Nature of weak inter- and intramolecular interactions in crystals
8.* Influence of intermolecular contacts on the strength of intramolecular O—H...N bonds in crystals of 3-(2-hydroxyphenyl)-1,2,4-triazoles

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The nature and energy of the intramolecular H-bond in 3-(2-hydroxyphenyl)-1,2,4-triazoles was studied by X-ray diffraction and quantum chemical methods. In this system, the conjugation does not additionally contribute to the enhancement of the H-bond energy. The cooperative effects lead to a strengthening of the intramolecular H-bond.

Key words: 3-(2-hydroxyphenyl)-1,2,4-triazoles, X-ray diffraction study, quantum chemical calculations, intramolecular O—H...N bond, cooperative effects.

As part of systematic studies of the electron density distribution ρ(r) in compounds with strong intramolecular H-bonds stabilized through conjugation (delocalization assistant H-bond, see the reviews[2]), we have earlier analyzed O—H...O bonds in ketoenols of β-diketones[3] and 3-(aryl)hetaryl-3-hydroxy-2-phosphoryl-substituted acrylonitriles,[4] N—H...S bonds in (2*Z*)-2-cyano-2-quinolin-2(1*H*)-ylideneethanethioamide,[5] and N—H...O bonds in methyl 2-{2-[(*E*)-(diethoxyphosphoryl)methylidene]-4-oxothiazolidin-5-ylidene}acetate.[6] In all the above systems, the H-bonds were characterized by a high energy and, according to the classification in terms of the theory of Atoms in Molecules (AIM),[7] were assigned to an intermediate type of interactions.[2—5] A comparison of the X-ray diffraction data and the results of quantum chemical calculations for analogous systems demonstrated that the H-bond strength substantially depends on the crystal packing effects, resulting in a weakening of the intramolecular H-bond due to competitive intermolecular interactions.[3—4]

Since the H-bond strength is determined by the nature of the proton donor and acceptor and the presence of intermolecular hydrogen bonds, in the present study we examined the characteristics of O—H...N and OH...O interactions in molecules, in which the nitrogen atom is involved in the triazole heterocycle. We studied hydroxyphenyltriazoles containing substituents of different nature at position 5, *viz.*, 3-(2-hydroxyphenyl)-5-methyl-2-phenyl-1,2,4-triazole (**1**), 5-[2-(4-hydroxy-3-methoxyphenyl)ethyl]-3-(2-hydroxyphenyl)-2-phenyl-1,2,4-triazole (**2**), and 5-[2-(3,4-dimethoxyphenyl)ethyl]-3-(2-hydroxyphenyl)-2-phenyl-1,2,4-triazole (**3**) (Fig. 1).

We evaluated the energy of the intramolecular O—H...N bond in compounds **1—3** as a function of the rotation angle of the hydroxyphenyl substituent and estimated the influence of competitive intermolecular interactions on the strength of this bond based on X-ray diffraction data and results of quantum chemical calculations.

Results and Discussion

In all the molecules under study, the heteroatom forms the intramolecular O(8)H(8)...N(4) hydrogen bond with the oxygen atom of the hydroxyphenyl substituent (see Fig. 1). In spite of the fact that the coplanar arrangement of the substituent and the heterocycle, by analogy with the systems studied earlier, should strengthen the intramolecular contact due to conjugation in the hydrogen-bonded ring,[2] this conformation is observed only in compound **1** (the molecule occupies a special position in a symmetry plane).

