

# REGIONAL FOCUS AND TAUTOMERICITY IN THE SERIES OF AROYLHYDRASONES OF $\beta$ -DICARBONYL COMPOUNDS

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DOI: 10.47750/pnr.2022.13.S06.040

## Abstract

Nitrogen derivatives of  $\beta$ -ketoaldehydes are capable of various tautomeric transformations [1–5]. The condensation products of aroylacetic aldehydes with aromatic acid hydrazides exist in linear, hydrazone, and enhydrazine forms. The appearance of an alternative cyclic 5-hydroxy-2-pyrazoline form is facilitated by the introduction of a strong electron-withdrawing substituent into the aromatic ring of 1,3-ketoaldehyde. In series of compounds, an increase in the volume of the substituent in the acyl moiety shifts the tautomeric equilibrium towards the enhydrazine form. The resulting organic substances were studied by elemental analysis, IR and <sup>1</sup>H NMR spectroscopy. The molecular structure of compound II was determined by X-ray diffraction analysis (CCDC no. 1826717).

**Keywords:** Aroylhydrazone, benzoylacetic aldehyde, crystal structure, X-ray diffraction analysis.

## INTRODUCTION

The interaction of 1,3-ketoaldehydes with acylhydrazines, proceeding exclusively through the aldehyde function, stops at the stage preceding the formation of 1-acylpyrazolines [1, 2, 5–9]. The condensation products, depending on the structure of the 1,3-dicarbonyl and hydrazine components, in the solid state can have a hydrazone, conjugated enhydrazine, or 5-hydroxy-2-pyrazoline structure. In solutions, they undergo a series of prototropic and ring chain equilibria with various combinations of the above tautomers [10–12].

## EXPERIMENTAL PART

Compounds I–IV synthesized according to [5–7] were studied in the work; pyridine (analytical grade) was used, as well as solvents EtOH, diethyl ether (reagent grade, distilled) [13, fourteen].

IR absorption spectra were recorded on a Specord 75IR spectrometer; samples were recorded in the range of 400–4000 cm<sup>-1</sup> in pressed KBr pellets. <sup>1</sup>H NMR spectra of 5–10% solutions I–IV were recorded on Unity 400plus spectrometers (Varian).

Synthesis of para-methylbenzoylhydrazone 3-phenyl-3-oxopropanal.

To a solution of 1.48 g (0.01 mol) of 3-phenyl-3-oxopropanal in 50 ml of ethanol was added dropwise with stirring 1.50 g (0.01 mol) of para-methylbenzoic acid hydrazide in 100 ml of ethanol. The reaction mixture was left for 1 day at room temperature. The precipitated polycrystalline precipitate of para-methylbenzoylhydrazone 3-phenyl-3-oxopropanal (II) with a mass of 2.02 g (72 %, T<sub>пл</sub> 157°C table 1), filtered, washed with a small amount of ethanol, diethyl ether and hexane. Recrystallization of II from ethanol and chloroform gave monoclinic crystals C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>.

Compounds I, III, and IV were obtained similarly (Table 1).

<sup>1</sup>H NMR spectra of solutions of the synthesized compounds I-IV in DMSO-d<sub>6</sub> (5-10%) were recorded on a Bruker DPX-300 spectrometer with an operating frequency of 300.13 MHz. signals were calibrated relative to the tetramethylsilane standard □ 0.00 ppm.

Table 1. Yields, melting points, and results of elemental analysis of aroylhydrazones of aroylacetic aldehyde (I-IV)

Compound	Exit, %	T <sub>пл.аб.</sub> , °C	Gross formula	Calculated/found, %		
				C	H	N
I	77	124	C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub>	71.93/72.16	5.22/5.30	10.68/10.52
II	72	157	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	72.86/72.84	5.72/5.75	10.02/9.99
III	83	163	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	68.94/68.91	5.49/5.44	9.63/9.45
IV	69	174	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	65.42/65.38	5.12/5.16	9.08/8.97

