

IR, NMR, AND X-RAY DIFFRACTION STUDY OF THE STRUCTURE OF ETHYL 5,5-DIMETHYL-2,4- DIOXOHEXANOATE BENZOYLHYDRAZONE

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Аннотация. Методами элементного анализа, ИК- и ПМР спектроскопии установлено состав и строение бензоилгидразона этилового эфира 5,5-диметил-2,4-диоксогексановой кислоты. Полученные монокристаллы лиганда изучены методом РСА.

Ключевые слова: бензоилгидразон, этиловый эфир, кристаллическая структура.

Annotatsiya. 5,5-dimetil-2,4-dioksogeksan kislotaning etil esferining benzoilgidrazoni tarkibi va tuzilishini elementar analiz, IQ va PMR spektroskopiyasi orqali aniqlandi. Ligandning yagona kristallari rentgen difraksiyasi usuli bilan o'rganildi.

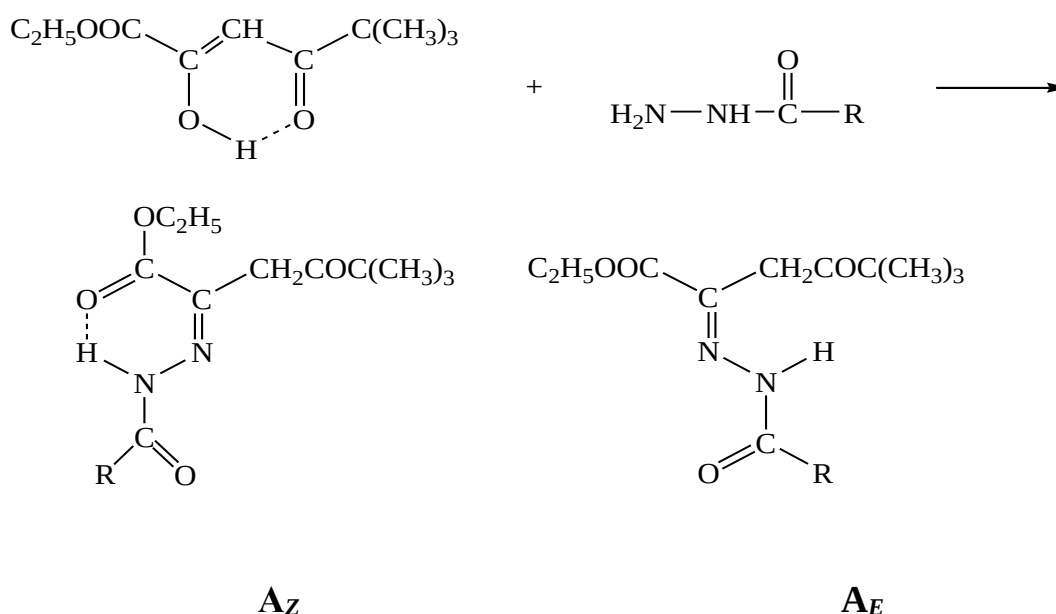
Kalit so'zlar: benzoilgidrazon, etil efir, kristall tuzilish.

Abstract. The composition and structure of benzoylhydrazone of the ethyl ester of 5,5-dimethyl-2,4-dioxohexanoic acid was established by elemental analysis, IR and PMR spectroscopy. The single crystals of the ligand obtained were studied by the X-ray diffraction method.

Key words: benzoylhydrazone, ethyl ester, crystalline structure.

In this paper, we discuss the structure of the benzoyl hydrazone of the ethyl ether of 5,5-dimethyl-2,4-dioxohexanoic acid. A mixture of hydrazone and 5-hydroxypyrazoline forms is potentially possible for it, which makes it possible to identify the relationship between the position of the ring-chain equilibrium. It is safe

to say that the resulting compound is a product of condensation over the carbonyl group adjacent to the ester group, which was established earlier. An attack on an alternative carbonyl group is not allowed by the large effective volume of the neighboring tert-butyl radical. When studying the IR spectrum of the H₂L compound in a pressed KBr tablet, a number of bands are observed in the region of valence oscillations of multiple bonds, including an absorption of about 1740 cm⁻¹ (Fig. 1). This means that the resulting H₂L compound in the solid state has a linear hydrazone (A_E) structure and the nucleophile condensation follows the carbonyl of the ester group [1-2]:



This conclusion is also confirmed by the absence of absorption bands of valence oscillations $V_{(O-H)}$ in the region ~3400-3600 cm⁻¹ and 1660 cm⁻¹, which we refer to the valence oscillations of the amide group $V_{(C=O)}$. The spectrum has an intense absorption band in the region of 1730-1750 cm⁻¹, which indicates the content of a free ketone group in the resulting reaction product. Separate absorption bands in the region of 2950 and 3030 cm⁻¹ were assigned to the valence oscillations of the $V_{(C-H)}$ CH₃- and CH - groups. In the presence of a small number of mixed configuration isomers of cyclic form in the solid state, absorption bands in the region of 3500-3600 cm⁻¹ were recorded in the IR spectrum, which are typical for the $V_{(O-H)}$ hydroxyl groups and doubling of the signals of carbonyl groups due to their steric non-equivalence. In the region of

valence oscillations of double bonds, intensive absorption bands are observed around 3200-3290, 1738-1750, 1660-1680, 1620-1630, 1535-1560, and 1260-1290 cm^{-1} .

