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X-RAY DIFFRACTION STUDY OF CRYSTAL AND MOLECULAR STRUCTURES OF AZO COMPOUNDS OF TWO β-DIKETONES

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Novel compounds 2-(2-(2-hydroxy-4-nitrophenyl) hydrazono)-1,3-diphenyl propane-1,3-dione and 2-(2-(2-hydroxy-4-nitrophenyl) hydrazono)-1-phenyl butane-1,3-dione are prepared on the base of β-diketones. Crystal and molecular structures of synthesized compounds are determined by X-ray diffraction analysis. The crystals are found to be monoclinic. The compounds are represented only by their hydrazo forms. The structural data for the two obtained compounds are compared with previously reported data.

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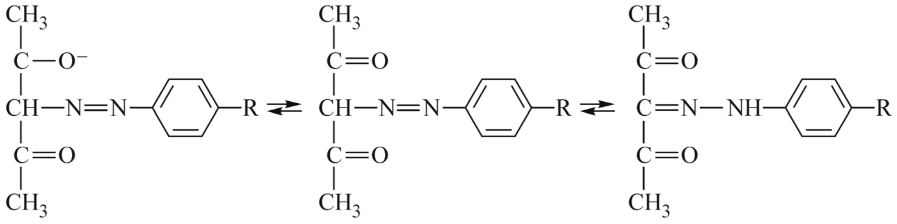
INTRODUCTION

It is known that β-diketone and its derivatives are widely used to identify different metals [1-3]. The ability of these ligands to form stable complexes with metals was discussed in [4]. The class of chelates capable of forming stable complexes with metals is extended by introducing nitrogen atoms in the ligand, including the substitution of oxygen atoms by one [5-7] or two imino groups [8] and by a hydrazone group [9]. The attachment of an azo group to the gamma carbon atom is another approach that is still little studied. Currently, these ligands are of particular interest, since azo derivatives of β-diketones can exist in solutions as three tautomeric forms: enol-azo, keto-azo, hydrazo [10] (Scheme 1).



Scheme 1.

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It was established by IR, NMR, and X-ray photoelectron spectroscopy methods that the hydrazo form is the most preferable form due to the presence of three conjugated double bonds and an intramolecular hydrogen bond (O…H).

This work aims at preparing azo compounds based on β-diketones and determining their structure using X-ray analysis.

EXPERIMENTAL

Synthesis. Compound $C_{23}H_{21}N_3O_6$ **I** was prepared by the azo coupling of diazotized *m*-nitrophenol with dibenzoylacetone in a weakly alkaline medium [10]: 3.475 g (0.025 mol) of *m*-nitrophenol was dissolved in 20 mL of water and slightly heated with the addition of 1 g of crystalline KOH. The obtained solution was cooled in an ice bath to 0 °C for 30 min with 1.725 g (0.025 mol) of $NaNO_2$ added in portions. The temperature did not exceed +3 °C.

A mixture of 5.6 g (0.025 mol) of dibenzoylacetone and 15 mL of ethanol was cooled down by adding 11.952 g (0.146 mol) of CH_3COONa. The solution was cooled in an ice bath with *m*-nitrophenol diazonium suspension. The next day the reagent residue was filtered off, washed with ethanol, and dried in air.

Compound $C_{16}H_{13}N_3O_5$ **II** was prepared according to the above procedure.

XRD. Unit cell parameters and the crystal space group were determined and refined on a Bruker SMART APEX II CCD automated diffractometer (θ/2θ scanning, MoK_α-radiation, $\lambda = 0.71073$ Å, graphite monochromator, $T = 100$ K). Table 1 shows experimental details and some crystallographic characteristics. All crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC numbers 1886864 **I** and 1886866 **II**).

The structures were solved by direct methods using the SHELXTL-2001 software [11] in automated mode and refined by the least squares method (LSM) in the anisotropic approximation for non-hydrogen atoms. The difference electron density synthesis showed that the solvate molecule of ethanol in structure **I** is disordered over three positions (in the 40:30:30 ratio). The positions of H atoms linked to carbon atoms were calculated geometrically using a riding model and refined isotropically.

