

Tautomeric Equilibrium Among the Derivatives of Benzoyl Vinegar Aldehydes

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Annotation: In this work, using modern physicochemical research methods, the interaction of various amino acid solutions with the Cu(II) ion, the structure and properties of the resulting complex compounds were studied. The influence of the environment on the formation of pure and mixed ligand complexes from various obtained amino acids and the constants of stability and instability were determined.

Keywords: amino acid, 2-aminobutanedicarboxylic acid, thermal analysis, thermal stability, thermolysis, infrared spectroscopy, Mossbauer spectroscopy, frequency of symmetric and asymmetric vibrations, stretching vibrations.

Introduction

The synthesis of derivatives of ketoaldehydes with nucleophilic reagents, the presence in solution and solid state of ring-chain tautomer forms in the form of hydrazone, jenhydrazine and ring oxypyrazole, the formation of complex compounds with various metals is of great interest to scientists. Because these substances are widely used as biocatalysts, drugs in medicine, as biologically active substances in agriculture.

The results of the study show that a series of different equilibria can be found among the acylhydrazones of β -ketoaldehydes (Table 1), which are: double-ring-chain between the ring (B) and hydrazone (A) or hydhydrazine (B) forms. equilibrium, tertiary ring-chain equilibrium, tautomeric equilibrium between linear (A) and (B) forms, Z, E-configuration equilibrium within the hydhydrazine form, conformational equilibrium relative to the amide bond in the hydrazone form, and so on. In solutions of some compounds, up to 5 interlocking structures can be found. Such equilibria were made in the presence of only one substitute and in the presence of only three solvents.

Material and Methods

According to previous studies, the condensation products of ketoaldehydes with aromatic acid hydrazides exhibit a ring-chain equilibrium in which the ring 5-hydroxypyrazoline form is present in addition to the hydrazone or hydhydrazine forms. In contrast to the products of condensation of benzoyl acetaldehyde with aliphatic acid acylhydrazones, solutions of condensation products of benzoyl acetaldehyde with interchangeable aroilhydrazides ($H_2L^1-H^2L^4$) are also linear: E-hydrazone (EZ-hydrazone and AE)) forms predominate. This is evidenced by the parameters of the spectra YaMR- 1H (Table 1).

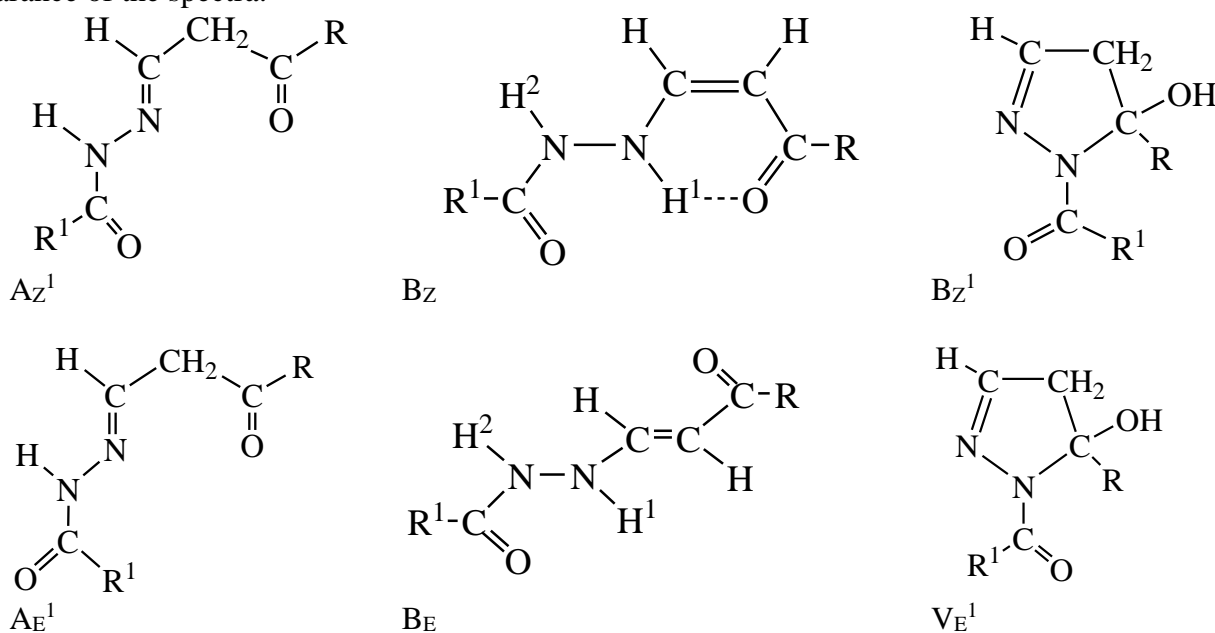
Table 1

Room temperature of benzoyl acetaldehyde ($H_2L^1 - H_2L^4$) aroilhydrazones and YaMR- 1H spectrum obtained in $CCl_4 + DMSO-d_6$ solution

