SYNTHESIS, IR, 1H NMR SPECTROSCOPY AND X-RAY DIFFRACTION ANALYSIS OF BENZOYLACETIC ALDEHYDE AROYLHYDRAZONES

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Abstract- Nitrogenous derivatives of β-ketoaldehydes are capable of various tautomeric transformations [1-5]. The condensation products of aldehydes with area luxury hydrazide aromatic acids exist in linear hydrazone and emigrating forms. The appearance of an alternative cyclic 5-hydroxy-2-pyrazoline form is facilitated by the introduction of a strong electron-acceptor substituent into the aromatic core of 1,3-ketoaldehyde. In a series of compounds, an increase in the volume of the substituent in the acyl part shifts the tautomerism equilibrium towards the enhydrazine form. The resulting ligands were studied by elemental analysis, IR and NMR spectroscopy. The molecular structure of compound II is determined by the method of RSA (CIF file CCDC №.1826717).

Keywords: aroylhydrazone, benzoylacetic aldehyde, crystalline structure. X-ray diffraction analysis.

I. INTRODUCTION

The interaction of 1,3-ketoaldehydes with acylhydrazones, which proceeds exclusively by 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 number of prototropic and ring-chain equilibria with various combinations of the above tautomers [10-14].

II. EXPERIMENTAL

2.1. Synthesis of para-methylbenzoyl hydrazone 3-phenyl-3-oxopropanal and its analogues.
Compounds I-IV synthesized according to [5-7] were studied, pyridine ("pure for analysis"), as well as solvents EtOH, diethyl ether ("chemical pure", distilled) [15, 16].

Synthesis of para-methylbenzoyl hydrazone 3-phenyl-3-oxopropanal. To a solution of 1.48 g (0.01 mol) of 3-phenyl-3-oxopropanal in 50 ml of ethanol, 1.50 g (0.01 mol) of para-methylbenzoic acid hydrazide in 100 ml of ethanol was added by stirring. The reaction mixture was left for 1 day at room temperature. The precipitated polycrystalline precipitate of para-methylbenzoyl hydrazone 3-phenyl-3-oxopropanal (II) with a mass of 2.02 g (72 %, $T_{melting}$ 157°C Table. 1), filtered, washed with a small amount of ethanol, diethyl ether and hexane. Recrystallization of II from ethanol and chloroform produced monoclinic crystals of $C_{17}H_{16}N_2O_4$.

Similarly, compounds I, III and IV were obtained (Table 1).

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

Compound	Yield, %	$t_{m,}$ ^oC	Brutto-formule	Found/calculated, %		
				C	H	N
I	77	124	$C_{16}H_{14}N_2O_2$	71.93/72.16	5.22/5.30	10.68/10.52

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II	72	157	$C_{17}H_{16}N_2O_2$	72.86/72.84	5.72/5.75	10.02/9.99
III	83	163	$C_{17}H_{16}N_2O_3$	68.94/68.91	5.49/5,44	9.63/9.45
IV	69	174	$C_{17}H_{16}N_2O_4$	65.42/65.38	5.12/5.16	9.08/8.97

2.2. Materials and characterization

IR spectra

IR absorption spectra were recorded on a Specord 75IR spectrometer, and samples were taken in the range of 400-4000 cm-1 in compressed KBr tablets.

1H NMR spectra

The 1H NMR spectra of 5-10% solutions I-IV were taken on Unity 400plus (Varian) spectrometers with an operating frequency of 300.13 MHz. The signals were calibrated relative to the tetramethylsilane standard δ 0.00 ppm.

X-ray diffraction analysis.