TABLE 1. Main Crystallographic Parameters and Characteristics of the X-Ray Diffraction Experiment for **I** and **II**

Parameter	**I**	**II**
Empirical formula	$C_{23}H_{21}N_3O_6$	$C_{16}H_{13}N_3O_5$
M	435.62	327.29
Crystal system	Monoclinic	
Space group; Z	$P2_1/n$; 4	
a, Å	12.443(1)	10.3659(3)
b, Å	10.1819(7)	8.8551(2)
c, Å	17.594(2)	16.9032(6)
β, deg	100.819(3)	93.306(1)
V, Å^3	2189.4(3)	1548.98(8)
d_{calc}, g/cm^3	1.322	1.403
μ, mm^{-1}	0.097	0.107
F(000)	912	680
Crystal size, mm	0.220×0.160×0.067	0.522×0.275×0.166
θ range, deg	2.604-26.401	2.367-30.035
h, k, l ranges	$-15 \le h \le 15$, $-11 \le k \le 12$, $-21 \le l \le 21$	$-14 \le h \le 12$, $-9 \le k \le 12$, $-23 \le l \le 14$
R ($I > 2\sigma_I$)	$R_1 = 0.0463$, $wR_2 = 0.1032$	$R_1 = 0.0510$, $wR_2 = 0.1321$
R ($I_{hkl\ \text{all data}}$)	$R_1 = 0.0889$, $wR_2 = 0.1273$	$R_1 = 0.0675$, $wR_2 = 0.1441$
$GOOF$ on F^2	1.002	1.005

RESULTS AND DISCUSSION

Crystal structure I. The $C_{23}H_{21}N_3O_6$ molecule (Fig. 1) is the building unit of compound **I**; its geometrical parameters (bond lengths and bond angles) are listed in Table 2.

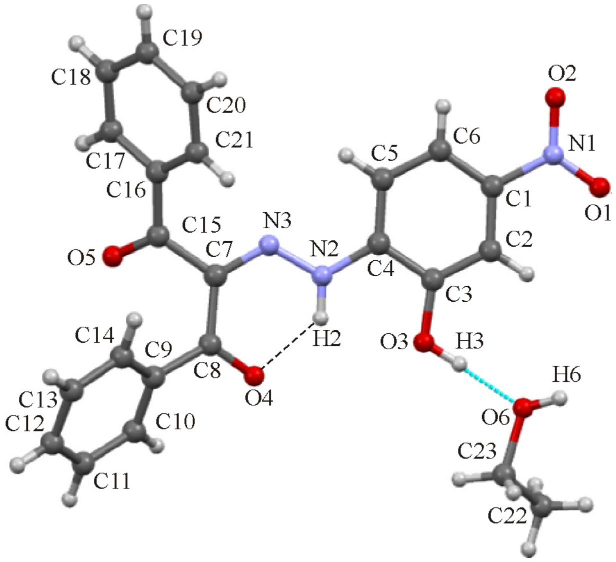

Fig. 1. Structure of molecule $C_{23}H_{21}N_3O_6$ **I** with numbered atoms.

