Full Articles

Nature of weak inter- and intramolecular interactions in crystals
6.* Intramolecular O—H...O bond in enol forms of (phosphoryl)acylacetonitriles**

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The nature of the intramolecular O—H...O bond was studied and its energy was estimated by X-ray diffraction analysis and quantum-chemical calculations (B3LYP/6-311G**) of (diphenylphosphoryl)acylacetonitriles. The influence of the nature of the substituents at the double bond in the H-bonded ring and the crystal packing effects on the hydrogen bond were investigated.

Key words: (phosphoryl)acylacetonitriles, tautomerism, enols, hydrogen bonds, supramolecular chemistry, topological theory of Atoms in Molecules, X-ray diffraction data.

We have studied keto enols of β-diketones by X-ray diffraction and quantum-chemical methods[2,3] and demonstrated that intramolecular O—H...O bonds in these symmetrical systems correspond to an intermediate type of interatomic interactions in terms of Bader's topological theory of Atoms in Molecules (AIM).[4] These interactions are characterized by a lower barrier to proton transfer and a high energy of the hydrogen bond, which is stabilized through π-electron density delocalization in the hydrogen-bonded six-membered ring. It was suggested that the O—H...O bond strength, for which the interatomic O...O distance serves as an estimate, depends on the nature of the substituents at the carbon atoms of the keto enol ring because these distances in structurally similar acetylacetone,[4] benzoylacetone,[5] and tetraacetylethane[3] differ in value (2.547(1), 2.502(4), and 2.450(1) Å, respectively). However, no such differences were observed in the isolated molecules of these compounds. Quantum-chemical calculations (DFT at the B3LYP level with the 6-31G** or larger basis set) showed that the O...O distance in the keto enol form is always approximately equal to 2.51 Å.[3,7,8] The same distance between the oxygen atoms was also obtained from gas electron diffraction data[9] for acetylacetone at 294 K. Hence, the difference in the hydrogen bond strength in the solid state for a series of compounds

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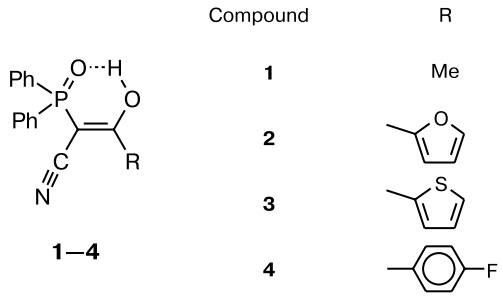
under consideration is, apparently, determined by the crystal packing effects.

However, the β-diketone fragment in all the above-considered cyclic systems with hydrogen bonds have a symmetrical structure. It was of interest to estimate the character of interatomic interactions in the vicinity of the intramolecular hydrogen bond in keto enols, in which the oxygen atoms would be characterized by strong chemical nonequivalence, and, consequently, the barrier to proton transfer along the hydrogen bond line in these molecules would also be high. In the present study, we considered the enol forms of (diphenylphosphoryl)acylacetonitriles **1—4** (see Refs 10—12) as such systems. These compounds contain the phosphoryl fragment instead of the second carbonyl group.



Interestingly, the first representatives of this class have been synthesized in 15—30% yields by acylation of potassium derivatives of dialkoxyphosphorylacetonitriles.[13] Based on the results of bromometric titration and IR spectroscopic data, it has been suggested[13,14] that these compounds exist as equilibrium mixtures of tautomers with a variable percentage of the ketone and enol forms. Recently, we have developed an efficient procedure for the synthesis of this class of compounds under phase-transfer catalysis conditions. This method is suitable for the preparation of compounds containing various substituents both at the phosphorus atom and the acyl fragment (see Refs 12 and 15 and references therein). Using spectroscopic methods and X-ray diffraction analysis, we demonstrated that these compounds exist as the corresponding enol forms both in the individual state and in solutions of nonpolar and polar solvents.

