Structural features and the nature of the hydrogen bond in the enol form of α-diphenylphosphoryl-α-acetylacetonitrile based on X-ray diffraction data

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It has been established by X-ray structural analysis that pure α-diphenylphosphoryl-α-acetylacetonitrile exists in the enol form (a *Z* isomer). In crystals, a strong intramolecular P=O...H...O hydrogen bond is formed; the O...O distance is 2.551 Å. It has been demonstrated that the H atom is characterized by a high lability along the hydrogen bond, which exhibits a covalent component in the H...O region.

Key words: α-diphenylphosphoryl-α-acetylacetonitriles, keto-enol tautomerism, *Z,E* isomers, X-ray structural analysis, hydrogen bond, electron density distribution.

Previously we reported[1] a simple method of acylation of phosphorylacetonitriles at the central carbon atoms under conditions of phase transfer catalysis. It was demonstrated by spectral methods that products of acylation exist in the pure form as well as in the form of a single geometric isomer of the corresponding enol form in aprotic solvents. The IR and ^1H NMR spectra of these compounds provide an indication of the presence of an intramolecular hydrogen bond (H-bond) between the phosphoryl oxygen atom and a hydroxyl proton when the phosphoryl and hydroxyl groups are in *cis* positions (a *Z* isomer).

In this connection it is of interest to study the structural features of one of the compounds of this series, namely, α-diphenylphosphoryl-α-acetylacetonitrile (**1**), by X-ray structural analysis for the purpose of establishing its structure and determining the peculiarities of H-bonds.

Results and Discussion

X-ray structural data for compound **1** confirm a *cis* orientation of the hydroxy group and diphenylphosphoryl fragment with respect to the double C(2)=C(3) bond (Fig. 1) proposed from the spectral data. As a result, a strong intramolecular O(2)—H(2)...O(1) H-bond is formed; the distance between oxygen atoms is equal to 2.551(1) Å and the closure of the nearly planar six-membered ring occurs (the r.m.s. deviation of the atoms of the cycle including the H(2) atom from the mean plane is 0.017 Å; the C(1) and N(1) atoms deviate from the plane of the cycle by 0.124 Å and 0.226 Å, respectively). The other parameters of the H-bond are as follows: O(2)—H(2) 0.76(2) Å, H(2)...O(1) 1.82(2) Å, and the angle at the H(2) atom is 160(3)°.

The geometric parameters of molecule **1** are close to the expected values.[2] The phosphorus atom is characterized by a slightly distorted tetrahedral coordination: the bond angles at the P(1) atom vary from 106.4(1) to 113.8(1)°, the O=P—C angles being slightly larger than the C—P—C angles (Table 1), as is usually the case[3] for organophosphorus compounds of the $R_3P=O$ type. Atoms at the double bond (N(1), C(1), C(2), P(1), C(3), O(2),

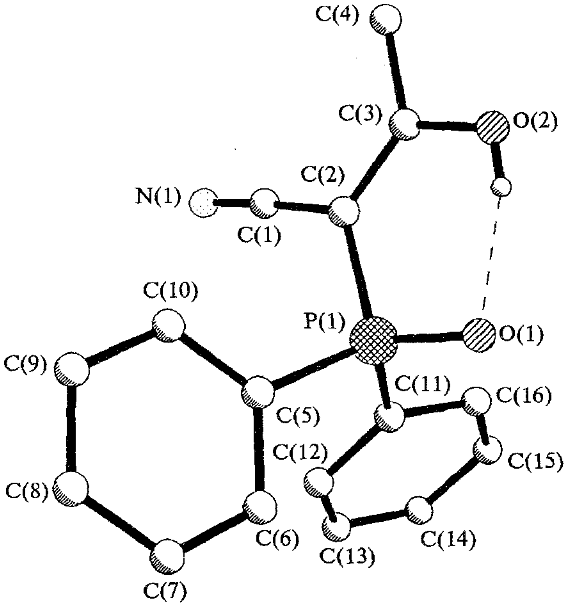

Fig. 1. Overall view of molecule **1** and the atomic numbering scheme.

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† Deceased.