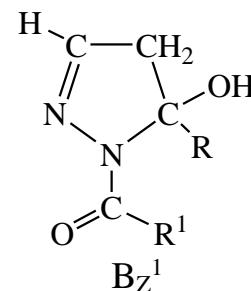
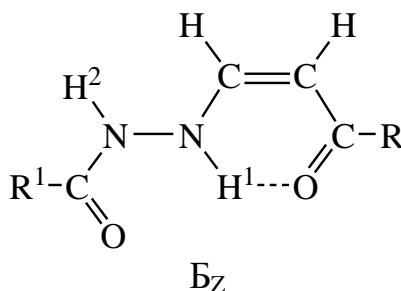
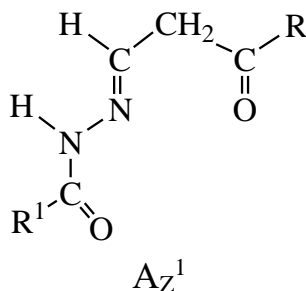
X-ray diffraction analysis. The experiments were carried out on an Xcalibur® Oxford Diffraction diffractometer at room temperature (CuKα radiation, graphite monochromator). The strategy for collecting experimental data was carried out using the CrysAlisPro program [15]. Absorption correction was made by the “multi-scan” method in the CrysAlisPro software package. The structures were solved by the direct method and refined by full-matrix least squares in F2 using the Olex2 [16] and SHELX [17] software packages. Some crystallographic characteristics and details of the experiment are presented in Table 4. All non-hydrogen atoms were refined anisotropically. The coordinates of hydrogen atoms (except for NH groups) in compound II are determined geometrically and refined with fixed isotropic displacement parameters (U<sub>iso</sub>=nU<sub>eq</sub>, where n=1.5 for methyl groups and 1.2 for others). The hydrogen atoms of the secondary amino group were found by the method of electron density difference synthesis and refined isotropically. Final divergence factors R=0.0726 (for I>2,0□(I)), (wR2=0.1588, for all reflections). Molecular graphics were constructed using the XP program in the SHELXTL-Plus software package [18].

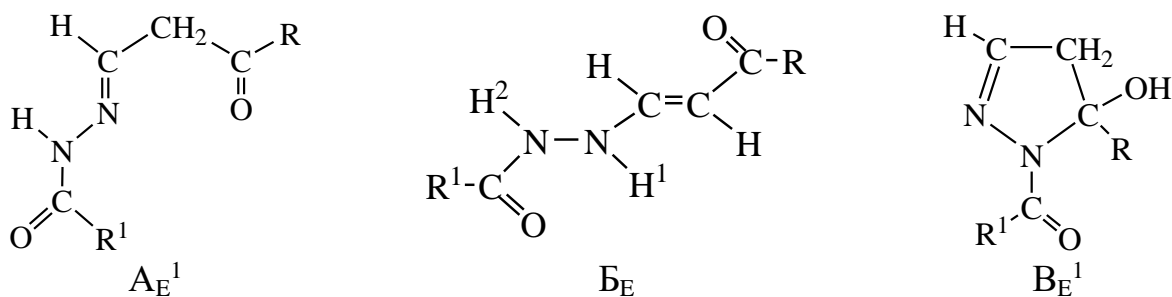
The structure was registered with the Cambridge Crystallographic Data Center (<http://www.ccdc.cam.ac.uk>, e-mail: deposit@ccdc.cam.ac.uk; deposit number CCDC 1826717).

## RESULTS AND ITS DISCUSSION

The products of the interaction of β-diketones with nitrogen-containing nucleophilic reagents are potentially tautomeric compounds, although most of them can exist in solutions of ringed 5-hydroxypyrazoline, hydrazone, and/or conjugated enhydrazine forms [1–7, 13, 14, 19].

In this work, we studied the structure of the synthesized condensation products of a number of benzoylacetic aldehydes with aromatic acid hydrazides (I-IV):