Therefore, we chose this class of compounds also because the presence of strong intramolecular hydrogen bonds in these compounds both in the crystalline state[10] and solution[11,12] was confirmed by experimental data. X-ray diffraction study revealed a strong hydrogen bond (O...O, 2.550 Å) in the crystal structure of α-acetyl-α-diphenylphosphorylacetonitrile (**1**).[10] The O...O distance **1** is comparable to the distances in the above-considered keto enols. In addition, the π-electron density delocalization in the hydrogen-bonded ring in these compounds, like that in keto enols, increases with increasing strength of intramolecular hydrogen bonds.[11]

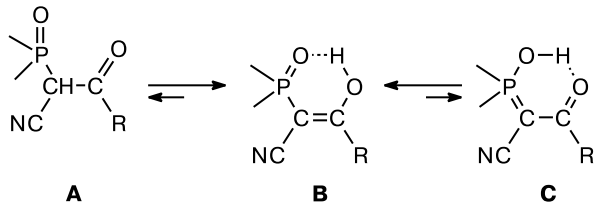
To estimate the influence of the substituent R at the double bond on the hydrogen bond strength in organophosphorus analogs of keto enols, we performed X-ray diffraction study of compounds containing the furan (**2**), thiophene (**3**), or *p*-fluorophenyl (**4**) group as the heterocyclic substituent at position 2. Data for methyl-substituted analog **1**, which has been studied earlier,[10] were used for comparison.

Molecular and crystal structures

X-ray diffraction studies demonstrated that compounds **2—4** crystallize without solvent molecules. In the crystals of compounds **3** and **4**, there is one crystallographically independent molecule per asymmetric unit. In the crystal structure of compound **2**, $Z' = 2$.

Compounds **2—4** exist as enols **B** of the corresponding acylacetonitriles **A**. These compounds, like compound **1**,[10] adopt a *Z* conformation to form a planar six-membered ring stabilized by an intramolecular O—H...O hydrogen bond (Scheme 1, Fig. 1). The maximum average deviation of the atoms from the plane of the H-bonded ring is observed in compound **3** (0.066 Å).

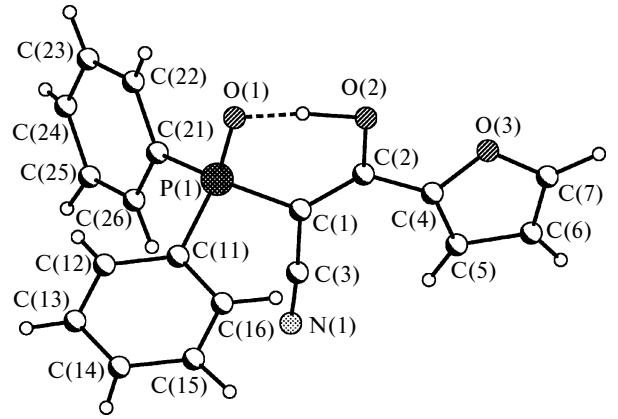
Scheme 1



In all compounds, the hydrogen bond is strong (see the O(1)...O(2) distances, Table 1). The shortest O...O distance is observed in **2** (O(1)...O(2), 2.522—2.528(3) Å). The replacement of the furan substituent with the thiophene group (**3**) leads to weakening of the hydrogen bond (O(1)...O(2), 2.607(2) Å). Other geometric parameters of the ring, *viz.*, the C—O and C=C bond lengths, are virtually equal to each other, in spite of variations in the O...O distances.

The heterocycles in compounds **2** and **3** are coplanar with the plane of the H-bonded ring (the twist angle is at most 2°) containing the heteroatom (O or S) in the *syn* orientation with respect to the hydroxy group. This orientation of the substituent relative to the keto enol fragment is indicative of the presence of conjugation between these two groups.* To the contrary, the *p*-fluoro-

* It should be noted that, according to the results of quantum-chemical calculations at the PBE/TZ2p level,[12] the conformer adopting this conformation does not correspond to the energy minimum.



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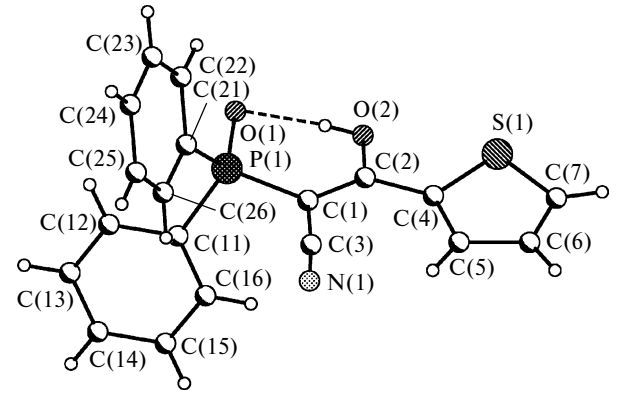