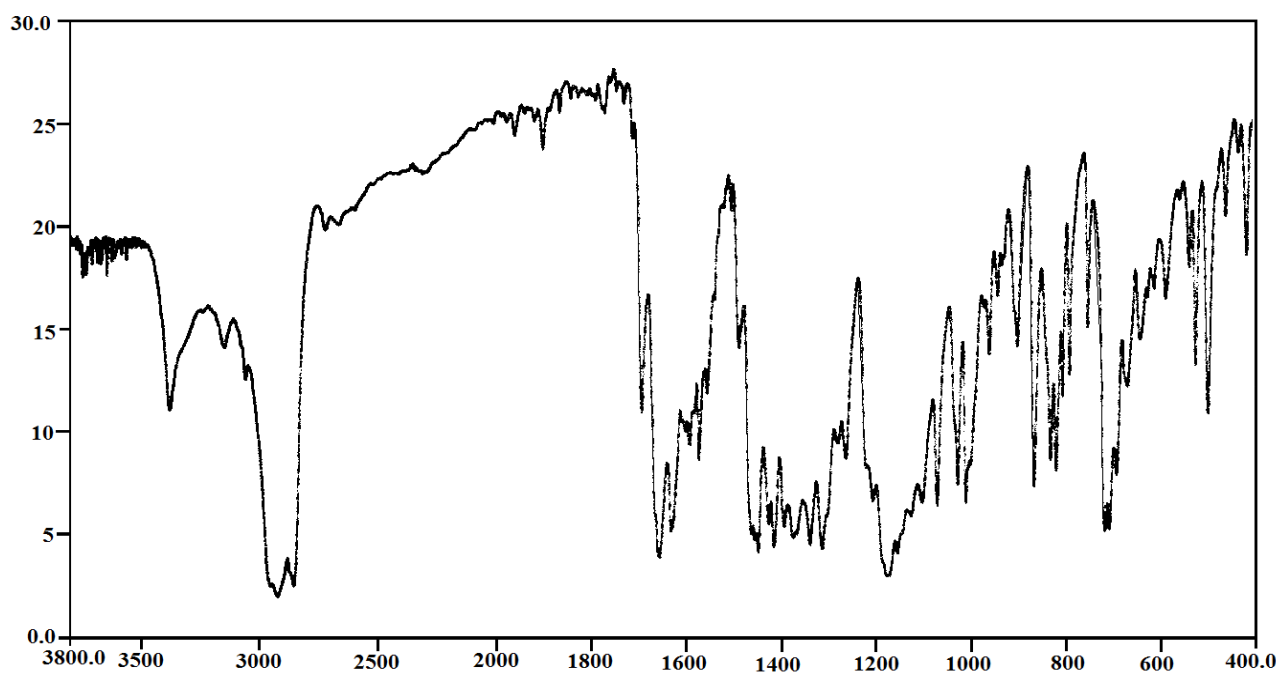


Fig. 1. IR spectrum of benzoyl hydrazone of the ethyl ether of 5,5-dimethyl-2,4-dioxohexanoic acid (H_2L).

The absorption band at 1633 cm^{-1} indicates the presence of a C=N bond, the remaining absorption bands belong to the fluctuations of the aromatic ring's half bonds and the deformation fluctuations of the NH bond. Obviously, if a tautomeric equilibrium is established, then the hydrazone form (A) remains predominant. However, IR spectroscopy does not allow us to indicate the regional direction of the condensation reaction on the carbonyl group of the adjacent $-\text{C}(\text{CH}_3)_3$ or $-\text{COOC}_2\text{H}_5$ molecule fragment β - ketoether and results are somewhat contradictory.

To unambiguously prove the inferences of IR spectroscopy about the hydrazone structure (A) of ligands, we recrystallized H_2L to grow single crystals of $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_4$ and decoded the structure using the RSA method (CCDC # 1508722). Crystals of the ligand belong to the tetragonal crystal structure. Cell parameters: $a=9.6114(10)$, $b=9.6114(10)$, $c=18.1664(6) \text{ \AA}$, $V = 1718.2(4) \text{ \AA}^3$, $Z = 2$, etc. gr. P43, $R_{\text{int}} t=0.035$.