Principal geometric parameters of compounds **1—3** are similar to those expected for this class of compounds (Table 1). In the crystals of compounds **2** and **3**, unlike

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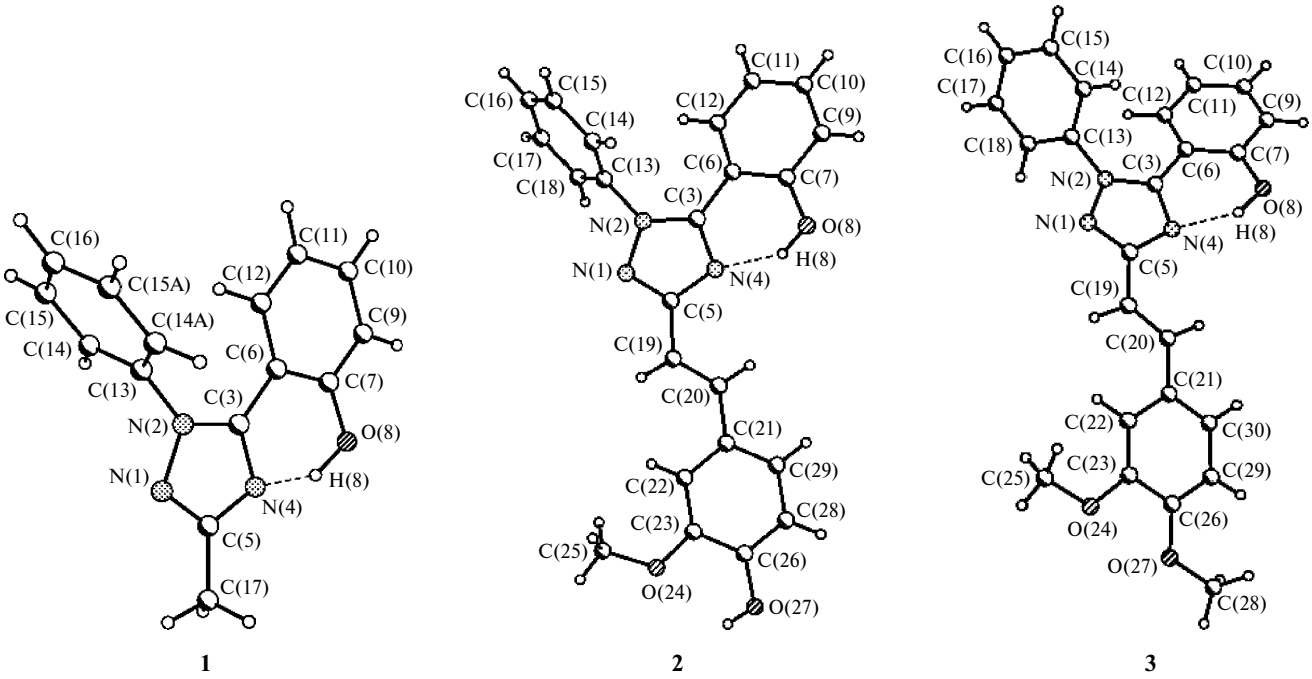

Fig. 1. Overall view of 3-hydroxyphenyltriazoles based on X-ray diffraction data.

Table 1. Bond lengths and bond angles in molecules **1—3** based on X-ray diffraction data

Parameter	**1**	**2**	**3**
Bond		*d*/Å	
C(3)—C(6)	1.465(2)	1.461(3)	1.464(2)
C(3)—N(4)	1.345(2)	1.333(3)	1.332(2)
C(6)—C(7)	1.404(2)	1.416(3)	1.406(2)
C(7)—O(8)	1.355(2)	1.358(3)	1.366(2)
N(4)...O(8)	2.555(2)	2.586(2)	2.655(2)
N(4)...H(8)*	1.77	1.84	1.91
Angle		ω/deg	
N(4)—H(8)—O(8)	152	145	145
N(4)—C(3)—C(6)	122.1(2)	122.8(2)	123.6(1)
C(3)—C(6)—C(7)	118.9(2)	118.2(2)	119.1(1)
C(6)—C(7)—O(8)	122.6(2)	122.1(2)	122.1(1)
Torsion angle		ϕ/deg	
N(4)C(3)C(6)C(7)	0.0	17.0	21.4

* In the calculations of the H-bond parameters, the hydrogen atom was normalized based on the results of B3LYP/6-311G** calculations.

compound **1**, the hydroxyphenyl substituent is substantially rotated with respect to the plane of the heterocycle (the N(4)C(3)C(6)C(7) torsion angle (ϕ) is 17 and 21.4°, respectively). The molecules differ also in the mutual orientation of the phenyl and hydroxyphenyl substituents (the dihedral angles between the planes of the rings in the crystals of **1**, **2**, and **3** are 90.2, 66.1, and 59.8°, respectively). In spite of the variations in the torsion angle ϕ, the C(3)—C(6) bond length and the bond lengths in the heterocycle in the structures of **1—3** are virtually equal (see Table 1).