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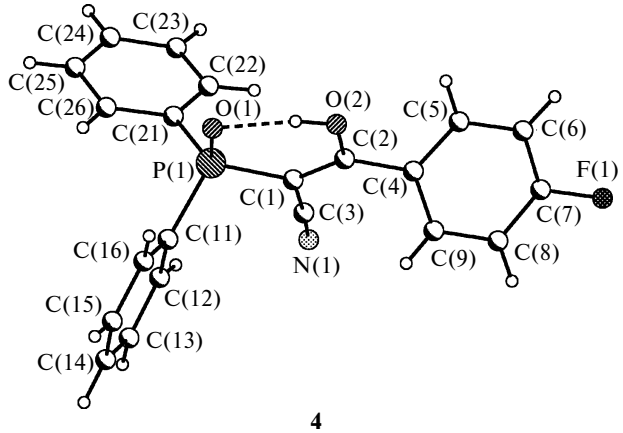

4

Fig. 1. Molecular structures of compounds **2—4**.

phenyl substituent in compound **4** is twisted with respect to the H-bonded ring by 38.8°, which should result in substantial weakening of the conjugation. Actually, the C(2)—C(4) bond in **4** is longer than the corresponding bonds in compounds **2** and **3** (by approximately 0.02—0.03 Å) and is only 0.01 Å shorter than that observed in compound **1** (see Table 1). Apparently, the observed twist of the *p*-fluorophenyl substituent is attributed to steric repulsions between the *ortho*-hydrogen atoms and the cyano group, although the influence of intermolecular interactions cannot be ruled out as well.

The crystal structures of **2—4** are characterized by the similar mutual arrangement of the phenyl substituents at the phosphorus atom with respect to the P(1)—O(1) bond. In all structures, one of the phenyl substituents is in the eclipsed conformation relative to the P=O bond (the twist angle is 4—14°), whereas another phenyl substituent lies in the plane perpendicular to the P=O bond, and the corresponding torsion angle varies over a wider range (70—109°). Taking into account that the P—Ph bond lengths in **2—4** are virtually equal to each other (1.793(3)—1.804(3)Å) and are independent of the arrangement of the phenyl groups with respect to the P=O bond, the observed conformations are presumably stabilized by intramolecular contacts.

Since compounds **1—4** differ only in the nature of the substituent at the C(2) atom, the change in the hydrogen bond strength, in particular, weakening of the hydrogen bond in compound **3**, can be attributed to specific stereoelectronic interactions between the S atom and the OH group.

Actually, the *syn* arrangement of the oxygen (or sulfur) atom and the hydroxy group gives rise to the forced shortened O(3)...O(2) and S(1)...O(2) contacts (2.557(5) and 2.736(2) Å, respectively). The presence of the shortened contact and its specific directionality (the S(1)O(2)H(2O) angle is 173°) suggest that the charge transfer from the sulfur lone pair (n_s) to the antibonding σ orbital of the O(2)—H(2O) bond (σ^*_{O-H}) can occur in **3**. An analogous hypothesis has been made in the study.[16] The corresponding angles in compound **2** also do not rule out the presence of the $n_O—\sigma^*_{O-H}$ interaction. However, taking into account the diffuse character of the sulfur lone pairs, the charge transfer to the O—H bond in **3** is, apparently, more pronounced.

Taking into account that the differences in the strength of intramolecular hydrogen bonds can be associated not only with the nature of the substituent but also with the crystal packing effects, we performed quantum-chemical calculations (B3LYP/6-311G**) of molecules **1—4** in the isolated state.