TABLE 2. Main Interatomic Distances and Bond Angles in $C_{23}H_{21}N_3O_6$ **I**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
O(1)–N(1)	1.227(2)	C(1)–C(6)	1.375(3)	C(11)–C(12)	1.369(4)
O(2)–N(1)	1.223(2)	C(2)–C(3)	1.378(2)	C(12)–C(13)	1.373(4)
O(3)–C(3)	1.350(2)	C(3)–C(4)	1.400(2)	C(13)–C(14)	1.379(3)
O(4)–C(8)	1.231(2)	C(4)–C(5)	1.379(3)	C(15)–C(16)	1.482(3)
O(5)–C(15)	1.218(2)	C(5)–C(6)	1.378(3)	C(16)–C(21)	1.386(3)
O(6)–C(23)	1.481(3)	C(7)–C(8)	1.477(2)	C(16)–C(17)	1.396(2)
N(1)–C(1)	1.458(2)	C(7)–C(15)	1.492(2)	C(17)–C(18)	1.371(3)
N(2)–N(3)	1.3184(19)	C(8)–C(9)	1.488(3)	C(18)–C(19)	1.379(3)
N(2)–C(4)	1.391(2)	C(9)–C(10)	1.377(3)	C(19)–C(20)	1.372(3)
N(3)–C(7)	1.313(2)	C(9)–C(14)	1.379(3)	C(20)–C(21)	1.379(3)
C(1)–C(2)	1.374(3)	C(10)–C(11)	1.371(4)	C(23)–C(22)	1.513(3)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(2)–N(1)–O(1)	122.9(2)	C(6)–C(5)–C(4)	119.7(2)	C(9)–C(14)–C(13)	120.2(2)
O(2)–N(1)–C(1)	119.3(2)	C(1)–C(6)–C(5)	118.6(2)	O(5)–C(15)–C(16)	121.0(2)
O(1)–N(1)–C(1)	117.8(2)	N(3)–C(7)–C(8)	121.1(2)	O(5)–C(15)–C(7)	117.8(2)
N(3)–N(2)–C(4)	120.1(2)	N(3)–C(7)–C(15)	115.1(2)	C(16)–C(15)–C(7)	121.2(2)
C(7)–N(3)–N(2)	120.3(2)	C(8)–C(7)–C(15)	120.2(2)	C(21)–C(16)–C(17)	118.5(2)
C(2)–C(1)–C(6)	122.8(2)	O(4)–C(8)–C(7)	119.9(2)	C(21)–C(16)–C(15)	124.1(2)
C(2)–C(1)–N(1)	119.0(2)	O(4)–C(8)–C(9)	118.7(2)	C(17)–C(16)–C(15)	117.3(2)
C(6)–C(1)–N(1)	118.2(2)	C(7)–C(8)–C(9)	121.3(2)	C(18)–C(17)–C(16)	120.5(2)
C(1)–C(2)–C(3)	118.7(2)	C(10)–C(9)–C(14)	119.7(2)	C(17)–C(18)–C(19)	120.0(2)
O(3)–C(3)–C(2)	124.8(2)	C(10)–C(9)–C(8)	118.4(2)	C(20)–C(19)–C(18)	120.5(2)
O(3)–C(3)–C(4)	116.1(2)	C(14)–C(9)–C(8)	121.9(2)	C(19)–C(20)–C(21)	119.6(2)
C(2)–C(3)–C(4)	119.1(2)	C(11)–C(10)–C(9)	120.3(3)	C(20)–C(21)–C(16)	120.9(2)
C(5)–C(4)–N(2)	122.9(2)	C(12)–C(11)–C(10)	119.8(3)	O(6)–C(23)–C(22)	118.0(1)
C(5)–C(4)–C(3)	121.0(2)	C(11)–C(12)–C(13)	120.6(2)		
N(2)–C(4)–C(3)	116.2(2)	C(12)–C(13)–C(14)	119.7(3)		

Atoms O(4), C(8), C(7), N(3), N(2), H(2) lie almost in the same plane (the mean square deviation of the atoms from the plane is 0.0632 Å).

Table 2 shows that all these bonds are single or double bonds. The bond lengths are distorted around atoms C(7)–C(8), N(2)–N(3), C(4)–N(2). Bond lengths C(4)–N(2) and N(2)–N(3) are 1.391 Å and 1.318 Å, respectively, which is typical of azo compounds. Bonds N(3)–C(7) and C(8)–O(4) are longer than standard bonds and are partially conjugated. These bonds along with the N(2)…O(4) distance (2.604 Å) testify that the molecule contains an intramolecular hydrogen bond (Fig. 1) [12, 13]. At first glance, both hydrogen bonds N–H…O=C (hydrazo) and O–H…O=C (keto-azo) seem to be strong; however, it is in the hydrazo form only that the hydrogen bond is additionally strengthened by the acyl group of the neighboring molecule. Therefore, hydrogen bond (N–H…O=C) is stronger than other similar bonds (O–H…O=C, O–H…N) in other tautomeric forms of this molecule.