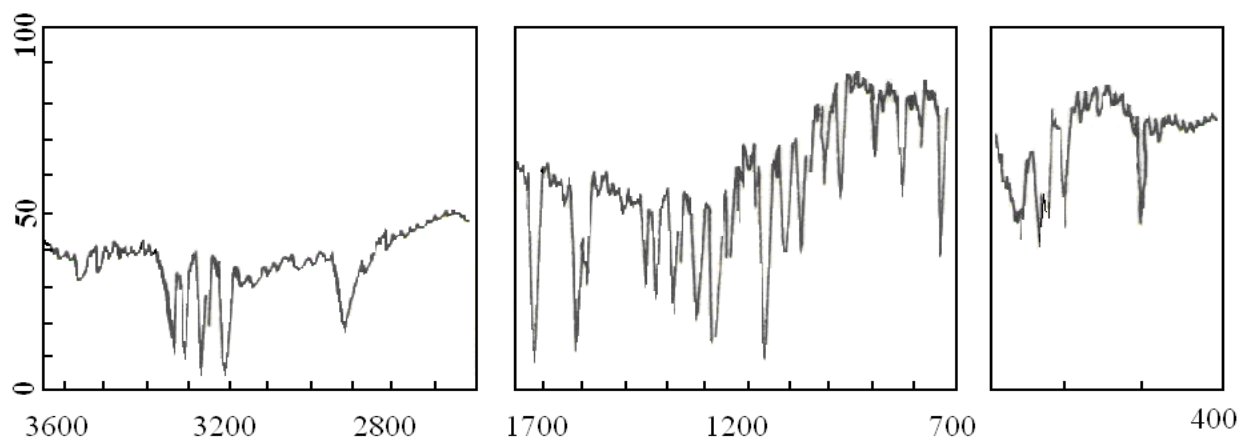
R=C<sub>6</sub>H<sub>5</sub>;R<sub>1</sub>=C<sub>6</sub>H<sub>5</sub> (I), *para*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> (II), *meta*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> (III);

R=*para*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>, R<sub>1</sub>=*ortho*-OHC<sub>6</sub>H<sub>4</sub> (IV).

The structure of the obtained organic compounds was established by the results of IR -, <sup>1</sup>H NMR spectroscopy and X-ray diffraction. In our opinion, in the case of ketoaldehydes, the condensation reaction proceeds at the aldehyde group adjacent to the benzoyl substituent [20, 21].

The aroylhydrazones of β-ketoaldehydes obtained in solutions exist as a tautomeric mixture, the composition of which is determined by the structure of the substituent in the acyl moiety and the nature of the solvent used.

Absorption bands at 1510, 1595, 1640, 1660, and 1730–1740 cm<sup>-1</sup> are observed in the IR spectrum of compound I, in a pressed KBr pellet, in the region of stretching vibrations of multiple bonds [5, 19, 22]. The form of the spectra is consistent with the linear structure (A and B) of compounds (I-IV) in the solid state (Fig. 1, Table 2).



Rice. 1. IR spectrum of compound I in a pressed KBr tablet.

Table 2. Assignment of stretching vibration frequencies (□, cm<sup>-1</sup>) in the IR spectra of ligands

Compound	NC=O	C=O	C=N	C-N	N-N	N-H	C-H
I	1740	1660	1590	1290	1080	3250	2970
II	1735	1665	1586	1280	1080	3260	3050
III	1740	1670	1587	1286	1090	3255	3060
IV	1730	1650	1550	1278	1040	3240	2950

In the IR spectrum of compound I in a pressed KBr tablet, in the region of stretching vibrations of multiple bonds, absorption bands are observed at 1590 cm<sup>-1</sup>, which we assigned to the stretching vibrations of amide II □(C=N). The bands at 1650–1670, 1730–1740, 1270–1290, 2959–3050, and 3280–3330 cm<sup>-1</sup> were assigned by us, respectively, to □(C=O), □(NC=O),

$\nu(\text{C-N})$ ,  $\nu(\text{C-H})$  и  $\nu(\text{N-H})$  oscillations [19, 23]. The shape of the spectra and their assignments are consistent with the linear structure (AE) in the solid state (Fig. 1, Table 2). In contrast to the condensation products of  $\alpha$ -diketones with acylhydrazides of aliphatic acids [5, 14, 19], in the condensation products of benzoylactic aldehyde with substituted aroylhydrazides (I-IV) in solution  $\text{CCl}_4 + \text{DMSO-d}_6$  linear ones predominate: hydrazone (AE) or enhydrazine (BE) forms [6,19]. This is evidenced by the parameters of the spectra  $^1\text{H NMR}$  (Fig. 2, Table 3). in solution  $\text{DMSO-d}_6$  there is a complex ring-chain transformation involving all of the above tautomeric forms. These paired ring-chain equilibria between cyclic (C) and hydrazone (A) or enhydrazine (B) forms, where the set of open forms (A) and (B) acts as an open tautomer, tautomeric equilibria between linear forms (A) and (B), as well as the configurational Z,E-equilibrium within the enhydrazine form, the conformational equilibrium relative to the amide bond for the hydrazone form. It should be noted, as the most characteristic, that the realization of this range of equilibrium forms was carried out by varying the structure of only one substituent in the N-acyl moiety and using only three solvents [5, 12].