Although the functional and the basis set used in the calculations rather well reproduce the experimental data (see Table 1), the P(1)—O(1) bond is substantially elongated (by 0.03 Å), which is typical of quantum-chemical calculations of P=O-containing compounds.[17]

The arrangement of the phenyl rings at the phosphorus atom, as well as the conformations of the substituents at the C(2) atom relative to the hydrogen-bonded ring, in the crystals are virtually equal to those in the isolated molecules. According to the results of calculations at the B3LYP/6-311G** level, one of the phenyl substituents is in the eclipsed conformation, whereas another phenyl substituent is perpendicular to the P=O bond. The corre-

Table 1. Selected interatomic distances in compounds **1**—**4**

Distance	X-ray diffraction data				Calculations			
	1	**2**[a]	**3**	**4**	**1**	**2**	**3**	**4**
P(1)—O(1)	1.507(1)	1.511/1.507(3)	1.496(2)	1.502(1)	1.521	1.521	1.522	1.522
P(1)—C(1)	1.788(1)	1.807/1.804(3)	1.796(2)	1.796(2)	1.816	1.816	1.818	1.821
C(1)—C(2)	1.376(2)	1.384/1.388(5)	1.391(4)	1.382(2)	1.380	1.392	1.391	1.387
C(2)—O(2)	1.326(2)	1.332/1.321(4)	1.328(3)	1.321(2)	1.319	1.320	1.325	1.323
C(1)—C(3)	1.425(2)	1.419/1.422(5)	1.410(3)	1.421(2)	1.415	1.408	1.409	1.412
C(2)—C(4)	1.488(2)	1.450/1.454(5)	1.449(3)	1.478(2)	1.497	1.454	1.457	1.481
O(1)...O(2)	2.550(2)	2.522/2.528(4)	2.607(3)	2.560(2)	2.557	2.547	2.532	2.537
O(2)...X[b]	—	2.559/2.555(4)	2.736(3)	2.809(2)	—	2.564	2.794	2.714

[a] Data for two crystallographically independent molecules in the unit cell are given.
[b] X = O(3) (**2**), S(1) (**3**), and C(5) (**4**).

sponding torsion angles vary in the ranges of 3.8—6.1 and 85.0—89.2°, respectively. The P—Ph bond lengths (1.813—1.814Å), like those in the crystals, are virtually independent of the twist angle. The twist angle of the *p*-fluorophenyl group in **4** also changes only slightly (in the isolated molecule, this angle is 27.2°), and the twist angle of the hetaryl substituent remains virtually unchanged.

The interatomic O(1)...O(2) distances in isolated molecules **1**—**4**, unlike those in the crystals, are virtually equal to each other. In isolated molecule **3**, this distance is even slightly shorter than that in the crystal (see Table 1). The distances between the oxygen atom of the hydroxy group and the heteroatom of the substituent R in **2** and **3** vary only slightly.

To estimate the barrier to proton transfer in this system, we made an attempt to optimize the potentially possible hydroxy ylide ketone tautomer **C** (see Scheme 1) using compound **1** as an example. However, calculations always gave phosphoryl enol **B** regardless of the starting geometry. We found the desired tautomer **C** only when we fixed the O(1)—H(1) distance. The energy of this tautomer appeared to be 15 kcal mol^{-1} higher than that of the tautomer **B**. Therefore, both the energy difference and the character of geometry optimization unambiguously indicate that the barrier to proton transfer in phosphorus-substituted acrylonitriles is very high, which is radically different from their keto enols.

To obtain more complete data on the influence of the substituent at the C(2) atom on the H-bonded ring, elucidate the type of the interatomic interaction in the vicinity of the hydrogen bond, and reveal the factors responsible for stability of the conformation of the phenyl substituents with respect to the P=O group, we performed topological analysis of the electron density distribution $\rho(\mathbf{r})$ in isolated molecules **1**—**4** using the results of B3LYP/6-311G** calculations.

A search for critical points (CP) of $\rho(\mathbf{r})$ showed that CP (3, −1) are localized not only in the vicinity of all covalent bonds and the intramolecular hydrogen bond but also near a series of intramolecular interactions between the hydrogen atoms of the phenyl groups and the substituents at the C(3) atom and the cyano group. In all structures, CP (3, −1) were localized in the vicinity of C—H...CN contacts formed by the CN group and the *o*-protons of the furan (2.531 Å), thiophene (2.445 Å), *p*-fluorophenyl substituents (2.428 Å), and the phenyl substituent (H...C, *ca.* 2.91 Å) located in the eclipsed conformation with the respect to the P=O group.