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Table 1. Bond lengths and bond angles in the structure of **1**

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
P(1)—O(1)	1.507 (1)	N(1)—C(1)	1.151 (2)	C(5)—C(10)	1.386 (2)	C(11)—C(12)	1.398 (2)
P(1)—C(2)	1.787 (1)	C(1)—C(2)	1.427 (2)	C(6)—C(7)	1.393 (2)	C(11)—C(16)	1.397 (2)
P(1)—C(5)	1.796 (1)	C(2)—C(3)	1.377 (2)	C(7)—C(8)	1.377 (3)	C(12)—C(13)	1.387 (2)
P(1)—C(11)	1.797 (1)	C(3)—C(4)	1.486 (2)	C(8)—C(9)	1.395 (2)	C(13)—C(14)	1.387 (2)
O(2)—C(3)	1.326 (2)	C(5)—C(6)	1.404 (2)	C(9)—C(10)	1.396 (2)	C(14)—C(15)	1.394 (2)
						C(15)—C(16)	1.387 (2)

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(1)—P(1)—C(2)	107.8 (1)	O(2)—C(3)—C(2)	122.3 (1)	C(5)—C(10)—C(9)	120.3 (1)
O(1)—P(1)—C(5)	113.8	O(2)—C(3)—C(4)	113.4 (1)	P(1)—C(11)—C(12)	123.8 (1)
O(1)—P(1)—C(11)	112.1 (1)	C(2)—C(3)—C(4)	124.2 (1)	P(1)—C(11)—C(16)	116.7 (1)
C(2)—P(1)—C(5)	108.7 (1)	P(1)—C(5)—C(6)	117.6 (1)	C(12)—C(11)—C(16)	119.5 (1)
C(2)—P(1)—C(11)	106.4 (1)	P(1)—C(5)—C(10)	122.2 (1)	C(11)—C(12)—C(13)	120.2 (1)
C(5)—P(1)—C(11)	107.8 (1)	C(6)—C(5)—C(10)	120.1 (1)	C(12)—C(13)—C(14)	120.1 (1)
N(1)—C(1)—C(2)	176.1 (1)	C(5)—C(6)—C(7)	119.1 (2)	C(13)—C(14)—C(15)	120.1 (1)
P(1)—C(2)—C(1)	118.4 (1)	C(6)—C(7)—C(8)	120.6 (1)	C(14)—C(15)—C(16)	120.0 (1)
P(1)—C(2)—C(3)	121.3 (1)	C(7)—C(8)—C(9)	120.5 (1)	C(11)—C(16)—C(15)	120.1 (1)
C(1)—C(2)—C(3)	120.1 (1)	C(8)—C(9)—C(10)	119.3 (2)		

and C(4)) are coplanar within 0.019 Å; the twisting (torsion distortion) of the double bond is no more than 3.0°. The C(2)=C(3) and C(1)≡N(1) bonds (1.377(2) and 1.151(2) Å, respectively) are slightly longer than the typical values (1.340 and 1.136 Å),[2] which is, apparently, caused by conjugation in the ethylene fragment of the molecule. The P(1)=O(1) phosphoryl bond length (1.507(1) Å) corresponds to the length of the double P=O bond involved in formation of a strong H-bond.[4] Note for comparison that in the monoclinic form of $Ph_3P=O$ the P=O distance is 1.492(2) Å.[5]

According to the available classification of H-bonds (see, for example, Refs. 6 and 7), the H-bond in crystals of **1** is classified as a strong short bond. As the analysis of the data in the literature on structural, spectral, and quantum-chemical studies of the systems with strong O—H...O hydrogen bonds demonstrates, when O...O distances are in the range 2.46—2.60 Å, the height of the barrier separating two possible minima in the potential curve of the H-bond is small and when O...O distances are shorter, this barrier is virtually absent (see Refs. 8 and 9).

When the above-mentioned short distances occur, the H atom should execute vibrations in a rather broad and flattened effective potential minimum, which may be unsymmetrical as well as symmetrical, and should have a high lability along the H-bond, which manifests itself in increased values of the parameters of the thermal displacements of this atom. When the parameters of such H atoms are refined anisotropically, the corresponding thermal ellipsoids appear to be substantially elongated along the O...O line.[4,8] The anisotropic refinement of the H(2) atom, which we have performed, demonstrated that its positional parameters were changed by no more than 2σ, whereas the ellipsoid of thermal vibrations (displacements) was substantially elongated along the O(2)...O(1) bond (Fig. 2). This result reflects qualitatively a high lability of the H(2) atom.