The strength of the O—H...N bond in molecules **1—3** would be expected to be determined exclusively by the angle ϕ. However, a comparison of the H-bond geometric parameters demonstrated that the strength of this bond depends, apparently, also on other factors. For example, the shortest intramolecular* O(8)—H(8)...N(4) hydrogen bond was found in compound **1** (O(8)...N(4), 2.555(2) Å). However, in spite of the fact that the rotation angle of the hydroxyphenyl substituent in compound **2** is similar to that in compound **3** (17 and 21.4°, respectively), the O(8)...N(4) distances in these compounds are substantially different (2.586(2) and 2.655(2) Å, respectively). The observed weakening of the intramolecular H-bond leads also to a slight variation in the geometry of the hydrogen-bonded ring. In particular, the shortest C(7)—O(8) bond is observed in compound **1** (1.354(2) Å), whereas the corresponding bond length in compound **3** is 1.366(2) Å.

It could be suggested that the H-bond in compound **3** is elongated due to the crystal packing effects. However, the strong intermolecular contacts were found only in molecule **2**, whereas only weak van der Waals interactions are observed in molecules **1** and **3**. In the crystal of **2**, the hydroxy group O(8)—H(8) forms not only the intramolecular bond with the N(4) atom but also the intermolecular O(8)....H(27)—O(27) hydrogen

* Hereinafter, the H-bond strength will be described with the use of the distance between the proton donor and acceptor as the geometric parameter.

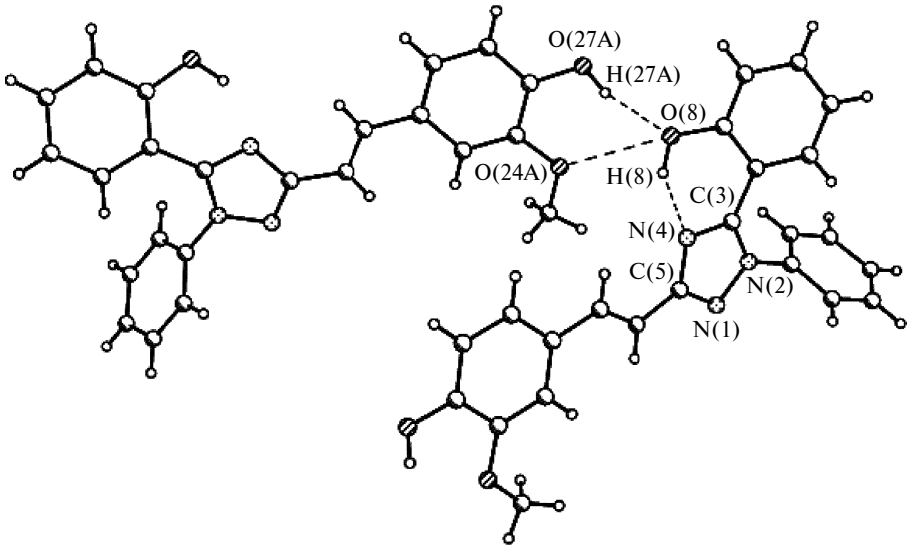

Fig. 2. Fragment of an O—H...O-bonded helix in the crystal of **2**.

bond (1/2 − *x*, 1/2 + *y*, *z*) (O(8)...O(27A), 2.762(2) Å; O(8)H(27)O(27A), 160°) serving as the proton acceptor. The molecules are linked to each other through these H-bonds to form helices along the *b* axis (Fig. 2). In the chains there are, along with the H-bonds, shortened contacts with the methoxy group (O(8)...O(24A), 3.006 Å), which are, apparently, forced.