Judging by the bond lengths, O(1)–C(7) (1,224 Å), O(2)–C(9) (1,203 Å) O(4)–C(13) (1,207 Å) N(2)–C(8) (1,290 Å) are double, although the bond length O(1)–C(7) (1,224 Å) falls somewhat out of this ensemble. This difference in the values of double bonds, in our opinion, is due to the fact that the π -bond C=O - fragment of the acyl part of the molecule is partially weakened, since it enters into π - π -conjugation with a single apomac-orbit of the aromatic nucleus. Atom C (7) has a flat-trigonal configuration (sp^2 -hybrid state), which results in a coplanar arrangement of the atoms of this fragment of the molecule in space (Fig. 2).

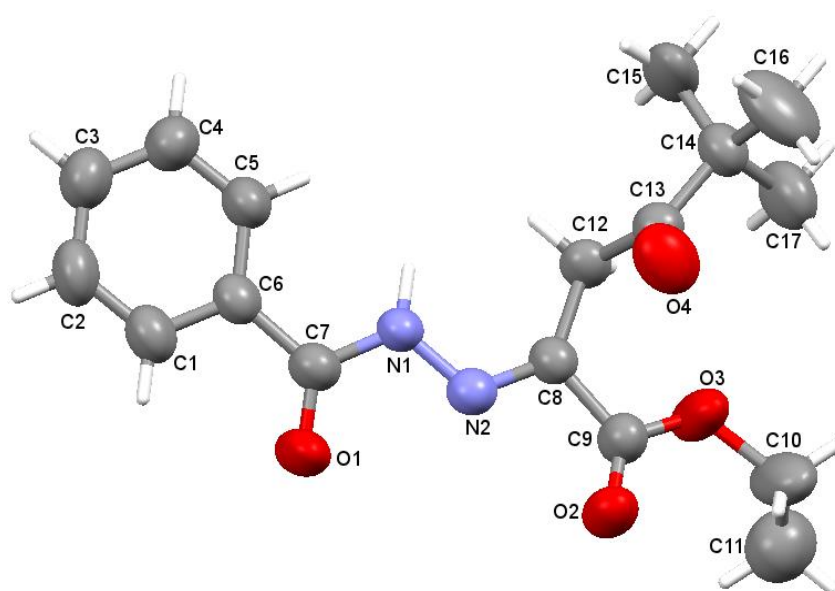


Fig. 2. Crystal structure of benzoyl hydrazone of the ethyl ether of 5,5-dimethyl-2,4-dioxohexanoic acid (H₂L).

This is clearly evidenced by the values of torsion angles N(2)–N (1) - C(7) - O (1); O (1)–C(7)–C (6)–C (5); N (1)–C(7)–C (6) - C (1) and N (2) - N(1)–C(7)–C (6) whose values are equal -3,3(8); -172,7(6); -174,5(5) and 177.3 (4)°, respectively. The same local conjugate systems are formed around the flat-trigonal atoms C (9) and C(13), which provides a coplanar arrangement of the associated atoms separately in the β -ketoester part of the molecule. As seen in Fig. 2, the ligand molecule is indeed in linear hydrazone (AE) form. The packaging of structural units in the H₂L crystal is shown in Fig. 3

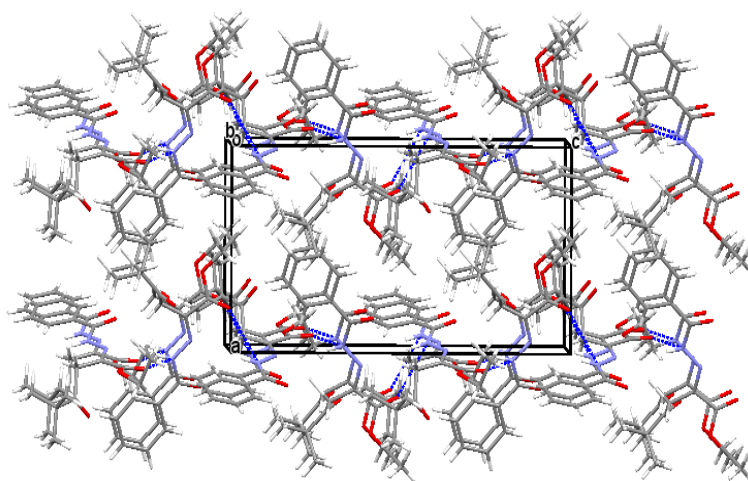


Fig. 3. Crystal packaging of H₂L molecules (projection on the ac plane).