The analysis of the parameters of anisotropic displacements of all nonhydrogen atoms within the rigid-body LTS model[10] demonstrated that molecule **1** in crystals may be only approximately considered as structurally rigid: the agreement between the U_{ij} values obtained in the least-squares refinement of the structure (in this refinement, the Seiler—Dunitz's quasi-high-order weighting scheme[11] with B = 5.0 Å^2 was used) and those calculated from the LTS model is characterized by a value of the corresponding reliability factor R_u equal to 0.146. When the phenyl atoms, which can execute librational vibrations around the P—C bonds in crystals, are excluded from calculations of the LTS tensors, the value of R_u decreases substantially and

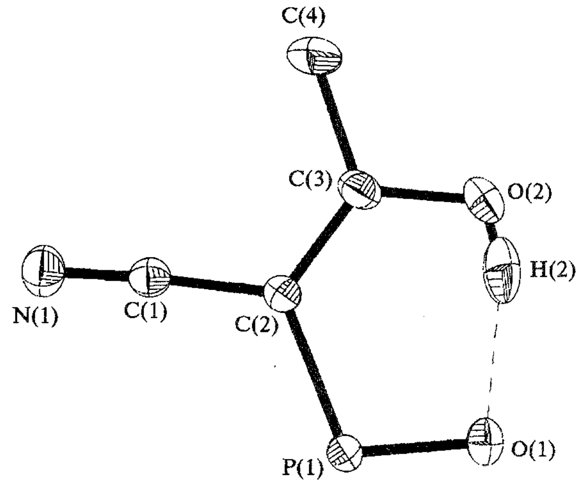

Fig. 2. Central fragment of the structure of **1**; atoms are represented by thermal ellipsoids drawn at the 50 % probability level.

becomes equal to 0.086, which is indicative of the structural rigidity of the central fragment with the H-bond. The libration corrections to bond lengths are no more than 0.002 Å. The rigid-bond test (the Hirshfeld test[12]) is also followed satisfactorily for chemically bonded atoms of the central fragment (the average value Δ is 0.0014 Å^2).

In this work, based on the parameters of anisotropic displacements of the H(2) atom obtained from the structure refinement and the analysis of displacements of nonhydrogen atoms within the rigid-body model we attempted to estimate the ν(OH) stretching frequency from the X-ray diffraction data. It is known[13] that besides the rigid-body motion of the molecule, rather high-frequency O—H stretching vibrations also contribute significantly to the thermal ellipsoid of the hydrogen atom involved in a strong H-bond (in this case, of the O—H...O type). In this case, the corresponding subtraction of the components of the rigid-body motion of the molecule from the ellipsoid of the H atom allows estimation of the degree of the residual motion (or disorder) of the H atom involved in an H-bond, *i.e.*, allows estimation of the ν(O—H) frequency. This approach was first proposed by Hamilton as early as in 1969[14] when he analyzed the neutron diffraction data for a number of crystals with strong H-bonds (see also Refs. 15 and 16). Clearly in the case of X-ray diffraction data, when the accuracy of location of H atoms is substantially lower, this approach may give only a qualitative result.

In this work, we used the difference Δ of mean-square amplitudes of the displacements of the H(2), O(1), and O(2) atoms in the projection onto the direction of the H-bond for estimating the residual motion of the H(2) atom along the H-bond. Taking into account a large error in determining the parameters of anisotropic displacements of the H(2) atom, we varied the calculated values of Δ over a rather wide range 0.023—0.014 Å^2, which corresponds to the ν(O—H) frequency range of ≈700—1200 cm^{-1}, within which the absorption band in the region of ν(O—H) skeletal vibrations (≈950 cm^{-1}) falls in the IR spectrum of compound **1**.

This analysis of the electron distribution pattern in the region of the H-bond under consideration is also of interest. It is known[17] that the electron density distribution in the region of H-bonds with a low and moderate density differs greatly from that for strong bonds exhibiting a substantial covalent component in the O—H...O hydrogen bridge. It is common practice to ignore the electron density of a spherically symmetrical H atom, which forms an H-bond, in the composition of a promolecule when traditional deformation electron density maps are calculated with the aim of determining this covalent component.[17,18] In this case, a covalent component of an H-bond manifests itself as a continuous