It should be noted that a similar strengthening of the H-bond in molecule **2** compared to that in molecule **3** in the presence of competitive interactions is observed also in other compounds containing the hydroxyphenyl substituent at the heterocyclic fragment.

An analysis of the published data based on the Cambridge Structural Database (CSD)* demonstrated that an analogous situation is observed also in the crystals of hydroxyphenylimidazole.[8] In the molecule of the latter, the oxygen atom of the OH group is involved not only in the intramolecular OH...N bond (O...N, 2.55) but also in the intermolecular NH...O contact (O...N, 2.83 Å). According to the results of quantum chemical calculations, the H-bond in the isolated molecule is substantially weaker (O...N, 2.68 Å) compared to that in the crystal. Although the observed weakening of the H-bond may be a consequence of the fact that the environment of the molecule in the crystal is ignored, the systematic error introduced by calculations in the description of H-bonds cannot be ruled out.

A similar strengthening of the H-bond is observed also in hydroxyphenyl derivatives of pyrazole.[9] In the crystals of 1,4-dihydroxy-2,5-bis(pyrazolyl)benzene and 1,4-dihydroxy-2-pyrazolylbenzene, the oxygen atoms of the OH groups are involved in intramolecular OH...N bonds with the O...N distances of 2.61 and 2.56 Å, respectively. The observed differences cannot be attributed to the structural features of the molecules. However, the oxygen atom of the hydroxy group in 1,4-dihydroxy-2-pyrazolylbenzene is additionally involved in the intermolecular OH...O contact (O...O, 2.74 Å), whereas analogous contacts in 1,4-dihydroxy-2,5-bis(pyrazolyl)benzene are absent.

Therefore, based on the published data and our experimental results, it can be suggested that intermolecular contacts formed by the oxygen atom of the hydroxy group can lead to a strengthening of the intramolecular H-bond.

With the aim of validating this hypothesis and obtaining detailed data on the nature of the H-bond in hydroxyphenyl-1,2,4-triazoles as well as on the influence of conjugation on the strength of this bond, we carried out quantum-chemical calculations (B3LYP/6-311G**) for compound **1** in the isolated state.

The geometry optimization of **1** in the point symmetry group C_s observed in the crystal led to a slight weakening of the O(8)H(8)...N(4) bond (O(8)...N(4), 2.594 Å) compared to the experimental value. The other bond lengths in compound **1** are in agreement with the X-ray diffraction data (the C(3)—C(6) bond length is 1.464 and 1.465(2) Å, respectively).

However, the geometry optimization of **1** without symmetry restrictions demonstrated that the global minimum is observed for the conformation with the substituent rotated by an angle of 15.8°, which is comparable with the corresponding angles in the crystal structures of **2** and **3**. It is of interest that, in spite of a considerable H-bond weakening (O(8)...N(4), 2.620 Å), the energy of this conformation is only 0.3 kcal mol^{-1} lower than that of the planar conformation.

To study the influence of the conformation of the substituent on the energy characteristics of the system, we scanned the potential energy surface along the coordi-

* Cambridge Crystallographic Database, release 2005.

nate, *viz.*, the N(4)C(3)C(6)C(7) torsion angle (ϕ), from 0 to 130° (Fig. 3). It should be noted that the energy of the conformation with the substituent rotated by an angle of up to ϕ < 35° is higher by only 0.65 kcal mol^{-1} than the global minimum. Taking into account such a small energy difference, it is hardly possible to state the presence of the global minimum, *i.e.*, conformations with the angle ϕ varying from 0 to 35° are observable with similar probability in the crystals and, apparently, in solution, which is confirmed by the experimental data for compounds **1—3**. A further increase in the torsion angle leads to a slight increase in the energy of the system due to a number of factors, such as a weakening of conjugation, an H-bond weakening, and the steric repulsion at ϕ > 90° as a result of a decrease in the distance between the hydroxy group and the phenyl substituent (see Fig. 3).

