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Article

IR and PMR Spectrum Analysis of 1-Benzoyl-3-(4 Bromophenyl)-5-Hydroxy-5-Trifluoromethyl-2 Pyrazoline Ligand

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Abstract: This study investigates the structural features of 1-benzoyl-3-(4-bromophenyl)-5-hydroxy-5-trifluoromethyl-2-pyrazoline through IR and PMR spectroscopy. While aroyltrifluoroacetylmethanes are known to exist in equilibrium between cis-enol tautomers, the exact behavior and structure of their condensation products with benzoyl hydrazine remain insufficiently explored, particularly under mild, catalyst-free conditions. Addressing this gap, the compound was synthesized via condensation in alcohol solution at room temperature, and its structure analyzed through spectral methods. IR spectroscopy confirmed functional group presence, including hydroxyl (νOH ~3400–3500 cm⁻¹), amide (νC=O ~1660 cm⁻¹), and azomethine (νC=N ~1633 cm⁻¹) functionalities, with additional signals indicative of aromatic and C–F bonds. PMR analysis showed spectral signals corresponding to the 5-oxypyrazoline form with no evidence of tautomeric transitions over time, indicating structural stability in $CDCl_3$. A quartet signal at δ 93.58 ppm in 13C NMR validated the substitution at position 5 by a trifluoromethyl group, confirming intramolecular cyclization and formation of the 5-oxypyrazoline ring. These results demonstrate that the synthesized ligand adopts a stable cyclic structure both in solid state and solution, with its configuration unambiguously supported by NMR and IR data. The findings contribute to the deeper understanding of structure–property relationships in heterocyclic ligands and offer implications for future coordination chemistry studies involving transition metals and fluorinated β-diketones.

Keywords: 1-Benzoyl-3-(4-Bromophenyl)-5-Hydroxy-5-Trifluoromethyl-2-Pyrazoline, IR and PMR Spectroscopy, Benzoyl Hydrazine

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1. Introduction

Aroyltrifluoroacetylmethanes exist in solutions as conjugated enols [1]. In the PMR spectra of these diketones that we specially recorded, in full accordance with the literature data, there are no signals that could be attributed to the diketone form [2].

According to previously performed spectroscopic studies, for these 1,3-diketones there is an equilibrium between two cis-enol structures, the mutual transition of which is carried out due to the rapid intrachelate migration of a proton from the carbon atom to the oxygen of the carbonyl group and the redistribution of bonds, and the cis-enol tautomers are present in fairly comparable quantities [3].

2. Materials and Methods

When conducting the interaction of benzoyl hydrazine with a series of aroyltrifluoroacetylmethanes $CF_3COCH_2COC_6H_4X$-4 (X=H, CH_3, CH_3O, Cl, Br, NO_2), where the substituent in the aromatic ring of the 1,3-dicarbonyl component was varied, under mild conditions (mixing alcohol solutions of reagents at room temperature (heating and the absence of any catalysts) condensation products at the aroyl carbonyl (compounds H_2L^1–H_2L^6 structure I) were obtained, the structure of which was proven by IR and NMR 1H and C spectroscopy methods.

Figure 1 describes the general structural framework of synthesized heterocyclic compounds, designated as A^1, B^1, and $B^{1'}$. Each compound features various substituent groups at the X position, including hydrogen (H), methyl (CH_3), methoxy (CH_3O), chloro (Cl), bromo (Br), and nitro (NO_2), corresponding to ligands H_2L^1 through H_2L^6. The left structure (A^1) illustrates a β-dicarbonyl-based framework; the middle structure (B^1) represents a hydrazone-type intermediate with an aryl substituent; and the right structure ($B^{1'}$) shows a pyrazoline ring substituted with trifluoromethyl and hydroxyl groups, highlighting the final product in the synthetic route. These structural representations form the basis for the IR and NMR characterization discussed in the subsequent sections.