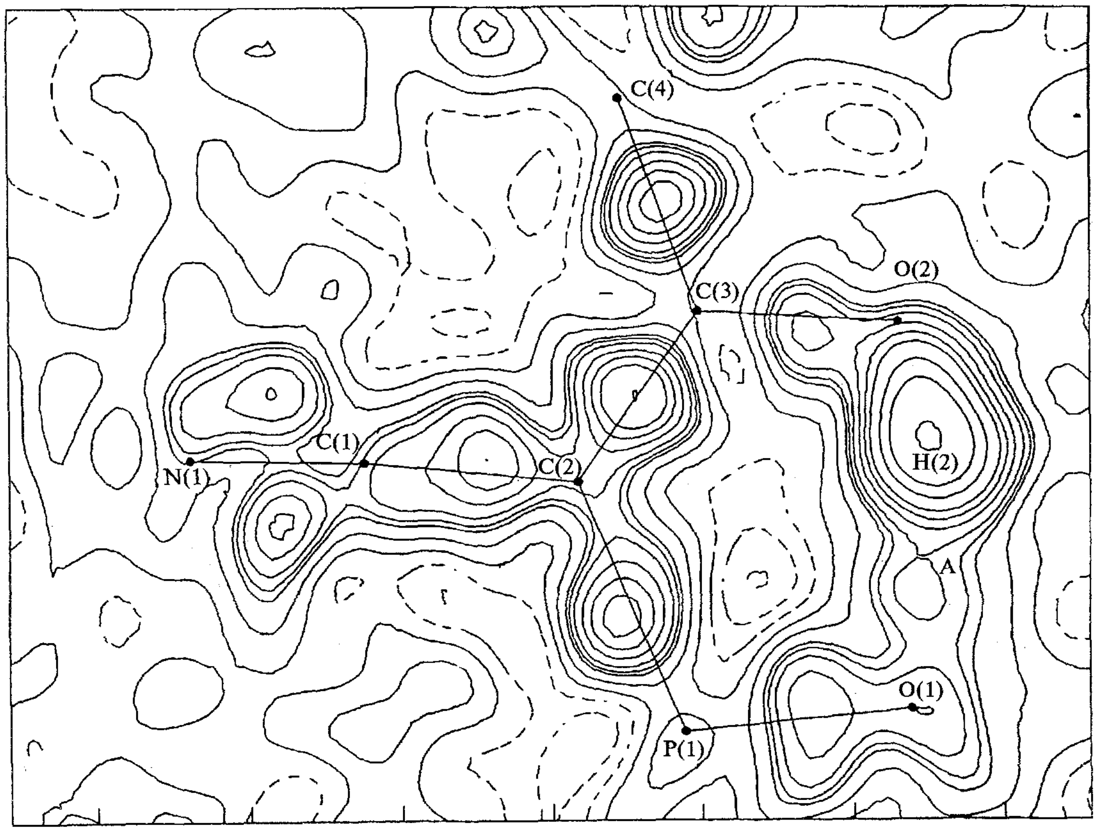

Fig. 3. Deformation electron density map of the central region of molecule **1**. Contour intervals are 0.05 *e* Å^{-3}. The electron density of the H(2) atom was not subtracted.

Table 2. Atomic coordinates for nonhydrogen atoms (×10^4) in the structure of **1** and their equivalent isotropic temperature factors

Atom	x	y	z	$U \cdot 10^3/\text{Å}^2$
P(1)	2974 (1)	272 (1)	807 (1)	17 (1)
O(1)	3480 (1)	1236 (1)	563 (1)	25 (1)
O(2)	2104 (1)	2241 (1)	1550 (2)	34 (1)
N(1)	587 (1)	−942 (1)	1704 (2)	28 (1)
C(1)	1107 (1)	−266 (1)	1626 (2)	19 (1)
C(2)	1800 (1)	528 (1)	1486 (2)	18 (1)
C(3)	1516 (1)	1475 (1)	1748 (2)	22 (1)
C(4)	539 (1)	1744 (1)	2273 (3)	33 (1)
C(5)	3868 (1)	−514 (1)	2297 (2)	19 (1)
C(6)	4789 (1)	−885 (1)	1906 (2)	26 (1)
C(7)	5539 (1)	−1441 (1)	3079 (2)	32 (1)
C(8)	5371 (1)	−1645 (1)	4589 (2)	31 (1)
C(9)	4461 (1)	−1275 (1)	4988 (2)	28 (1)
C(10)	3713 (1)	−703 (1)	3831 (2)	22 (1)
C(11)	2498 (1)	−402 (1)	−1094 (2)	19 (1)
C(12)	2626 (1)	−1414 (1)	−1221 (2)	23 (1)
C(13)	2204 (1)	−1884 (1)	−2725 (2)	28 (1)
C(14)	1655 (1)	−1352 (1)	−4113 (2)	29 (1)
C(15)	1520 (1)	−344 (1)	−3996 (2)	29 (1)
C(16)	1940 (1)	130 (1)	−2493 (2)	26 (1)