Apparently, it is the H-bond that is responsible for the high barrier to rotation of the hydroxyphenyl substituent in **1** (7.95 kcal mol^{-1} at ϕ = 90°). For example, the barrier to rotation in biphenyl is 1.6 kcal mol^{-1},[10] whereas this barrier in 4,6-bis(2-hydroxyphenyl)-2-dimethyl-1,3,5-triazine is 11 kcal mol^{-1}.[11] It should be noted that the rotation angle ϕ estimated by optimization of **1**, in which the H-bond is absent and the hydroxy group is rotated off (the H(8)O(8)C(7)C(9) torsion angle is 0°), is 63.5°. The energy difference between the conformer of **1** containing an H-bond and the conformer without this bond is 4 kcal mol^{-1}.

Therefore, although the H-bond undoubtedly stabilizes **1**, its presence leads to a change in the equilibrium angle ϕ. Consequently, while loosing energy at each point on the potential energy surface due to an H-bond weakening, the molecule gains in energy due to a decrease in the steric repulsion.

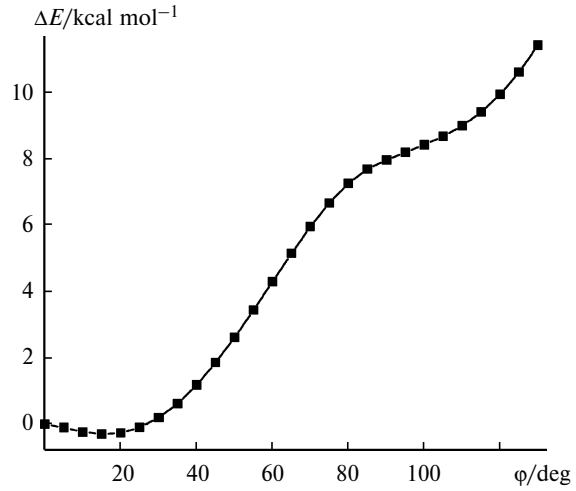

Fig. 3. Scan profile of the potential energy surface (Δ*E*) along the coordinate of the change in the N(4)C(3)C(6)C(7) torsion angle (φ) in molecule **1**.

Actually, the steric interactions between the aryl substituents at positions 2 and 3 of molecule **1** are partially responsible for a high energy of the conformation characterized by the coplanar arrangement of the phenol and heterocyclic fragments. For example, in the conformation observed in the crystal of **1**, the C(12)—H(12) bond in the hydroxyphenyl fragment points toward the π density of the phenyl substituent with the shortest H(12)...C(13) distance of 2.43 Å. The role of the steric factors is confirmed by the correlated changes in the rotation angles of the aryl substituents. At the minimum point, the rotation angle of the phenyl substituent is 59°, whereas this angle is 83.9 and 43.5° at ϕ = 0 and 90°, respectively.

Let us consider in more detail the degree of conjugation of the aromatic and heterocyclic fragments and the H-bond strength as a function of the angle ϕ.

An analysis of the geometry of molecule **1** at different angles ϕ revealed changes exclusively in the hydrogen-bonded ring. In spite of the fact that an increase in the angle ϕ leads to the loss of conjugation and a considerable H-bond weakening, the bond lengths change by no more than 0.03 Å. For example, the O(8)—C(7) and C(6)—C(3) distances monotonically increase from 1.341 to 1.368 Å and from 1.464 to 1.482 Å, respectively, whereas the C(6)—C(7) and N(4)—C(3) distances monotonically decrease from 1.425 and 1.336 Å to 1.398 and 1.322 Å, respectively, with increasing rotation angle of the 1-hydroxyphenyl substituent.

The O(8)—H(8) bond length, whose value is determined primarily by the presence and strength of the H-bond, remains virtually unchanged up to the rotation angle of 20° (0.991—0.988 Å), then this length sharply decreases to 0.972 Å at 20° < ϕ < 65°, after which the O—H-bond length remains virtually unchanged as the rotation angle further increases. Therefore, an analysis of the geometry of **1** as a function of the angle ϕ, revealed that the conjugation has only a slight effect on the bond length distribution, whereas the intramolecular H-bond is retained up to 65°.