The experiments were carried out on an Xcalibur® Oxford Diffraction diffractometer at room temperature (CuK$_\alpha$ radiation, graphite monochromator). The strategy of collecting experimental data was implemented using the CrysAlisPro program [17]. The correction for absorption was made by the "multi-scan" method, in the CrysAlisPro software package. The structures were solved by the direct method and refined by the full-matrix F^2 OLS using the Olex2 [18] and SHELX [19] 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 the hydrogen atoms (except for NH groups) in compound II are determined geometrically and refined with fixed isotropic displacement parameters (U_{iso}=nU_{eq}, where n=1.5 for the methyl groups and 1.2 for the others). The hydrogen atoms of the secondary amino group were found by the electron density difference synthesis method and refined isotropically. The final divergence factors are R=0.0726 (for I>2.0σ(I)), (wR2=0.1588, for all reflections). Molecular graphics constructed using the XP program in the SHELXTL-Plus software package [20, 21].
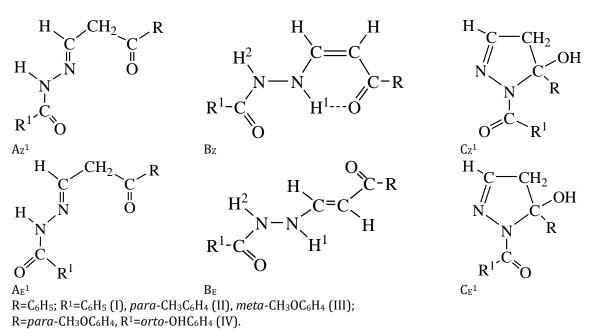
The structure registered in the Cambridge Structural Data Bank (http://www.ccdc.cam.ac.uk, e-mail: deposit@ccdc.cam.ac.uk; deposit number CCDC 1826717).

III. RESULTS AND DISCUSSIONS

3.1. Tautomerism

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 the annular 5-hydroxypyrazoline, hydrazone and / or conjugated enhydrazine forms, [1-7, 14, 15, 22-25].

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

R=C_6H_5; R^1=C_6H_5 (I), *para*-$CH_3C_6H_4$ (II), *meta*-$CH_3OC_6H_4$ (III);
R=*para*-$CH_3OC_6H_4$, R^1=*orto*-OHC_6H_4 (IV).

The structure of the obtained organic compounds established by the results of IR-, 1H NMR spectroscopy and X-ray structural analysis. In our opinion, in the case of ketoaldehydes, the condensation reaction proceeds at the aldehyde group adjacent to the benzoyl substituent [26, 27].

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

3.2. Infrared spectra

In the IR spectrum of compound I in a pressed KBr pellet in the region of stretching vibrations of multiple bonds, absorption bands are observed at 1590 cm^{-1}, which we assigned to stretching vibrations of amide II $\nu_{(C=N)}$.

Table 2.

Assignment of stretching vibration frequencies (ν, см$^{-1}$) in the IR spectra of ligands

Соединение	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

The bands at 1650-1670, 1730-1740, 1270-1290, 2959-3050, 3280-3330 cm^{-1} were assigned by us, respectively, to $\nu_{(C=O)}$, $\nu_{(NC=O)}$, $\nu_{(C-N)}$, $\nu_{(C-H)}$ and $\nu_{(N-H)}$ vibrations [22, 28, 29]. The form of the spectra and their assignment are consistent with the linear structure (A_E) in the solid state (Fig. 1, Table 2).
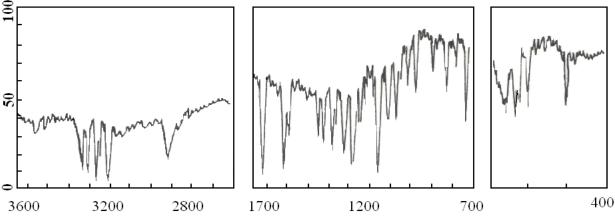

Fig. 1. IR spectrum of compound I in a pressed KBr tablet.