By contrast, CP (3, −1) were not found for the O(2)...O(3) (**2**) and O(2)...S(1) (**3**) pairs. This unambiguously indicates that these forced contacts do not correspond to attractive interactions. The latter are absent due to the unfavorable arrangement of the sulfur lone pairs with respect to the O(1)—H(1) bond. Actually, the Laplacian of the electron density $\nabla^2\rho(r)$ in the plane of the hydrogen-bonded ring in **3** shows that neither n_S of the S atom nor n_O of the O atom of the hydroxy group is directed toward the regions of charge depletion in the O(1)—H(1) and C(8)—S(1) bonds, respectively (Fig. 2).

The topological parameters of $\rho(\mathbf{r})$ at CP (3, −1) for the covalent bonds are close to the expected values (Table 2). All bonds, except for P—O, are characterized by the negative Laplacian of the electron density $\nabla^2\rho(\mathbf{r})$ and, consequently, correspond to shared interatomic interactions. In spite of the positive value of $\nabla^2\rho(\mathbf{r})$ (27.82—27.96 e Å^{-3}) at CP (3, −1), the P(1)—O(1) bond is characterized by the negative electron energy density $H_e(r)$ (−0.159 a.u.) and, hence, corresponds to an intermediate type of interatomic interactions in terms of the AIM theory.[4]

Analysis of the ellipticities ε (which reflect the degree of deviation of $\rho(\mathbf{r})$ from cylindrical symmetry in the map perpendicular to the bond line) revealed considerable π-electron density delocalization in the H-bonded ring in compounds **1**—**4**. First, noteworthy are high ε at CP (3, −1) for the P(1)—C(1) (0.120—0.129) and C(1)—C(2) (0.330—0.348) bonds. The ellipticity ε (0.02)

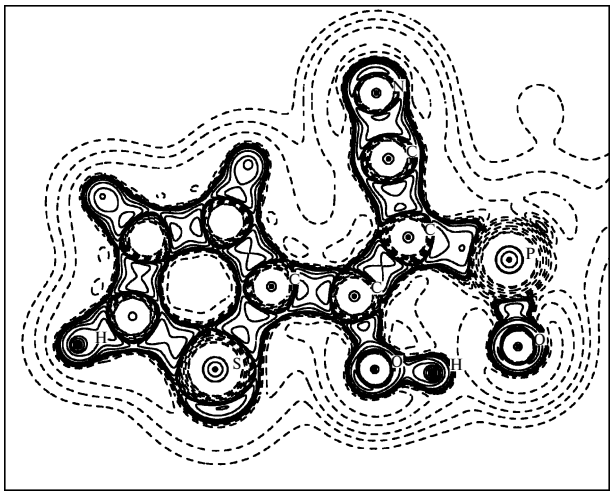

Fig. 2. Electron density distribution $-\nabla^2\rho(\mathbf{r})$ in the plane of the H-bonded ring in enol **3**.

at CP (3, −1) for the P(1)—O(1) bond is small due both to high polarity of the bond (positive $\nabla^2\rho(\mathbf{r})$ at CP (3, −1)) and the unusual character of binding, *viz.*, back donation from the oxygen lone pairs to the antibonding orbitals of the P—C bonds (see Refs 18 and 19).

The large ellipticities ε for the C(1)—C(3) and C(2)—C(4) bonds indicate that both the CN group and the aryl and hetaryl substituents at the C(2) atom are involved in conjugation with the hydrogen-bonded ring. Analysis of ε for the C(2)—C(4) bonds in compounds **1**—**4** shows that the maximum conjugation between the hydrogen-bonded ring and the substituent at the C(2) atom is observed in the case of furan, whereas ε in the thiophene-containing compound is only slightly larger than that in **4** in spite of the twisting of the *p*-fluorophenyl substituent (for comparison, ε for the C(2)—C(4) bond in **1** is 0.058).

It should be noted that, although the P—Ph bond lengths are equal in different conformations, the corresponding ellipticities ε for the P—C bond for the phenyl substituent in the eclipsed conformation are systematically larger (0.092—0.095) than those for another phenyl substituent (0.01—0.013). Hence, it can be concluded that stability of the mutual arrangement of the phenyl substituents at the P atom and the P=O group observed in the crystals is determined primarily by conjugation with the phosphoryl group rather than by the presence of weak intramolecular contacts. In turn, this effect suggests that the bond lengths for third-period elements are not informative for analysis of the contribution of the π component.