Taking into account that the geometric parameters are rather conservative with respect to the above-described electronic effects, we performed the topological analysis of the electron density distribution in terms of the AIM theory[7] based on the results of calculations by the B3LYP/6-311G** method. To estimate the energies of weak intramolecular H-bonds and contacts, we used an empirical correlation between the potential energy density ($v(\mathbf{r})$) at the critical point (3, −1) and the energy of interactions (E_{cont}).[12] Earlier,[1,13] this correlation has been successfully applied to investigations of different types of intermolecular and intramolecular interactions with the use of both experimental and theoretical data on the function ρ(**r**).

An analysis of the critical points (CP) demonstrated that the characteristic set in the structure of **1** for the

angle ϕ varying from 0 to 60° remains unchanged and includes the CP (3, −1) for all the expected bonds and also for the intramolecular O—H...N and C—H...π (C(12)—H(12)...C(13)) interactions. At ϕ = 65°, the O—H...π interaction, *viz.*, O(8)—H(8)...C(3) (H(8)...C(3), 2.309 Å), is present in molecule **1** instead of the O—H...N bond, and a further rotation of the phenyl ring leads to the disappearance of the intramolecular H-bond involving the hydroxy group. The C—H...π contact is retained up to ϕ = 85°, and an increase in the rotation angle gives rise to the H(12)...O(8) contact.

An analysis of the topological parameters at the CP (3, −1) demonstrated that at the minimum of the potential energy and at all other points on the potential energy surface for rotation of the hydroxyphenyl substituent, all bonds, except for the hydrogen bond and C—H...π and C—H...O contacts, correspond to shared interactions (covalent bonds); $\nabla^2\rho(r)$ are always negative. The topological parameters of the covalent bonds remain virtually unchanged with changing angle ϕ. The only exception is the ellipticity (ε) of the C(3)—C(6) bond, which decreases from 0.15 at ϕ = 0 to zero at ϕ = 90°. However, it is interesting that ε decreases by no more than 30% even if the rotation angle increases to 50°.

The C—H...π and C—H...O interactions belong to closed-shell interactions; $\nabla^2\rho(r)$ and the local energy densities ($h_e(r)$) at the CP (3, −1) are positive. The strength of C—H...π interactions estimated based on the above-described correlation scheme decreases from 2.1 to 1.25 kcal mol^{-1} as the angle ϕ changes,[12] and the energy of the C—H...O bond is 1.65 kcal mol^{-1}.

The hydrogen bond is also characterized by the positive value of $\nabla^2\rho(r)$; however, the sign of $h_e(r)$ depends on the rotation angle and changes at 45°. Therefore, the H-bond corresponds to the intermediate interactions ($h_e(r)$ changes from −0.00997 to −0.00067 au) up to ϕ = 45°, whereas this bond belongs to closed-shell interactions ($h_e(r)$ = 0.00154—0.00230) at ϕ > 45°. The change in the character of the H-bond is accompanied by a substantial decrease in ρ(r) and $\nabla^2\rho(r)$ (from 0.35 and 2.93 eÅ^{-5} to 0.19 and 2.17 eÅ^{-5}, respectively) and an increase in ε from 0.02 to 0.10 at the CP (3, −1) for the H-bond at ϕ of 0 and 45°, respectively. It should be noted that the maximum value of ε for the H-bond (1.01) is observed at 60°. Such a behavior of the ellipticity of the H-bond is associated with the fact that an increase in the rotation angle leads to a substantial decrease in the distance between the CP (3, −1) of the H-bond and the CP (3, +1) of the hydrogen-bonded ring, with the result that, in the limit, the points merge and, consequently, the molecular graph changes.[10]

An estimation of the H-bond strength based on the correlation scheme[12] demonstrated that the H-bond energy monotonically decreases from 15.8 kcal mol^{-1} with increasing angle ϕ and stops short of reaching the zero

