C}H_3CH$, *J* = 2.5 Hz); 72.15 (d, OCH, *J* = 6.9 Hz); 120.59, 126.05, and 129.09 (all s, *o*-, *m*-, *p*-C_6H_5); 149.28 (d, O—C(Ar), *J* = 6.5 Hz); 167.8 (d, C(O) *J* = 175.9 Hz). Found (%): C, 54.12; H, 6.31; P, 12.89. $C_{11}H_{15}O_4P$. Calculated (%): C, 54.55; H, 6.20; P, 12.81.

IR spectra were measured on a UR-20 spectrophotometer in KBr pellets (crystalline sample) and in solutions. The concentrations of solutions were as follows: 0.1, 0.03, and 0.005 mol L^{-1} in $CDCl_3$; 0.13, 0.017, and 0.005 mol L^{-1} in CH_3CN; 0.04 mol L^{-1} in CH_3OH. The cell path lengths were 0.067, 0.215, 0.496, and 0.121 mm. The positions of the most important absorption bands are given for the spectrum (*c* = 0.1 mol L^{-1}) of a solution in $CHCl_3$, and the assignment was made using the reference data[20] (ν/cm^{-1}): 1000 v.s (ν(PO—C)); 1165, 1180 v.s, doublet (ν($(CH_3)_2$—C)); 1245 s (ν(P=O)); 1260 sh (γ((CH_3)P)); 1310 m (δ((CH_3)P)); 1730 s (ν(C=O)).

X-ray diffraction study for compound **1** ($C_{11}H_{15}O_4P$) was carried out at 110 K on an automated three-circle Smart CCD 1000K diffractometer (Mo-Kα radiation, graphite monochromator, ω scanning technique, $2\theta_{\max} \leq 82°$). Crystals are monoclinic, at 110 K: *a* = 19.5777(4) Å, *b* = 8.5579(2) Å, *c* = 14.8518(4) Å, β = 102.556(1)°, *V* = 2428.82(10) Å^3, d_{calc} = 1.325 g cm^{-3}, M = 242.20, *F*(000) = 1024, μ = 2.23 cm^{-1}, *Z* = 4 (*Z*′ = 1), space group *C*2/*c*. Of a total of 30 000 measured reflections, 7711 independent reflections were used in calculations. The semiempirical absorption correction was applied based on equivalent reflections with the use of the SADABS program.[21] The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares method against F^2_{hkl}. The hydrogen atoms were located from difference Fourier syntheses and refined isotropically. The final *R* factors were as follows: $R = 0.0363$ for 6581 reflections with $I > 2\sigma(I)$, $wR_2 = 0.0929$ and GOOF = 1.099 for all reflections. All calculations were carried out using the SHELXTL PLUS program package.[22]

The experimental electron density function was determined in the analytical form by the multipole refinement of X-ray diffraction data in terms of the Hansen—Coppens model[23] using the XD program package.[24] In the multipole refinement, the coordinates, anisotropic displacement parameters, and the multipole parameters up to the octupole level ($l = 3$) were refined for all nonhydrogen atoms against F_{hkl}. The multipole parameters of the carbon atoms of the phenyl ring were refined taking into the local symmetry m.[25] The positions of the hydrogen atoms and their isotropic displacement parameters remained fixed. Before the refinement, the C—H distances were normalized to the ideal distance (1.08 Å) determined by neutron diffraction. In the multipole refinement, the H atoms were refined up to the dipole level ($l = 2$) taking into account the cylindrical symmetry. The correctness of the anisotropic atomic displacement parameters were estimated using the Hirshfeld test,[26] which was at most $9 \cdot 10^{-4}$ Å^2 for the bonds. The results of the multipole refinement are characterized by the following parameters: $R = 0.0286$, $wR = 0.0341$, GOOF = 1.118 using 6500 reflections with $I > 3\sigma(I)$. The residual electron density ($\rho(\mathbf{r})_{\text{exp}} - \rho(\mathbf{r})_{\text{mult}}$) was at most 0.20 e Å^{-3}. The electron localization function (ELF)[27] was calculated from X-ray diffraction data using the WINXPRO program.[28,29]

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