Analysis of the topological characteristics of $\rho(\mathbf{r})$ in the vicinity of the hydrogen bond demonstrated that the hydrogen bonds in compounds **1**—**4**, like those in the keto enol systems studied earlier, correspond to an intermediate type of intermolecular interactions ($\nabla^2\rho(\mathbf{r})$ = 3.72—3.85 e Å^{-5}, $H_e(\mathbf{r})$ = −0.14—0.12 a.u.). Therefore, the intermediate type of interatomic interactions for strong hydrogen bonds is not characteristic of low-barrier hydrogen bonds and is observed also for hydrogen bonds with a high barrier to proton transfer.

Table 2. Main topological characteristics at CP (3, −1) in compounds **1**—**4** calculated at the B3LYP/6-311G** level

Bond	Compound	$\rho(\mathbf{r})$ /e Å^{-3}	$\nabla^2\rho(\mathbf{r})$ /e Å^{-5}	ε	$H_e(\mathbf{r})$
P(1)—O(1)	**1**	1.442	27.94	0.019	−0.159
	2	1.443	27.96	0.020	−0.159
	3	1.440	27.82	0.021	−0.159
	4	1.440	27.86	0.020	−0.159
P(1)—C(1)	**1**	1.126	−3.88	0.110	−0.168
	2	1.122	−3.75	0.121	−0.167
	3	1.121	−3.93	0.119	−0.167
	4	1.119	−4.11	0.114	−0.167
C(1)—C(2)	**1**	2.110	−20.25	0.348	−0.327
	2	2.061	−19.45	0.330	−0.312
	3	2.062	−19.46	0.331	−0.313
	4	2.080	−19.73	0.335	−0.317
C(2)—O(2)	**1**	2.161	−9.77	0.022	−0.481
	2	2.171	−11.09	0.006	−0.483
	3	2.141	−11.05	0.000	−0.474
	4	2.145	−10.29	0.012	−0.476
C(1)—C(3)	**1**	1.900	−17.82	0.118	−0.281
	2	1.918	−18.01	0.131	−0.287
	3	1.918	−18.02	0.130	−0.287
	4	1.908	−17.87	0.121	−0.283
C(2)—C(4)	**1**	1.760	−15.70	0.058	−0.226
	2	1.916	−18.40	0.195	−0.261
	3	1.884	−17.53	0.155	−0.254
	4	1.820	−16.66	0.113	−0.238
O(2)—H(2O)	**1**	2.114	−51.23	0.013	−0.598
	2	2.103	−50.78	0.013	−0.595
	3	2.075	−49.63	0.014	−0.584
	4	2.087	−50.05	0.013	−0.588
O(1)...H(2O)	**1**	0.402	3.72	0.015	−0.012
	2	0.419	3.79	0.014	−0.013
	3	0.440	3.84	0.014	−0.015
	4	0.433	3.83	0.015	−0.014

The hydrogen bond energy in molecules **1**—**4** was estimated with the use of a correlation scheme, which relates the energy of the contact to the potential energy density at CP (3, −1).[20] The semiquantitative estimation of the hydrogen bond energy gave the following values: −19.45, −20.57, −21.92, and −21.49 kcal mol^{-1} for compounds **1**—**4**, respectively. The strongest hydrogen bond (according to the results of calculations) is present in compound **3**, which is in complete agreement with the analysis of the molecular geometry in the isolated state. It should be noted that the energies of the O—H...O bonds are somewhat lower than those in 3-acetyl-4-hydroxycoumarin (33.8 kcal mol^{-1})[2] and tetraacetylethane (37.65 kcal mol^{-1})[3] and are similar to

those found in Schiff bases with strong intramolecular N—H...O hydrogen bonds (16—21 kcal mol^{-1}; O...N, 2.6668(5)—2.6379(5) Å).[18]

Hence, weakening of the hydrogen bond observed in the crystal structure of **3** containing the thiophene group is not observed in the isolated molecules.

The observed differences in the hydrogen bond strength can be attributed also to the crystal packing effects. The crystal packings of compounds **2—4** are stabilized primarily by weak C—H...O and C—H...N contacts. In particular, such interactions give rise to the structural unit of the packing of compound **2**, in which two crystallographically independent molecules are linked by asymmetric bifurcate C—H...O bonds (H...O, *ca.* 2.28 and 2.52 Å; C—H—O, 136 and 156°) (Fig. 3) to form dimers. These dimers are additionally stabilized by stacking interactions between the furan rings. The furan rings in the dimers are located parallel to each other at a distance of 3.36 Å with the shortest C(4)...C(4′) distance of 3.363(3) Å.