3.3. ¹H NMR spectra

In contrast to the condensation products of β-diketones with acylhydrazides of aliphatic acids [5, 16, 22], in the condensation products of benzoylacetic aldehyde with substituted aroylhydrazides (I-IV) in a solution of the CCl$_4$ + DMSO-d$_6$ mixture, linear: hydrazone (A_E) or enhydrazine (B_E) forms [6, 19]. This is evidenced by the parameters of the ¹H NMR spectra (Fig. 2, Table 3). In a DMSO-d$_6$ solution, paired ring-chain equilibria are observed between cyclic (C) and hydrazone (A) or enhydrazine (B) forms, where a set of open forms (A) and (B) acts as an open tautomer, tautomeric equilibria between linear forms (A) and (B), as well as conformational equilibrium relative to the amide bond for the hydrazone form. Note, as the most characteristic, that the realization of this range of equilibrium forms was carried out by us earlier by varying the structure of only one substituent in the N-acyl part and using only three solvents [6, 7, 22].
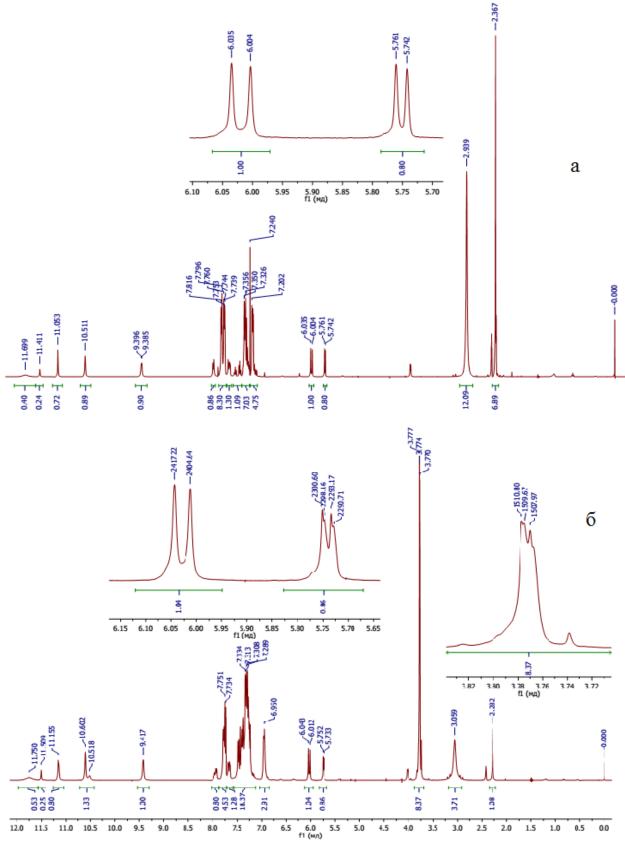
Fig. 2. 1H NMR spectrum of para-methylbenzoylhydrazone 3-phenyl-3-oxopropionic aldehyde (II) - a, meta-methoxybenzoylhydrazone 3- (4-methoxyphenyl) -3-oxopentanal (III) –b in CCl₄ + DMSO-d₆ solution.

The condensation products of ketoaldehydes with hydrazides of aliphatic acids, according to previous studies [15, 22], show 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 benzoylacetic aldehyde with acylhydrazines of aliphatic acids, for the condensation products of benzoylacetic aldehyde with substituted aroylhydrazides (I – III), linear forms prevail in solutions: E-hydrazone (A_E) and E-enhydrazine (B_E) [9, 15]. This is evidenced by the parameters of the ^{1}H NMR spectra (Fig. 2, Table 3) [6]. For example, compound II is in the enhydrazine tautomeric form with the B_E configuration (Table 3).

Table 3.
^{1}H NMR Spectra of aroylhydrazones of aroylacetic aldehyde
I – IV in CCl_4 + DMSO-d_6 solution at room temperature

Compound	NH[1]	NH[2]	HC-N	HC-C	C_6H_5	Protons R	
						X	C_6H_4
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

The enhydrazine form of these organic compounds is characterized in the ^{1}H NMR spectra by two doublet signals in the higher-field region (δ 6.08 ppm) with a coupling constant *J*=12-12,5 and in the relatively low-field part of the spectrum (δ 5.74 ppm). The magnitude of the CVC was *J*=7,0-8,0 Hz, which indicates the presence, along with the B_E-configuration, of the Z-enhydrazine form (B_Z). The form of 1H NMR spectra for compounds II and III (Fig. 2 a, b) slightly differs from spectrum I (Table 3) by the presence of signals from the protons of substituted para-CH_3- and meta-CH_3O-substituents of the phenyl ring of the hydrazide part of the molecules. The difference in the signals of the protons of these two substituents differs in that the protons from the CH_3-group in the para-position of the benzene ring of the hydrazide part of molecule II resonate at δ 2.42 ppm, and the protons of the CH_3O-group in the meta-position of the benzene ring of compound III - in a weaker field (δ 3.06 ppm), which should be expected [9, 15]. In fairness, 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}H NMR spectra are partially overlap with the signals of the protons of the aroyl fragments of the hydrazide part of the molecules, thus complicating the form of the spectra.

The set of spectral data shows that by varying the structure of the β-ketoaldehyde part of the molecule, the nature of the solvent used in the series of β-ketoaldehyde acylhydrazones, various tautomeric forms can be realized. Some of them can have complex ones, including up to five, and sometimes up to six, determined by the ^{1}H NMR method, slow in the time scale of this method, mutually transforming into each other tautomeric forms.