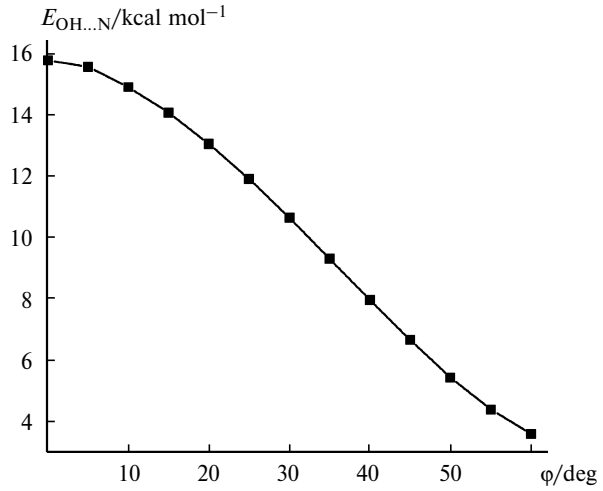

Fig. 4. Energy of the intramolecular OH...N hydrogen bond *vs.* the N(4)C(3)C(6)C(7) torsion angle (φ) in molecule **1**.

(E_{cont} = 3.59 kcal mol^{-1}) at ϕ = 60°. The O—H...π interaction occurs only at ϕ = 65° and its energy is virtually equal to the above-mentioned value (3.50 kcal mol^{-1}). It should be noted that this estimate the energy of the O—H...π interaction is in surprisingly good agreement with the energy difference between the conformers at ϕ = 65° with the H-bond and in the absence of this bond (see above).

As can be seen from a comparison of Figs 3 and 4, the conformers do not virtually differ in the energy at ϕ < 35° (see above), whereas the H-bond energy, on the contrary, decreases by more than 6.5 kcal mol^{-1}. Apparently, the energies of the conformers remain unchanged, whereas the H-bond energy substantially decreases, due to the fact that the H-bonding leads to a substantial deviation of the angle ϕ from the equilibrium value (63.5°) observed for an analogous system, in which an H-bond is absent but the OH group is rotated off. The H-bonding not only leads to flattening of the hydrogen-bonded ring but also additionally fix the aromatic fragments. For example, the B3LYP/6-311G** calculations of the energy of molecule **1** at ϕ = 0 containing the rotated-off OH group, the other geometric parameters being fixed, demonstrated that the energy of this conformer is 11 kcal mol^{-1} higher than that of the corresponding conformer containing the H-bond.

However, the above-considered rotation of the hydroxyphenyl substituent does not account for an H-bond strengthening n molecule **2** compared to that in the crystal of **3**. Since, according to the published data (see above), the presence of intermolecular interactions can also influence the H-bond strength, it is presumably the presence of intermolecular hydrogen bonds that causes a strengthening of the O(8)H(8)...N(4) bond.

To validate this assumption, we modelled the intermolecular O(27A)H(27A)...O(8) contact, which, taking into account the directionality and a shorter O...O dis-

tance, should also influence predominantly the strength of the intramolecular interaction (see Fig. 2). We chose compound **1** involved in the H-bond with the methanol molecule as a model. The choice of this model compound for studying the role of intermolecular bonding allowed us to simplify the system under consideration. It should be noted that, according to the experimental data, the replacement of the substituent at position 5 of molecule **1** with the methyl group does not lead to a considerable change in the geometric parameters of compound **1**.