Table 3. Atomic coordinates for hydrogen atoms (×10^3) in the structure of **1** and their equivalent isotropic temperature factors

Atom*	x	y	z	$U \cdot 10^2/\text{Å}^2$
H(2)	258 (1)	206 (1)	125 (3)	36 (12)**
H(4a)	14 (2)	115 (2)	232 (3)	5 (1)
H(4b)	10 (2)	213 (2)	140 (4)	11 (1)
H(4c)	75 (2)	202 (2)	333 (4)	9 (1)
H(6)	490 (1)	−76 (1)	81 (3)	3 (1)
H(7)	617 (1)	−172 (1)	279 (2)	3 (1)
H(8)	594 (1)	−202 (1)	547 (3)	4 (1)
H(9)	435 (1)	−146 (1)	608 (3)	2 (1)
H(10)	311 (1)	−45 (1)	412 (3)	4 (1)
H(12)	307 (1)	−179 (1)	−31 (2)	3 (1)
H(13)	228 (2)	−252 (2)	−284 (3)	6 (1)
H(14)	135 (2)	−167 (2)	−511 (3)	6 (1)
H(15)	113 (2)	0 (2)	−501 (3)	7 (1)
H(16)	187 (1)	76 (1)	−235 (3)	4 (1)

* The H atoms are assigned the numbers of the C and O atoms bonded to the corresponding H atoms.

** For the H(2) atom the equivalent isotropic thermal factor ($U \cdot 10^3/\text{Å}^2$) is given.

bridge of electron density with a saddle point in the H...O region, which was first established in precise study of electron distribution in crystals of oxalic acid dihydrate,[18] in which the O...O distance for a strong H-bond is 2.487 Å.

The corresponding deformation electron density map in the plane of the six-membered H-bonded cycle of the structure of **1** is shown in Fig. 3. The data of the above-mentioned quasi-high-order refinement were used as a model of the structure for calculating the deformation electron density map. The deformation electron density map contains all characteristic features in the region of chemical bonds of atoms of the H-cycle under consideration; among these characteristic features, the most interesting feature is the presence of a continuos bridge of electron density in the O(2)—H(2)...O(1) region with the saddle point (A) between the H(2) and O(1) atoms with a height of 0.14 e Å^{-3}, which is indicative of a covalent component in the H-bond under consideration. Note that in oxalic acid dihydrate, the corresponding value of electron density in the saddle point is higher and is equal to 0.25 e Å^{-3}, which may result from a higher strength of this bond as well as from a higher experimental resolution.

Experimental

X-ray diffraction study of compound **1** was performed at −120 °C on an automated four-circle Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, $\theta/2\theta$ scanning technique, $2\theta < 75°$). The crystals are monoclinic, at −120 °C: a = 12.801(1), b = 13.653(2), c = 8.424(3) Å, β = 106.39(1)°, V = 1412.5(4) Å^3, mol. weight 283.25, space group $P2_1/c$, Z = 4, d_{calc} = 1.332 g cm^{-3}, μ = 0.19 mm^{-1}. Of a total of 5426 reflections collected, 3832 independent observed reflections with $|F| > 4\sigma(F)$ were used in subsequent calculations and refinement. The structure was solved by the direct method and refined anisotropically by the full-matrix least-squares method.

Positions of hydrogen atoms were located from the difference electron density synthesis; these atoms were included in the final refinement with isotropic thermal parameters. In the final stage of refinement, the H(2) atom involved in a hydrogen bond was refined anisotropically. The final values of R factors are as follows: R = 0.037, R_w = 0.043, GOF = 1.19. All calculations were performed on an IBM PC/AT computer using the SHELXTL PLUS program package.[19] The bond lengths and bond angles are given in Table 1; atomic coordinates and thermal parameters are listed in Tables 2 and 3.

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