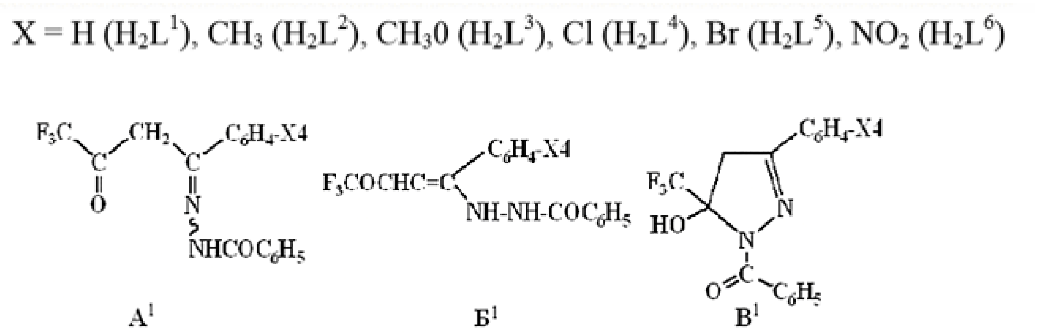

Figure 1. Spectroscopy methods

3. Results and Discussion

With an intensity of three protons, corresponding to the CH3 group of the aromatic ring of the β-dicarbonyl part of the molecule, a signal at δ 6.82 ppm with an intensity of one proton – the OH group, a set of signals in the region of δ 6.91-8.03 ppm, belonging to 9 protons of the aromatic rings, see Figure 2 and Figure 3.

Figure 2 illustrates the ^1H NMR (proton nuclear magnetic resonance) spectrum of the ligand 1-benzoyl-3-(4-bromophenyl)-5-hydroxy-5-trifluoromethyl-2-pyrazoline (H_2L^5) insolution. The spectrum displays a distinct set of signals corresponding to the various proton environments in the molecule.

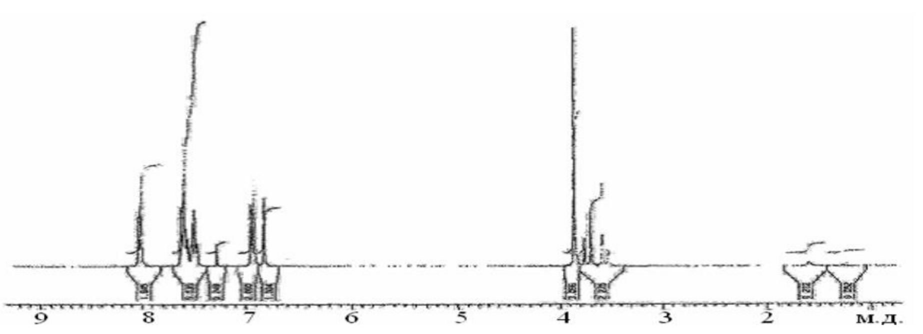

Figure 2. IR spectrum of the ligand 1-benzoyl-3-(4-bromophenyl)-5-hydroxy-5-trifluoromethyl-2-pyrazoline H2L5 structure I.

Figure 3 illustrates the IR (infrared) spectrum of the ligand 1-benzoyl-3-(4-bromophenyl)-5-hydroxy-5-trifluoromethyl-2-pyrazoline (H_2L^5), confirming the functional groups present in the molecule. The spectrum displays a broad absorption band in the 3400–3500 cm⁻¹ region, attributed to O–H stretching vibrations of the hydroxyl group located on the fifth carbon of the pyrazoline ring. Additionally, a sharp band around 1660 cm⁻¹ corresponds to C=O stretching vibrations from the amide (hydrazone) fragment.