Compound **I** crystallizes in a cell with one ethanol molecule to form a hydrogen bond between the hydrogen atom H(3) of the $C_{23}H_{21}N_3O_6$ molecule **I** and the oxygen atom O(6) of ethyl alcohol (Fig. 2). Fig. 3 shows the projection of the packing of molecules **I** on the (010) plane.

Crystal structure II. Fig. 4 shows the structure of molecule $C_{16}H_{13}N_3O_5$ **II**; its geometrical parameters (main bond lengths and bond angles) are listed in Table 3.

Atoms O(1), C(2), C(3), N(1), N(2), H(2) lie almost in the same plane (the mean square deviation of the atoms from the plane is 0.0613 Å).

As can be seen from Table 3, the lengths of all these bonds correspond to single or double bonds [12]. There are strong distortions around C(3)–C(2), N(1)–N(2), C(11)–N(2) atoms. The length of C(11)–N(2) and N(1)–N(2) bonds is 1.399 Å and 1.307 Å, respectively, which is typical of azo compounds. N(1)–C(3) and C(2)–O(1) bonds are longer than standard bonds and are partially conjugated. These bonds along with the distance between N(2)…O(1) atoms (2.565 Å) testify the existence of an intramolecular hydrogen bond in this part of the molecule (Fig. 4) [12, 13]. Compound **II** also exhibits additional strengthening of N–H…O=C (hydrazo) and O–H…O=C (keto-azo) hydrogen bonds due to the neighboring acyl group, which is typical of the hydrazo form.

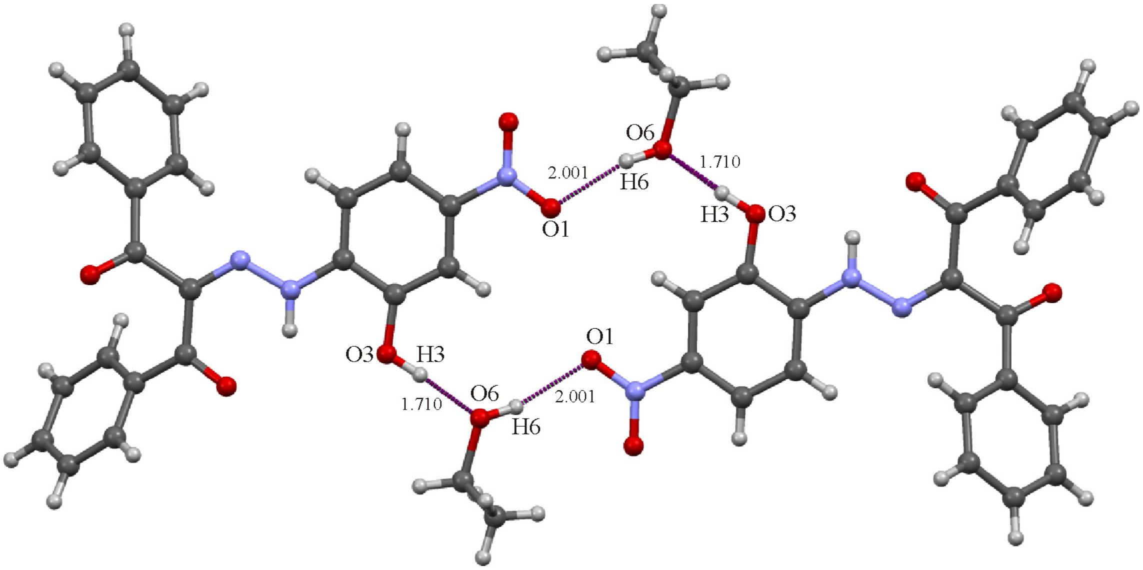

Fig. 2. Hydrogen bonds in structure **I**.