According to previous studies [13, 19], the condensation products of ketoaldehydes with hydrazides of aliphatic acids show a ring-chain equilibrium in which, along with the hydrazone or enhydrazine forms, the cyclic 5-hydroxy-pyrazoline form also participates. In contrast to the condensation products of benzoylactic aldehyde with acylhydrazines of aliphatic acids, for the products of condensation of benzoylactic aldehyde with substituted aroylhydrazides (I-III), linear reactions predominate in solutions: E-hydrazone (AE) and E- enhydrazine (BE and BZ) forms [9, 13]. This is evidenced by the parameters of the  $^1\text{H NMR}$  spectra (Fig. 2, Table 3) [6]. For example, compound II is in enhydrazine tautomeric form with BE- configuration (Table 3). The enhydrazine form of these organic compounds is characterized in the spectra  $^1\text{H NMR}$  with two doublet signals in a higher field region ( $\delta$  6.08 ppm) with VSWR  $J=12-12.5$  and in a relatively low-field part of the spectrum ( $\delta$  5.74 ppm). The SSCC value was  $J=7.0-8.0$  Hz, which indicates the presence, along with the BE configuration, of the Z-enhydrazine form (BZ). The shape of the  $^1\text{H NMR}$  spectra for compounds II and III (Fig. 2 a, b) somewhat differs from the spectrum of II (Table 3) by the presence of signals from substituted protons *para*- $\text{CH}_3$ - and *meta*- $\text{CH}_3\text{O}$ - substituents of the phenyl ring of the hydrazide part of the molecules. The difference in the proton signals of these two substituents differs in that the protons from  $\text{CH}_3$ -group in the *para*-position of the benzene ring of the hydrazide part of the molecule II resonates at  $\delta$  2,42 v  $\text{CH}_3\text{O}$ - groups in the *meta*-position of the benzene ring of compound III - in a weaker field ( $\delta$  3,06 ppm), what researched to expect [9, 13]. To be fair, it should be noted that the signals of the protons of the phenyl substituent in the terminal position of the ligands of the ketoaldehyde fragment of compounds I-IV in all four  $^1\text{H NMR}$  spectra partially overlap with the signals of the protons of the aroyl fragments of the hydrazide part of the molecules, thus complicating the shape of the spectra.

Thus, the totality of spectral data shows that by varying the structure of the  $\alpha$ -ketoaldehyde part of the molecule, the nature of the solvent used in the series of acylhydrazones of  $\alpha$ -ketoaldehydes, various tautomeric forms can be realized. Some of them may have complex, including up to five, and sometimes up to six, determined by  $^1\text{H NMR}$ , slow in the time scale of this method, mutually passing into each other tautomeric forms.