The hydrogen atom of N–H amide fragment, molecules of the ligand participates in the formation of intermolecular hydrogen bonds N(1)–H(1)...O(2) oxygen atom and the C(12)–H(12A)...N(1), leading to the formation of centrosymmetric dimer: N(1)–H(1) 0,86, H(1)...O(2) Of 2.56, N(1)–O(2) Å 3,068, the angle N(1)H(1)O(2) 118,66°; C(12)–H(12A) of 0.97, H(12A)...N(1) of 2.56, C(12)–N(1) Of 2.92 Å, the angle C(12)H(12A)N(1) 102,22°. The molecules are arranged in a centered motif [3-7].

Thus, as a result of studies using IR spectroscopy and RSA, it was found that the ligand in the solid state is in the hydrazone (A_E) form.

In the PMR spectrum of the H₂L ligand, the AB- system signals with SWR J_{AB}=19 Hz are clearly fixed (Fig. 4) at δ 2.90 and 3.31 m. d. These signals indicate the presence of a CH₂ group in the fourth position of the pyrazoline ring (B), adjacent to the asymmetric carbon atom (C*) in the 5-position of the heterocycle.

The singlet signal from 9 protons of the C (CH₃)₃-fragment resonates at δ 1.03 m. d., the signal of the proton of the OH-function of the heterocycle associated with the 5 carbon atom is fixed at δ 6.00 m.d. the Protons of the C₂H₅ radical of the β-ketoester residue manifest as a triplet and a quadruplet at δ1.26; 3.84 m. d. with an intensity ratio of 3:2. The phenyl protons of the acyl part of the molecule were detected as a complex multiplet at δ 7.34; 7.40 and 7.91 m. d. With all this, the presence of a

signal in the PMR spectrum of the H₂L ligand from a single proton at δ 11.18 m. d. indicates the existence of a ligand in the hydrazone (AZ) tautomeric form.

The material discussed shows that in the case of benzoyl hydrazone of the ethyl ether of 5,5-dimethyl-2,4-dioxohexanoic acid, the use of such a polar solvent as DMSO-d₆ does not contribute to the appearance of the enhydrazine tautomeric form (B). The equilibrium includes geometric isomers of linear (A) and cyclic (B) forms with their spatial isomers [2].

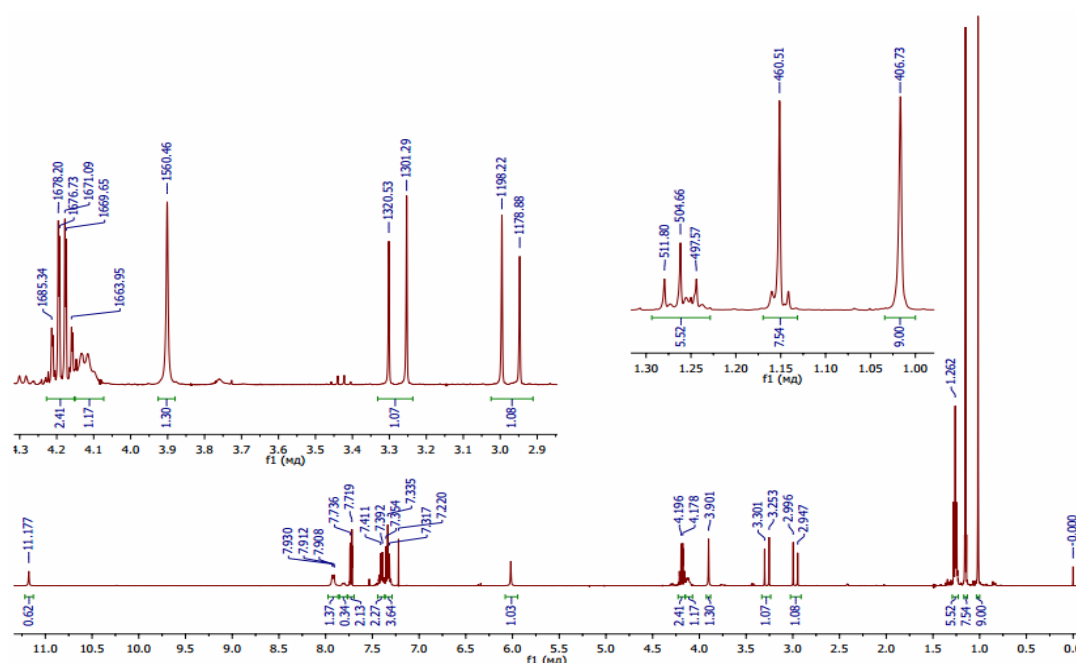


Fig. 4. PMR spectrum of benzoyl hydrazone of 5,5-dimethyl-2,4-dioxohexanoic acid (H₂L) ethyl ether in CCl₄+DMSO-d₆ solution.

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