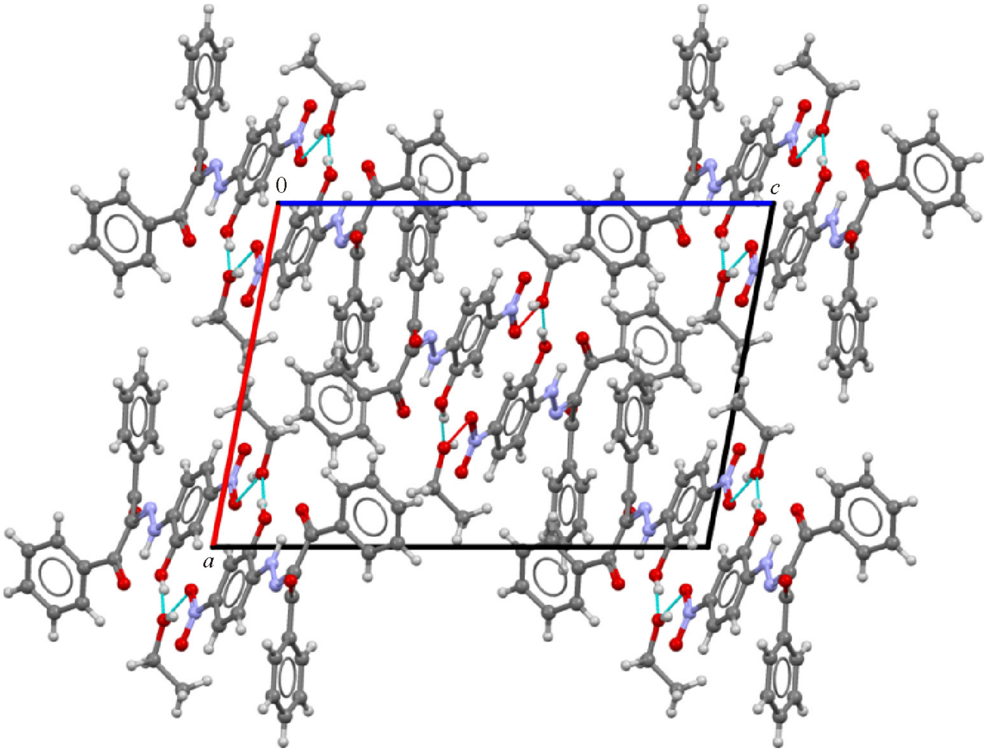

Fig. 3. Molecular packing in structure **I** in the projection onto the (010) plane.

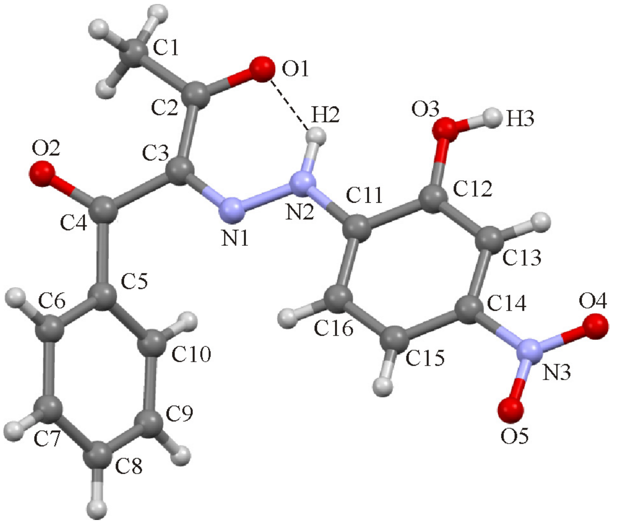

Fig. 4. Structure of molecule $C_{16}H_{13}N_3O_5$ **II** with numbered atoms.