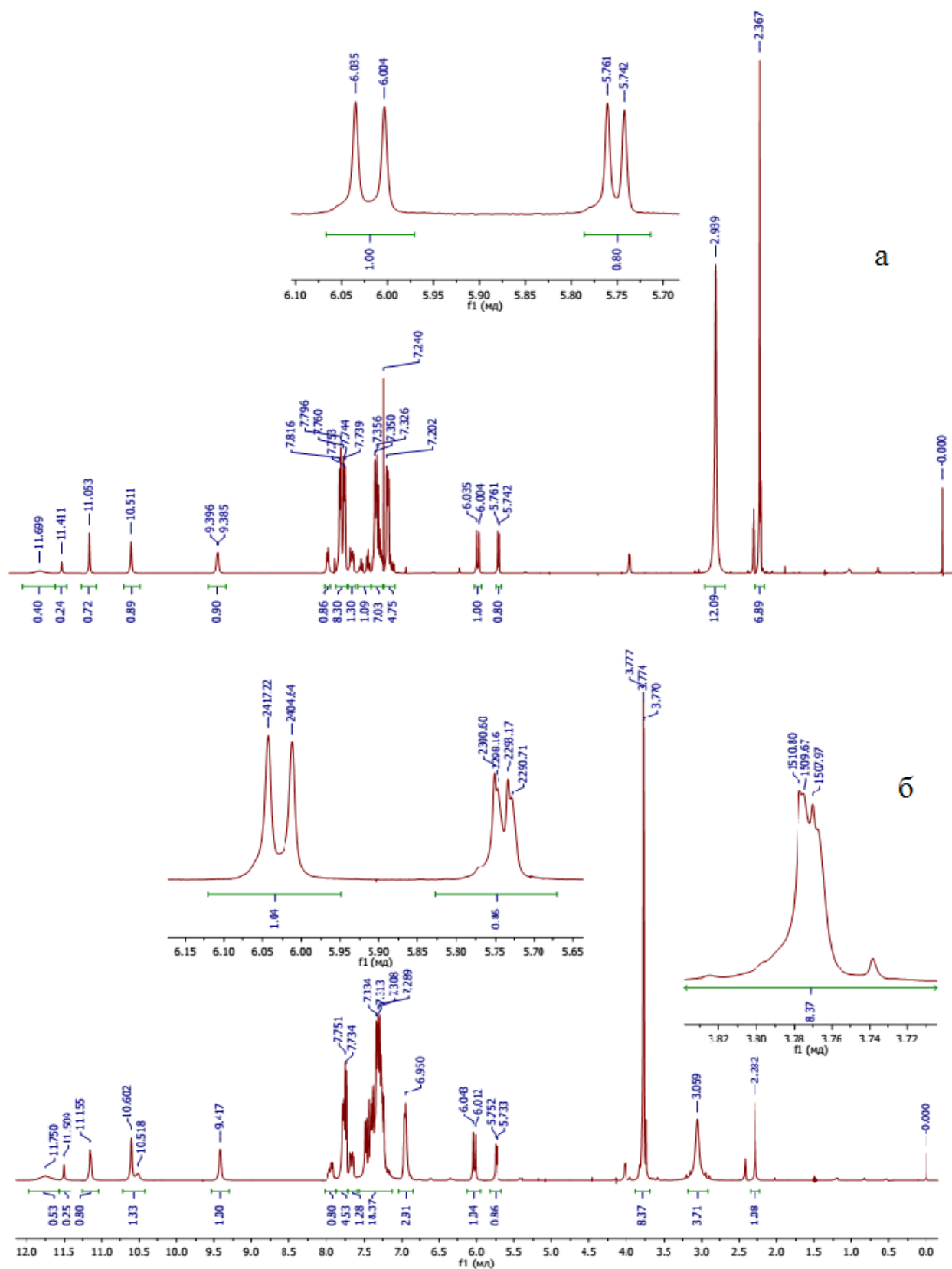


Fig.2. <sup>1</sup>H NMR spectrum of para-methylbenzoylhydrazone of 3-phenyl-3-oxopro-pionic aldehyde (II) - a, meta-methoxybenzoylhydrazone 3-(4- methoxyphenyl)-3-oxopentanal (III)-b in solution CCl<sub>4</sub>+ DMSO -d<sub>6</sub>.

Table 3. <sup>1</sup>H NMR spectra of aroylhydrazones of aroylacetic aldehydeI–IV in CCl<sub>4</sub>+DMSO-d<sub>6</sub> solution at room temperature

Compound	NH <sup>1</sup>	NH <sup>2</sup>	HC-N	HC-C	C <sub>6</sub> H <sub>5</sub>	Protons R	
						X	C <sub>6</sub> H <sub>4</sub>
I	10.05	9.39	5.75	6.02	7.43; 7.53; 7.80	7.02; 7.32; 7.96	
II	10.11	9.47	5.83	6.08	7.32; 7.65; 8.02	2.42	7.06; 7.49
III	11.16	9.42	5.74	6.04	7.28; 7.73; 7.90	3,06	6.95; 7.34;
IV	10.12	9.45	5.73	6.06	7.28; 7.55; 7.95	12.68	7.22; 8.05

Regardless of the type of equilibrium, for derivatives of substituted aroylhydrazones I–IV, the presence of a cyclic (B) form is simply excluded and is not fixed in the time scale of <sup>1</sup>H NMR spectra from this tautomer; in the solid state and in solutions, they exist only in the form of Z, E-enhydrazine tautomeric forms (BZ and BE) [12, 19].