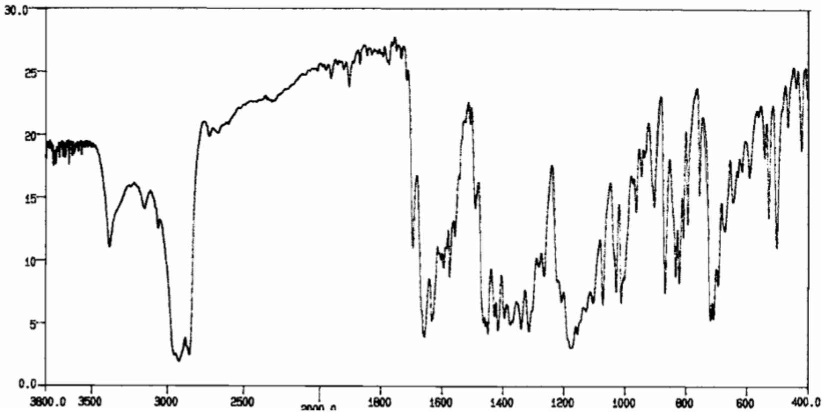

Figure 3. 9 protons of the aromatic rings.

This conclusion is also confirmed by the absorption bands ν(O–H) in the region of ~3400–3500 cm–1 and 1660 cm–1, which we attributed to the stretching vibrations of the hydroxyl group associated with the fifth carbon atom of the heterocyclic pyrazoline ring in the H2L5 molecule of structure (I) and the amide fragment ν(C=O) of the hydrazone part of the molecule [4], [5].

In the IR spectra of the type I ligands under consideration, in the region of stretching vibrations of multiple bonds, intense absorption bands were recorded at 1633, 1594, 1574, 1558, and 1490 cm–1. The absorption band at 1633 cm–1 indicates the presence of the C=N bond, while the remaining absorption bands belong to vibrations of the one-and-a-half bonds of the aromatic ring and deformation vibrations of the NH bond [6].

The spectrum in Figure 3 also contains absorption bands characteristic of C–F–bonds. Bands of medium and strong intensity at 1238–1277, 1119–1131 and 1039–1059 cm–1 have been assigned by us to νs and νas of the C–F–bond. Bands of medium intensity at 755 cm–1 correspond to fan vibrations, weak absorption bands at 528 cm–1 are caused by deformation vibrations, and 541 cm–1 is due to torsional vibrations of these bonds [7], [8].

The IR spectra of the remaining compounds of type I largely coincide with the IR spectrum of H2L1, with a small difference. However, IR spectroscopy does not allow us to indicate the regional direction of the condensation reaction at the carbonyl group adjacent to the –CF3 or –C6H4X-4 fragment, and the results are somewhat contradictory [9], [10], [11].

In order to unambiguously prove the conclusions about the structure of the obtained ligands in the solid state and in solutions, we recorded the PMR spectra of these compounds immediately after preparing the solutions and after some time [12].

For example, in the PMR spectrum of a solution of the compound H2L3 in CDCl3, taken immediately after preparation and reflecting the structure of the substance in the solid state, a set of signals corresponding to the 5-hydroxypyrazoline structure is observed.

Two asymmetric doublets with a total intensity of two protons, at δ 3.57 and 3.73 ppm and with a spin-spin interaction constant (SSIC) of 20 Hz, belonging to the methylene group of the ring, a singlet signal at δ 3.87 ppm [13].

Study of the IR spectrum of the compound H2L5 in a pressed KBr tablet, in the region of stretching vibrations of multiple bonds a number of bands are observed, including absorption at about 1730 cm–1, see Figure 3. This means that the obtained compound H2L5 in the solid state has a cyclic 5-oxypyrazoline structure and the condensation of the nucleophile occurs at the carbonyl of the aroyl group [14].

Figure 4 illustrates the ^{1}H NMR spectrum of 1-benzoyl-3-(4-methoxyphenyl)-5-hydroxy-5-trifluoromethyl-2-pyrazoline (H_2L^3) in $CDCl_3$ solution, highlighting the proton environments within the molecule. The spectrum shows multiple distinct peaks, including aromatic proton signals in the region of δ 6.5–8.5 ppm, as well as characteristic signals corresponding to the methylene and methoxy groups of the molecule.

Notably, the spectrum remains unchanged over time, which indicates the absence of tautomeric transitions to hydrazone (A1) or enehydrazine (B1) forms. This stability suggests a fixed 5-oxypyrazoline ring structure in solution.