TABLE 3. Main Interatomic Distances and Bond Angles in $C_{16}H_{13}N_3O_5$ **II**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
O(1)–C(2)	1.232(2)	C(1)–C(2)	1.499(2)	C(8)–C(9)	1.373(3)
O(2)–C(4)	1.230(2)	C(2)–C(3)	1.479(2)	C(9)–C(10)	1.385(2)
O(3)–C(12)	1.348(2)	C(3)–C(4)	1.480(2)	C(11)–C(16)	1.386(2)
O(4)–N(3)	1.210(2)	C(4)–C(5)	1.487(2)	C(11)–C(12)	1.405(2)
O(5)–N(3)	1.220(2)	C(5)–C(10)	1.385(2)	C(12)–C(13)	1.383(2)
N(1)–N(2)	1.307(1)	C(5)–C(6)	1.390(2)	C(13)–C(14)	1.377(2)
N(1)–C(3)	0.321(2)	C(6)–C(7)	1.383(2)	C(14)–C(15)	1.381(2)
N(2)–C(11)	1.399(2)	C(7)–C(8)	1.375(3)	C(15)–C(16)	1.383(2)
N(3)–C(14)	1.467(2)				
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
N(2)–N(1)–C(3)	121.3(1)	O(2)–C(4)–C(5)	121.1(1)	C(16)–C(11)–C(12)	120.9(1)
N(1)–N(2)–C(11)	119.4(1)	C(3)–C(4)–C(5)	117.7(1)	N(2)–C(11)–C(12)	116.2(1)
O(4)–N(3)–O(5)	123.8(2)	C(10)–C(5)–C(6)	120.0(1)	O(3)–C(12)–C(13)	124.6(1)
O(4)–N(3)–C(14)	118.1(2)	C(10)–C(5)–C(4)	120.6(1)	O(3)–C(12)–C(11)	116.3(1)
O(5)–N(3)–C(14)	118.1(2)	C(6)–C(5)–C(4)	119.4(1)	C(13)–C(12)–C(11)	119.1(1)
O(1)–C(2)–C(3)	118.6(1)	C(7)–C(6)–C(5)	119.5(2)	C(14)–C(13)–C(12)	118.9(1)
O(1)–C(2)–C(1)	119.7(1)	C(8)–C(7)–C(6)	120.1(2)	C(13)–C(14)–C(15)	122.9(1)
C(3)–C(2)–C(1)	121.7(1)	C(9)–C(8)–C(7)	120.6(2)	C(13)–C(14)–N(3)	117.9(1)
N(1)–C(3)–C(4)	111.9(1)	C(8)–C(9)–C(10)	119.8(2)	C(15)–C(14)–N(3)	119.2(2)
N(1)–C(3)–C(2)	124.1(1)	C(5)–C(10)–C(9)	119.9(2)	C(14)–C(15)–C(16)	118.4(1)
C(4)–C(3)–C(2)	124.0(1)	C(16)–C(11)–N(2)	123.0(1)	C(15)–C(16)–C(11)	119.8(1)
O(2)–C(4)–C(3)	121.2(1)				