To unambiguously prove the conclusions of IR spectral studies on the linear structure of the obtained organic compounds, we

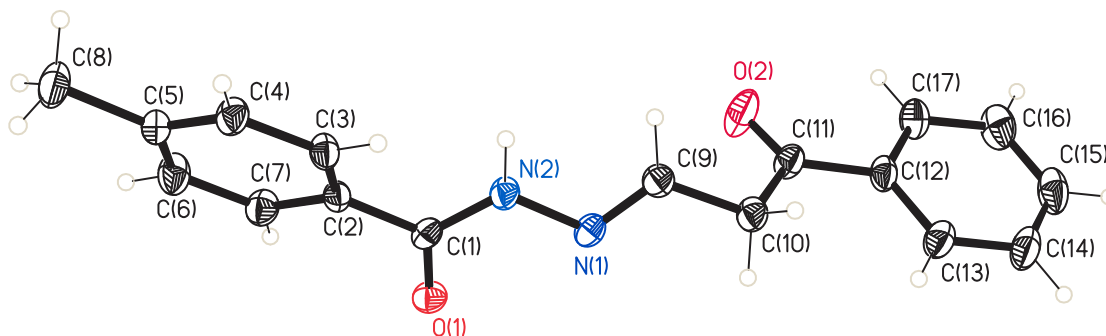


Figure 3. The structure of molecule II with the numbering of non-hydrogen atoms. Thermi-

The spherical ellipsoids are shown at the 30% probability level.

C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> single crystals were grown by recrystallization of II, and the crystal structure was analyzed by X-ray diffraction analysis. Molecule II crystallizes in the space group P2<sub>1</sub>/c of the monoclinic system and one molecule II crystallizes in an independent part of the unit cell (Fig. 3, Table 4). By means of hydrogen bonds of two types C10-H10B...O2 (2.445 Å long and 142.33°) and N2-H2...O1 (2.076 Å and 157.77° long), II molecules are combined into infinite chains going along the c axis. The cycles formed by hydrogen bonds in structure II can be represented using graph theory [24–26] as R22(14) (fig.4). In addition, there are additional □-□ interactions [Cg1...Cg1 = 3.932(3), as a result of the lateral shift 1.501 Å symmetry code: 1-x, 2-y, 1-z; Cg1 is the center of the benzene (C2-C7) ring] between the benzene fragments of the II molecule.

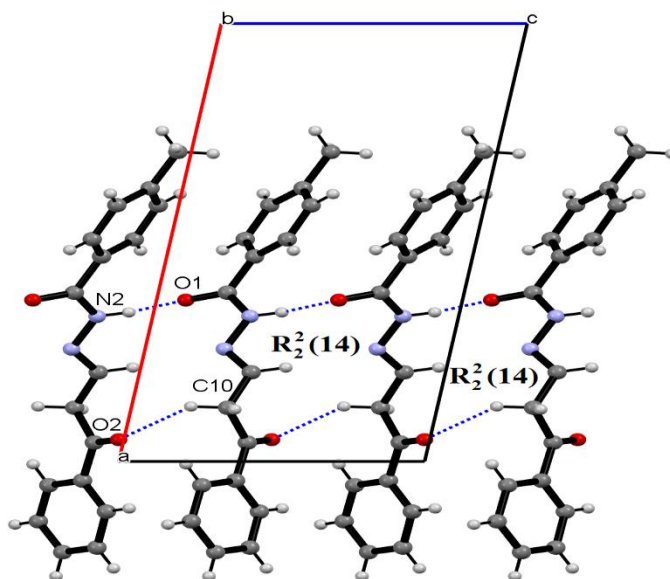
Table 4. Crystallographic data and XRD characteristics of compound II

Compound	II
Gross formula	C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>
<i>M</i>	280.32
Syngony	Моноклинная

space group	<i>P2<sub>1</sub>/c</i>
Elementary Cell Parameters <i>a, b, c, Å</i>	15.6942(13), 12.1515(13), 8.0046(10)
$\beta$ , hail.	99.853(9)
$V, \text{Å}^3$	1504.0(3)
$Z$	4
Density (calculated), $\text{g/cm}^3$	1.238
Temperature, K	293
Radiation, Å	CuKa, 1.54184
Crystal size, mm	0.32x0.24x0.18
Scan area $2\theta$ (min,max), deg.	4.6, 75.8
Data index range	-19: 19 ; -12: 15 ; -5: 9
$I_{hkl}$ tr./ independent./ $R_{\text{int}}$	5672, 3020, 0.094
Observed reflections [ $I > 2.0 \sigma(I)$ ]	1085
$N_{\text{ref}}, N_{\text{par}}$	3020, 196
GOOF ( $F^2$ )	0.92
$R_1, wR_2 (I > 2\sigma(I))$	0.0726, 0.1588
$R_1, wR_2$ (all reflections)	0.072, 0.157
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} (e \text{ Å}^{-3})$	<u>0.15</u> , <u>-0.24</u>