Calculations by the B3LYP/6-311G** method for the solvate **1**·MeOH demonstrated that the rotation angle of the hydroxyphenyl substituent differs only slightly from the torsion angle for isolated molecule **1** (15.8°). However, in spite of the similarity of the geometric parameters in two modelled systems, the formation of the intermolecular hydrogen bond of the hydroxy group in **1**·MeOH leads to a decrease in the intramolecular O(8)...N(4) distance from 2.620 to 2.594 Å. The degree of H-bond strengthening in the solvate **1**·MeOH compared to the experimental data is, apparently, associated with a weakening of the calculated intermolecular H-bond (2.888 Å) compared to that in the crystal of **2** (2.762 Å). The estimates of the H-bond energy demonstrated that an intermolecular interaction leads to an increase in the energy from 14.0 to 15.66 kcal mol^{-1}, the maximum value of E_{cont} being achieved for **1** (see Fig. 3). The energy of the intermolecular O(27A)—H(27A)...O(8) interaction is 5.64 kcal mol^{-1}.

The nature of this effect is, apparently, similar to the cooperative effects in water clusters.[14] Actually, it is known[13,14] that the stabilization energy per water molecule almost linearly increases with increasing cluster size. The nature of the observed effect is associated with the polarizing effect of H-bonds, resulting in a weakening of the O—H-bond and, consequently, in an increase in the positive charge on the hydrogen atom.

Summarizing the results of quantum chemical calculations, it can be concluded that flattening of the hydrogen-bonded ring in the hydroxyphenyltriazoles under consideration destabilizes the system due, apparently, to steric repulsion. Therefore, unlike ketoenols considered earlier,[3] the intramolecular OH...N interactions in the crystals of these compounds do not belong to H-bonds stabilized by conjugation according to Gilli's classification.[2] Moreover, this conclusion, apparently, can be, with high probability, extended to other similar systems, in which two aromatic rings share the hydrogen-bonded ring. To the contrary, an increase in the energy of the intramolecular H-bond due to cooperative effects observed in

Table 2. Crystallographic data and details of X-ray diffraction study for compounds **1—3**

Parameter	**1**	**2**	**3**
Molecular formula	$C_{15}H_{13}N_3O$	$C_{23}H_{19}N_3O_3$	$C_{24}H_{21}N_3O_3$
Molecular weight	251.28	385.41	399.44
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	*Pnma*	*Pbca*	$P\bar{1}$
T/K	120	120	120
$Z(Z')$	4(0.5)	8(1)	2(1)
a/Å	17.475(1)	13.700(4)	9.082(2)
b/Å	6.9937(6)	12.926(3)	9.413(2)
c/Å	10.2220(9)	22.116(5)	13.063(2)
α/deg	—	—	80.279(4)
β/deg	—	—	88.637(4)
γ/deg			64.294(3)
V/Å^3	1249.28(18)	3916.5(15)	990.2(3)
d_{calc}/g cm^{-3}	1.336	1.307	1.340
Absorption coefficient μ/mm^{-1}	0.87	0.88	0.90
$F(000)$	528	1616	420
$2\theta_{max}$/deg	60.12	55.98	60
Number of measured reflections	11351	14377	11802
Number of independent reflections	1960	4684	5706
R_{int}	0.0335	0.0432	0.0253
Number of parameters in refinement	142	271	355
GOOF	1.004	1.001	1.001
Number of reflections with $I > 2\sigma(I)$	1379	2392	3817
R_1	0.0550	0.0611	0.0559
wR_2	0.1284	0.1330	0.1376
Residual electron density/e A^{-3}, min/max	−0.209/0.354	−0.245/0.313	−0.244/0.392

compounds **1—3** has, apparently, a general character and calls for further investigation.

Experimental

Compounds **1—3** were prepared according to a procedure described earlier.[15] The single-crystal X-ray diffraction data sets for compounds **1—3** were collected 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°). The X-ray data were processed and merged using the SAINT Plus program package, and semiempirical absorption corrections were applied.[16]

The structures of compounds **1—3** were solved by direct methods and refined in the anisotropic approximation by the full-matrix least-squares method with the use of successive electron density maps. The refinement was carried out against F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. The H(8) atom was located from electron density maps and refined isotropically. The coordinates of the 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.[17] The crystallographic data and parameters of the structure refinement of compounds **1—3** are given in Table 2.

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 03 W program.[18] The topological analysis of the theoretical electron density distribution was performed using of the MORPHY 98 program.[19]

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