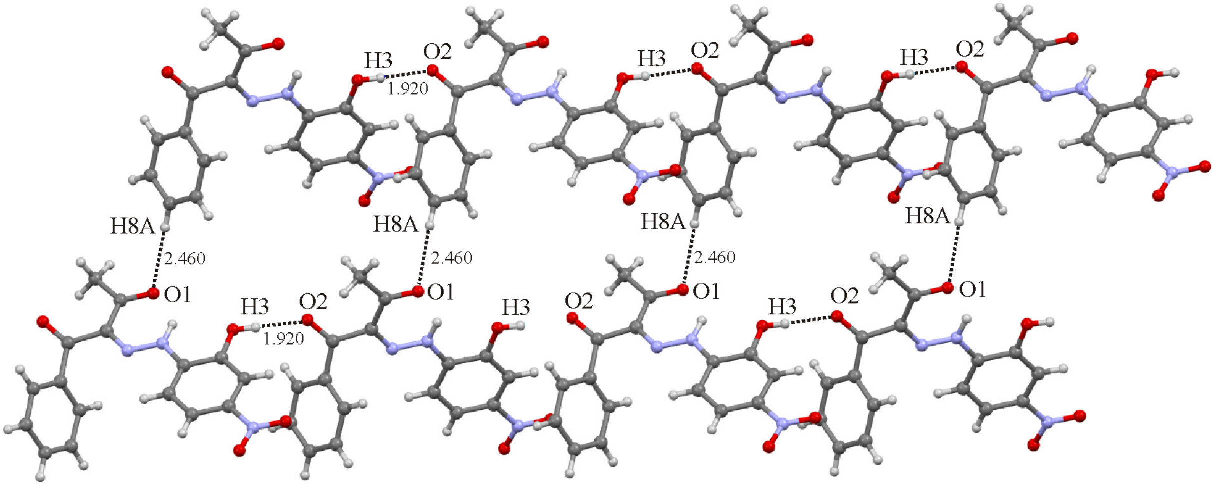

Fig. 5. Hydrogen bonds in structure **II**.

The crystal packing of molecules **II** is formed due to strong intermolecular hydrogen bonds O(3)–H(3)…O(2). The O(3)–H(3) distance is 0.832 Å; the O(2)…H(3) distance is 1.918 Å (*x*+1/2, –*y*+1/2, *z*+1/2); the O(3)H(3)O(2) angle is 176°.

A more detailed study of crystal structure **II** revealed weak intermolecular hydrogen bonds occurring between hydrogen atoms H(8) of the phenyl group and the oxygen O(1) of the carbonyl group C(8)–H(8)…O(1). Due to these weak contacts, the molecules are arranged parallel to each other. The C(8)–H(8) distance is 0.930 Å; the O(1)…H(8) distance is

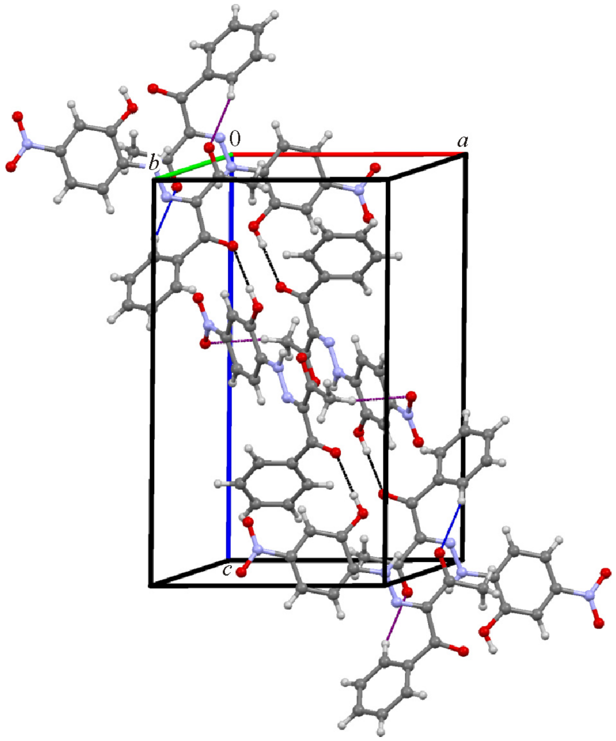

Fig. 6. Molecular packing in structure **II**.

2.460 Å (–1/2+*x*, 1/2+*y*, 1/2+*z*); the C(8)H(8)O(1) angle is 172° [12, 13]. Strong O(3)–H(3)…O(2) and weak C(8)–H(8)…O(1) contacts are shown by dotted lines in Fig. 5. The molecular packing of structure **II** is shown in Fig. 6.

Thus, X-ray diffraction revealed that the synthesis of ligands based on β-diketones lead to the formation of hydrazo forms of compounds **I** and **II**.

CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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