In the crystal structure of compound **4**, the system of intermolecular contacts involves also C—H...F interactions (H...F, 2.42 Å; CHF, 137°) due to the presence of the *p*-fluorophenyl substituent.

The crystal packing of **3** is of particular interest. This crystal structure has interactions involving the H(2O) atom, which already participates in the intramolecular hydrogen bond. The formation of competitive intermolecular O—H...O bonds leads to the formation of centrosymmetric dimers (Fig. 4). These bonds are substantially weaker than the intramolecular O—H...O bonds. The O...O distance increases to 2.899(3) Å, and the angle at the hydrogen atom is 112°. For comparison, the corresponding parameters for the intramolecular hydrogen bond are 2.607(3) Å and 159°.

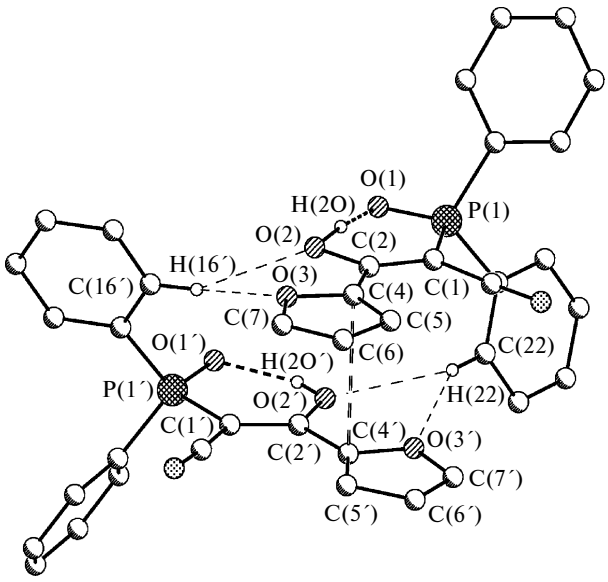

Fig. 3. Dimer formed through a stacking interaction and C—H...O contacts in the crystal of **2**.

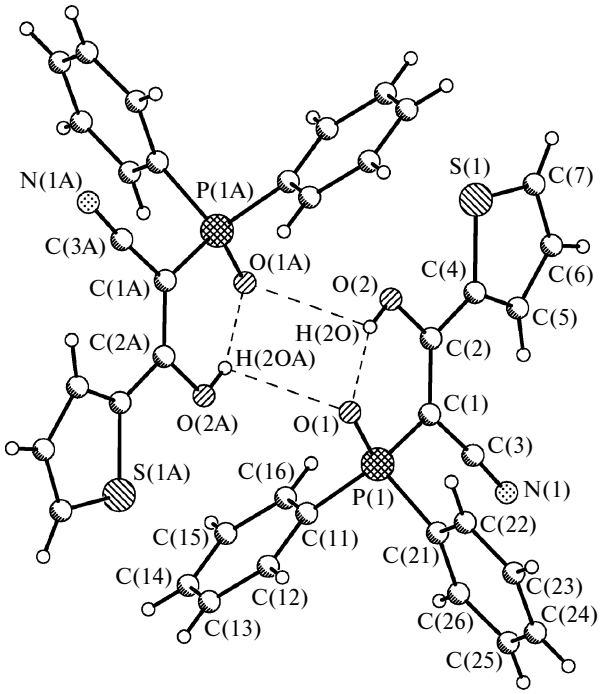

Fig. 4. The O—H...O-bonded dimer in the crystal of **3**.

These intermolecular contacts for hydrogen-bonded rings are rather often observed in the crystal structures (see Refs 3 and 21). In particular, an analogous centrosymmetric dimer (the distance between the oxygen atoms of the hydroxy groups is 2.849(1) Å) was observed in the crystal structure of 3-acetyl-4-hydroxycoumarin.[3] In spite of the relatively high energy of this contact (1.75 kcal mol^{-1}),[3] its presence in the crystal of 3-acetyl-4-hydroxycoumarin does not lead to considerable weakening of the intramolecular hydrogen bond.