Regardless of the type of equilibrium, for derivatives of substituted aroylhydrazones I – IV, the presence of the cyclic (B) form is simply excluded and is not recorded in the time scale of ^{1}H NMR spectra from this tautomer; in the solid state and in solutions, they exist only in the form of Z, E-hydrazone tautomeric forms (A_Z and A_E) [12, 22].

3.4. X-ray diffraction analysis.

To the unambiguously prove the conclusions of IR spectral studies on the linear structure of the obtained organic compounds, we grew single crystals of $C_{17}H_{16}N_2O_4$ by recrystallization of II, and the crystal structure as deciphered by X-ray diffraction. Molecule II crystallizes in the *P2₁/c* space group of the monoclinic system in the independent part of the unit cell (Fig. 3, Table 4).
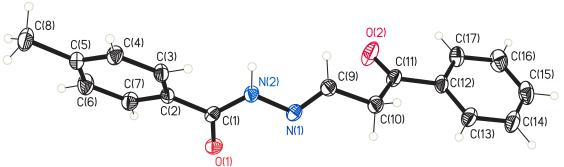
Fig.: 3. The structure of molecule II with the numbering of non-hydrogen atoms. Thermal ellipsoids are shown at the 30% probability level.

Table 4.
Crystallographic data and XRD characteristics of compound II

Compound	II
Brutto-formula	$C_{17}H_{16}N_2O_2$
M	280.32
Syngony	Monoclinic
Sp. Gr.	$P2_1/c$
Unit cell parameters a, b, c, Å	15.6942(13), 12.1515(13), 8.0046(10)
β, deg.	99.853(9)
V,Å³	1504.0(3)
Z	4
ρ (calc), g/sm³	1.238
Temperature, K	293
Ray, Å	CuKa, 1.54184
Crystal sizes, mm	0.32x0.24x0.18
Scanning region by 2θ (min,max), deg.	4.6, 75.8
Index area	-19: 19 ; -12: 15 ; -5: 9
I_{hkl} change / independent./R_{int}	5672, 3020, 0.094
Observed reflections [$I > 2{,}0\,\sigma(I)$]	1085
N_{ref}, N_{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
Δρ$_{max}$, Δρ$_{min}$ (e Å⁻³)	0.15, –0.24

By hydrogen bonds of two types C10-H10B···O2 (length 2.445 Å and angle 142.33°) and N2-H2···O1 (length 2.076 Å and angle 157.77°) molecules II are combined into infinite chains running in the direction of the **c** axis. The cycles formed by hydrogen bonds in structure II can be represented using graph theory [30-32] in the form of $R^2_2(14)$ (Fig.4).

In addition, additional π-π interactions arise [Cg1···Cg1= 3.932(3), because 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 molecule II.

Judging by the values of the relations: 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 single (table. 5). A small difference in the values of double bonds, in our view, due to the fact that π-connection C=O fragment aldehyde part of the molecule is partially weakened, as it comes into π-π-pairing with a single π-orbital of the aromatic ring. The C(1) atom has a planar-trigonal configuration (sp2-hybrid state), as a result of which the coplanar arrangement of the atoms of this fragment of the molecule in space is observed (Fig. 5). As can be seen from Figure 3, molecule II is indeed in a linear hydrazone (A$_E$) form [22]. The packing of structural units in crystal II is showing in Fig. 4.
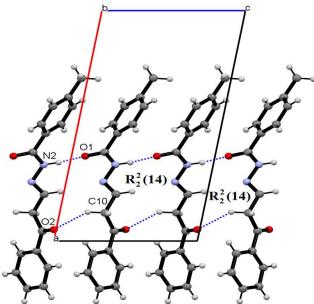
Fig. 4. Crystal structure II. Formation of directed chains, built at the expense of hydrogen bonds. Hydrogen bonds shown in dotted lines.

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), the values of which 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 plane-trigonal atom C(9), which provides a coplanar arrangement of the atoms associated with them separately in the β-ketoester part of the molecule.

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

Bond	d, Å	Bond	d, 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)		
Angle	ω, deg.	Angle	ω, 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)

IV. CONCLUSION

Thus, as a result of studies by IR and ^{1}H NMR spectroscopy, it was established that the condensation products of aroylacetic aldehydes with hydrazides of aromatic acids in the solid state and in solutions exist in linear hydrazone and enhydrazine forms.

It was unambiguously proved by X-ray structural analysis that the synthesized compound (II) in crystalline form is in the linear hydrazone form (A_E).

Acknowledgements

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