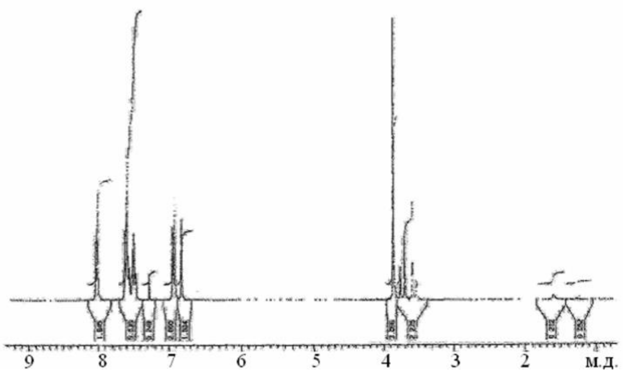

Figure 4. NMR spectrum of 1-benzoyl-3-(4-methoxyphenyl)-5-hydroxy-5-trifluoromethyl-2-pyrazoline (H2L3) structure I in CDCl3 solution.

The appearance of the spectrum does not change over time, indicating the absence of possible tautomeric transitions to the hydrazone A1 or enehydrazine B1 forms [15].

These data, of course, do not allow us to conclude that we are dealing with a condensation product precisely at the aroyl carbonyl. This conclusion follows from examining the 13C NMR spectrum. The most characteristic feature of it is the presence of a quartet signal at δ 93.58 ppm (SSCC 32 Hz).

It belongs to the carbon atom in position 5 of the ring, the cleavage is due to the interaction with the adjacent trifluoromethyl group [12]. The signal of the carbon of the methoxy group of the aromatic ring is recorded at δ 153.36 ppm, the C=N bond at δ 162.33 ppm, and the C=O bond at δ 171.36 ppm. Parameters of the NMR spectra of 1-benzoyl-3-aryl-5-hydroxy-5-trifluoromethyl-2-pyrazolines (I), in CDCl3 solution (δ, ppm) [13].

Table 1 illustrates the ^{1}H NMR spectral parameters of a series of 1-benzoyl-3-aryl-5-hydroxy-5-trifluoromethyl-2-pyrazoline ligands (H_2L^1–H_2L^6), each featuring different substituents (X) on the aryl ring. The table provides chemical shift data (in ppm) for the following proton environments:

a. CH_2 group within the pyrazoline ring (appearing as two doublets),
b. OH proton attached at position 5 of the ring,
c. C_6H_5 aromatic ring protons,
d. and the X substituent where applicable.

Table 1. Parameters of the NMR spectra of 1-benzoyl-3-aryl-5-hydroxy-5-trifluoromethyl-2-pyrazolines.

Соединение	X	**CH_2***	**OH**	C_6**H_5**	X
H_2L^1	H	3.59; 3.73	6.72	7,45м;7,55м;7,96м	–
H_2L^2	CH_3	3.57; 3.75	6,77	7,25м;7,56м;8,02м	2,44
H_2L^3	OCH_3	3.57; 3.73	6.82	6,91м; 8,03м	3,87
H_2L^4	Cl	3,58;3,76	6.72	7,45м; 8,01м	–
H_2L^5	Br	3,56; 3,75	6,74	7,50м; 7,95м	–
H_2L^6	NO_2	3.61; 3.80	6.60	7,48м;7,63м;8,05м	–

4. Conclusion

a. Using the PMR spectroscopy method, it was established that the synthesized organic ligands based on aroyltrifluoroacetylmethanes in the crystalline state and in CDCl3 solution are in the 5-oxypyrazoline form, and in DMSO-d6 solution the cyclic form is in equilibrium with the linear hydrazone form.

b. The presence of aroyltrifluoroacetylmethanes in the enol state in solution was determined by the results of their PMR spectrum.

c. These ligands are 5-oxypyrazoline in the solid state, when the nucleophilic condensation of the aroyl carbonyl is studied by IR spectroscopy.

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