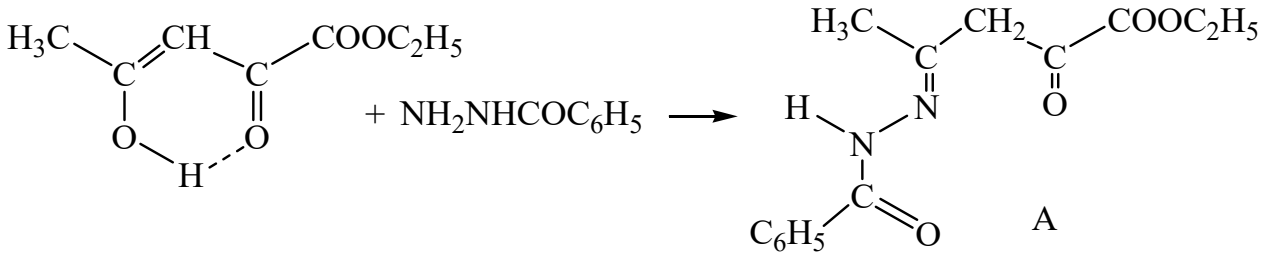
SYNTHESIS AND STRUCTURE OF THE BENZOYLHYDRAZONE OF ETHYL 2,4-DIOXOPENTANOATE

Tursunov Murod Amonovich
Bukhara State University
Research Institute of Natural Sciences and Agroinnovations
Professor of the Department of Chemistry and Oil and Gas Technologies

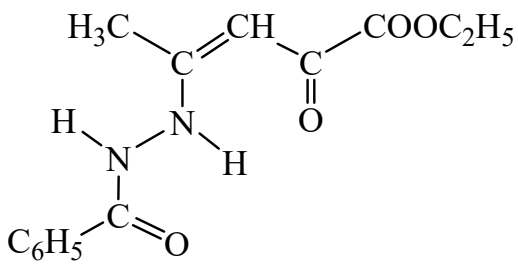
Shukurov Hidoyat O‘ktam o‘g‘li
Bukhara State Medical Institute
Assistant at the Department of Medical and Biological Chemistry
E-mail: tursunovma@mail.ru
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Acyl- and aroylhydrazones of 1,3-diketones are an important class of compounds in terms of their tautomeric possibilities, and scientific interest in them continues to grow. Aroylhydrazones of ethyl 2,4-dioxopentanoate can exist in various tautomeric forms. Depending on the structural features of the dicarbonyl component, aroylhydrazones of β-diketones can exhibit ring–chain equilibrium between the open-chain hydrazone and enehydrazine forms and the cyclic 5-hydroxy-2-pyrazoline tautomer. Paired prototropic equilibria are observed for derivatives of 1,3-ketoesters.

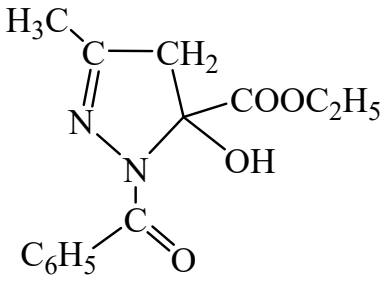
We studied the structure of the condensation product of ethyl 2,4-dioxopentanoate with benzoic acid hydrazide. According to proton NMR spectroscopy, ethyl 2,4-dioxopentanoate exists in the keto–enol form. Investigation of the composition and structure of the aroylhydrazone (H_2L^1) obtained from the ketoester by IR and proton NMR spectroscopy revealed the following structures:



A



Б



B

H_2L^1

H_2L^1 shows C=O stretching bands at 1750–1765 cm^{-1} for the ethyl ester fragment of its β-diketone moiety. The IR spectra of these compounds exhibit a broad stretching band at ~3400 cm^{-1}

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$\nu_{(O-H)}$, and an absorption band of the amide fragment at 1660–1680 cm^{-1}. Intense absorption bands in the multiple-bond stretching region occur at 1633, 1595, 1574, 1558 and 1490 cm^{-1}. The band at 1633 cm^{-1} indicates a C=N bond, while the remaining bands are assigned to aromatic ring bonds and N–H bending vibrations. IR analysis indicates that the synthesized compound H_2L^1 exists in the solid state as the cyclic 5-hydroxy-2-pyrazoline tautomer (B).