Therefore, X-ray diffraction and quantum-chemical studies of the enol forms of (diphenylphosphoryl)acylacetonitriles **1—4** demonstrated that, in spite of the high barrier to proton transfer, the intramolecular hydrogen bonds in this series of compounds are similar in properties to analogous intramolecular hydrogen bonds in keto enols. However, due to a decrease in the hydrogen bond energy, the latter depends more substantially on even weak intermolecular contacts rather than on the nature of the substituents at the carbon atoms of the hydrogen-bonded ring.

These data suggest that the correlations between the hydrogen bond strength and the electronic effects of the substituents in the hydrogen-bonded ring determined by systematic X-ray diffraction studies of strong intramolecular hydrogen bonds, in which the hydrogen donor and acceptor differ substantially in the chemical nature, as well as of N—H...O, O—H...N, and N—H.....S interactions, can include systematic errors because the crystals

Table 3. Crystallographic data and details of X-ray diffraction study for compounds **2—4**

Parameter	**2**	**3**	**4**
Molecular formula	$C_{19}H_{14}O_3NP$	$C_{19}H_{14}O_2NSP$	$C_{21}H_{15}O_2NFP$
Molecular weight	335.28	351.34	363.31
Crystal system	Hexagonal	Triclinic	Monoclinic
Space group	$P6_5$	$P\bar{1}$	$P2_1/c$
T/K	150	150	110
Diffractometer	«Syntex-$P2_1$»	«Syntex-$P2_1$»	«SMART CCD»
Z	12	2	4
a/Å	8.805(3)	8.722(2)	8.755(2)
b/Å	8.805(3)	9.353(2)	26.003(5)
c/Å	71.20(4)	11.458(2)	8.501(2)
α/deg	90.00	80.13(3)	90.00
β/deg	90.00	69.71(3)	114.87(1)
γ/deg	120.00	77.28(3)	90.00
V/Å^3	4781(3)	850.5(3)	1755.8(6)
d_{calc}/g cm^{-3}	1.398	1.372	1.374
Absorption coefficient μ/mm^{-1}	0.189	0.295	0.182
F(000)	2088	364	752
θ Scan range/deg	2.7—29	1.9—25.1	1.6—30.1
Number of measured reflections	27316	3172	19419
Number of independent reflections	7981	2958	5081
R_{int}	0.0488	0.0272	0.0270
Number of parameters in refinement	546	221	295
GOOF	1.053	1.008	1.008
Number of reflections with $I \geq 2\sigma(I)$	7219	2601	3885
Final R factors (for reflections with $I \geq 2\sigma(I)$):			
R_1	0.0599	0.0557	0.0508
wR_2	0.1273	0.1625	0.1161
R factors for all reflections:			
R_1	0.0664	0.0634	0.0635
wR_2	0.1301	0.1671	0.1215
Residual electron density (min/max)/e A^{-3}	−0.38/0.41	−0.54/0.96	−0.26/0.41

can contain weak competitive interactions and it is not always possible to clearly distinguish their role.

Experimental

Compounds **2—4** were prepared according to a procedure described earlier.[12] The single-crystal X-ray diffraction data sets for compounds **2** and **3** were collected on an automated four-circle Syntex-$P2_1$ diffractometer (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, θ/2θ scanning technique). The X-ray diffraction data for compound **4** were measured on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω scanning technique with a step of 0.3°, exposure time per frame was 15 s). The X-ray data were processed and merged using the SAINT Plus program package,[22] and semiempirical absorption corrections were applied.[23]

The structures of compounds **2—4** were solved by direct methods and refined isotropically by the full-matrix least-squares method with the use of successive electron density maps. All nonhydrogen atoms were located from electron density maps. The refinement was carried out against F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. The H(2O) atom was also located from electron density maps and refined isotropically. The coordinates of other hydrogen atoms were calculated geometrically and refined using a riding model. The structures were refined with the use of the SHELXTL 5.10 program package.[24] The crystallographic data and parameters of structure refinement of compounds **2—4** are given in Table 3.

Quantum-chemical calculations were performed by density functional theory with the use of the B3LYP hybrid functional and the 6-311G(d,p) basis set using the Gaussian 03W program.[25] The topological analysis of the theoretical electron density distribution was performed with the use of the MORTHY98 program.[26]

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