Judging by the magnitude of the connections: O(1)–C(1) (1.230Å), O(2)–C(11) (1.207Å), N(1)–C(9) (1.246Å) are double, but the bond length N(2)–C(1) (1.345Å) corresponds to a single one (Table 5). The small difference in the values of double bonds, in our opinion, is explained by the fact that  $\pi$ - $\pi$ -conjugation with a single  $\pi$ -orbital of the aromatic ring. The C(1) atom has a planar trigonal configuration ( $sp^2$  hybrid state), as a result of which a coplanar arrangement of the atoms of this fragment of the molecule in space is observed (Fig. 3, Table 5). As can be seen from fig. 3, molecule II, is indeed in the linear hydrazone (AE) form [19]. The packing of structural units in crystal II is shown in fig. four.

This is unambiguously evidenced by the values of the torsion angles N(1)N(2)C(1)C(2), N(1)N(2)C(1)O(1), C(1)C(2)C(3)C(4), C(8)C(5)C(6)–C(7), whose values are 173.2(4)o, -4.3(6)o, 179.8(4)o, 177.9(5) o respectively. The same local conjugated system is formed around the planar trigonal C(9) atom, which ensures the coplanar arrangement of the atoms bound to them separately in the  $\pi$ -ketoester part of the molecule.



Rice. 4. Crystal structure II. Formation of directed chains, built by hydrogen bonds. Hydrogen bonds shown by dotted line.

Table 5 Bond lengths and bond angles in the structure of para-methylbenzoylhydrazone of aroylacetic aldehyde (II)

Connection	<i>d</i> , Å	Connection	<i>d</i> , Å
O(1)–C(1)	1.230 (5)	O(2)–C(11)	1.207 (6)
N(1)–N(2)	1.401 (4)	N(1)–C(9)	1.246 (6)
N(2)–C(1)	1.345 (5)	C(1)–C(2)	1.491 (5)
C(2)–C(3)	1.374 (5)	C(2)–C(7)	1.374 (6)
C(3)–C(4)	1.391 (5)	C(4)–C(5)	1.375 (6)
C(5)–C(6)	1.370 (6)	C(5)–C(8)	1.523 (5)
C(9)–C(10)	1.500 (6)	C(10)–C(11)	1.495 (6)
C(11)–C(12)	1.496 (6)		
Corner	$\omega$ , deg.	Corner	$\omega$ , deg.
O(1)–C(1)–C(2)	122.2 (4)	O(1)–C(1)–N(2)	121.8 (4)
C(1)–N(2)–N(1)	119.5 (4)	N(2)–C(1)–C(2)	115.9 (4)
C(9)–N(1)–N(2)	114.9 (4)	O(2)–C(11)–C(10)	119.8 (5)
O(2)–C(11)–C(12)	120.6 (5)	N(1)–C(9)–C(10)	120.1 (4)
C(10)–C(11)–C(12)	119.5 (5)	C(6)–C(5)–C(8)	121.1 (5)
C(11)–C(12)–C(13)	122.1 (5)	C(11)–C(12)–C(17)	118.0 (5)

Thus, as a result of studies by IR and <sup>1</sup>H NMR spectroscopy, it was found that the products of condensation of aroylacetic aldehydes with aromatic acid hydrazides in the solid state and in solutions exist in linear hydrazone and enhydrazine forms. Molecule II was unambiguously proved by IR and X-ray diffraction studies that the synthesized compounds in crystalline form are in the linear hydrazone form (AE).

## CONCLUSION

1. As a result of studies using IR, <sup>1</sup>H NMR spectroscopy and X-ray diffraction analysis, it was found that the condensation products of aroylacetic aldehydes with aromatic acid hydrazides in the solid state and in solutions exist in linear hydrazone and enhydrazine forms.
2. In the process of recrystallization of compound II (para-methylbenzoylhydrazone of 3-phenyl-3-oxopropanal), crystals precipitate from a solution of ethanol and chloroform C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>. X-ray diffraction analysis proved the conclusion that II in the solid state is indeed in the linear hydrazone form (AE).

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