H_2L^1 was studied in solution by analysing its proton NMR spectrum in deuterated chloroform, $CDCl_3$. The spectral parameters indicate that the cyclic tautomer (B) is retained. The methylene protons of the pyrazoline ring give asymmetric doublet signals at δ 2.98–3.03 ppm, forming a typical AB system (chemical shifts of two sterically nonequivalent protons) with a spin–spin coupling constant J_{AB} = 21 Hz. This is explained by the presence of a chiral centre in the molecule, identified as the carbon atom at the fourth position of the 5-hydroxy-2-pyrazoline ring.

To confirm the cyclic structure inferred from the IR and proton NMR spectra, X-ray diffraction analysis was performed on single crystals grown from the ligand H_2L^1. The analysis was carried out using an automated "**Xcalibur, Oxford Diffraction**" diffractometer (λ = 1.5418 Å, CuKα radiation, graphite monochromator, ω scanning). The H_2L^1 ligand crystals, $C_{14}H_{16}N_2O_4$, are monoclinic and have the following unit-cell parameters: a=14.1683(5), b=8.28854(18), c=25.5886(9), α=90.0, β=111.457(4), γ=90.0°, V=2796.71(15) Å, Z=2, space group C2/c (Fig. 1).

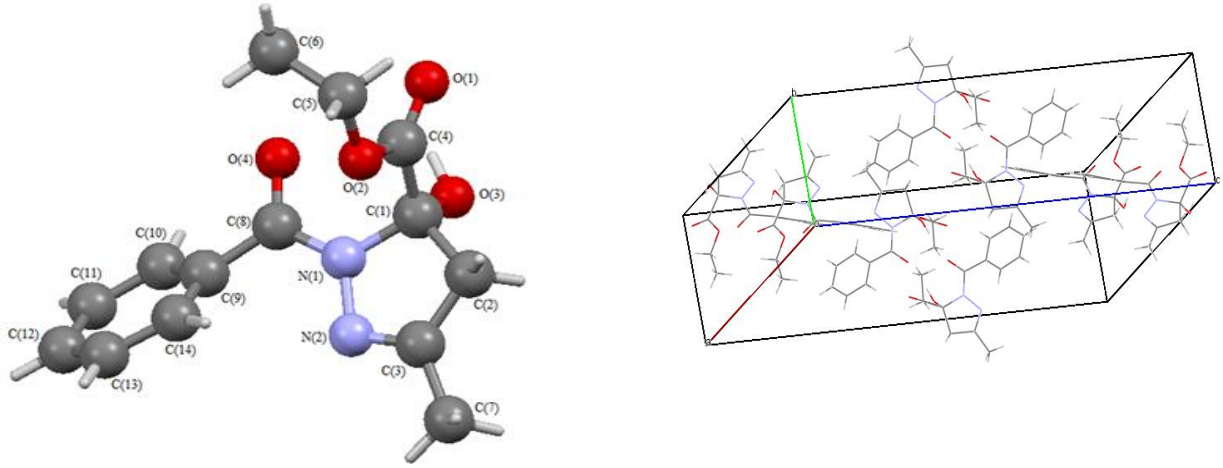


Fig. 1. H_2L^1 ligand molecular structure and projection of the molecules onto the ac plane of the crystal unit cell

The five-membered heterocyclic pyrazoline ring formed by the C(1)C(2)C(3)N(2)N(1) atoms and the benzene ring in the acyl part of the molecule are nearly planar. The maximum atomic deviations from the heterocyclic plane are 0.0022–0.011 Å, while the deviation for the phenyl ring is 0.0095 Å. Bond-length analysis reveals several double bonds in the molecule: N(2)=C(3), 1.28 Å; O(1)=C(4), 1.20 Å; and O(4)=C(8), 1.28 Å. The difference between the O(1)=C(4) and O(4)=C(8) bond lengths can be explained by the participation of the nonbonding p electron of O(4) in p–π conjugation with the delocalized π orbital of the phenyl ring. The bond angles O(1)C(4)O(2), 125.57°; N(2)C(3)C(7), 121.8°; and O(4)C(8)C(9), 122.04°, indicate that the C(4), C(3) and C(8) atoms are sp^2-hybridized and have a trigonal planar configuration. The bond angles and interatomic bond lengths indicate that the requirements of Hückel's aromaticity rule are fulfilled. One distinctive feature of the molecule is that the C(2) carbon atom in the pyrazoline ring is sp^3-hybridized.

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