Compounds	R	NH ¹	NH ²	HC-N	HC-C	C ₆ H ₅	R protons	
							X	C ₆ H ₄
H ₂ L ¹	C ₆ H ₅	10,03	9,41	5,72	6,04	7,42; 7,52; 7,81	7,03; 7,33; 7,93	
H ₂ L ²	<i>p</i> -CH ₃ C ₆ H ₄	10,12	9,45	5,82	6,11	7,34; 7,67; 8,03	2,44	7,09; 7,52
H ₂ L ³	-CH ₃ OC ₆ H ₄	11,14	9,41	5,76	6,01	7,23; 7,76; 7,91	3,08	6,92; 7,36;

H ₂ L ⁴	HOC ₆ H ₄	10,13	9,47	5,72	6,04	7,24; 7,59; 7,90	12,65	7,24; 8,07
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For example, the H₂L¹ ligand is present in the form of a BE-configured nebula. The enhydrazine form of these compounds is in the strong field region of the NMR-¹H spectra (d 6.04 m.h., SSTK J = 12-12.5 Gs) and in the relatively weak field region (d =5.72 m.h., SSTK J = 7.0-8.0 Gs) is characterized by two doublet signals, which indicate the presence of the form Z- enhydrazine (BZ) along with the BE-configuration. For H₂L² and H₂L⁴ compounds, the appearance of the YaMR-¹H spectra is slightly different from that of the H₂L¹ spectrum, as the signal of the para-CH₃- and meta-CH₃O substituent protons in the phenyl ring of the hydrazide part is observed. The signal of the protons of these two substituents differs in that the protons of the CH₃-group in the benzene ring of the hydrazide part of the H₂L² ligand molecule are d =2.44 mH, and the protons of the CH₃O-group in the meta-state of the benzene ring of the H₂L³ ligand are d =3.08. gives a signal in m.h. because it is bound to an oxygen atom. It should be noted that in the ketoaldehyde fragment of H₂L¹ – H₂L⁴ compounds, the signals of the terminal phenol substituent protons are obscured by the signals of the protons of the aryl fragment of the hydrazide part of the molecule in all three spectra of YaMR-¹H, complicating the appearance of the spectra.



Conclusion

Thus, the spectral data show that by changing the structure of the ketoaldehyde part of the molecule, the nature of the solvent, it is possible to achieve different tautomeric equilibria along with the β-ketoaldehydes acylhydrazones. Some of them are complex and can store 5, sometimes 6 tautomeric, configurational and conformational forms that rotate with each other.

Regardless of the equilibrium type, the ring (B) form does not exist at all for the H₂L¹ – H₂L³ derivatives of the exchanged aroilhydrazones and is not recorded in the YaMR-¹H spectra; in solids and solutions, they are mainly present in the form of Z, E-hydhydrazine tautomer (BZ and BE).

To confirm the IR spectroscopic conclusions about the linear structure of the obtained ligands, C₁₇H₁₆N₂O₄ single crystals have been recrystallized by recrystallization of the H₂L₂ ligand and the structure of the crystal was determined by the RSA method. The crystals of the ligand belong to the triclin syngonium and have the following parameters of the elemental cell: a = 15.6942 (13), b = 12.1515 (11), c = 8.0046 (10), α = 90, β = 99.853 (9), γ = 90°, V = 1504.0 (3) Å³, Z = 4, pr.gr. R21 / s. X-ray diffraction analysis was performed on an Xcalibur, Oxford Diffraction automatic diffractometer (λ = 1.5418 Å, CuKα radiation, graphite monochromator, θ-scan, θmax = 75.8°, θmin = 4.6°). The structure of the association was discovered directly by the SHELXS-97 program, and the MNC was determined using the SHELXL-97 program.

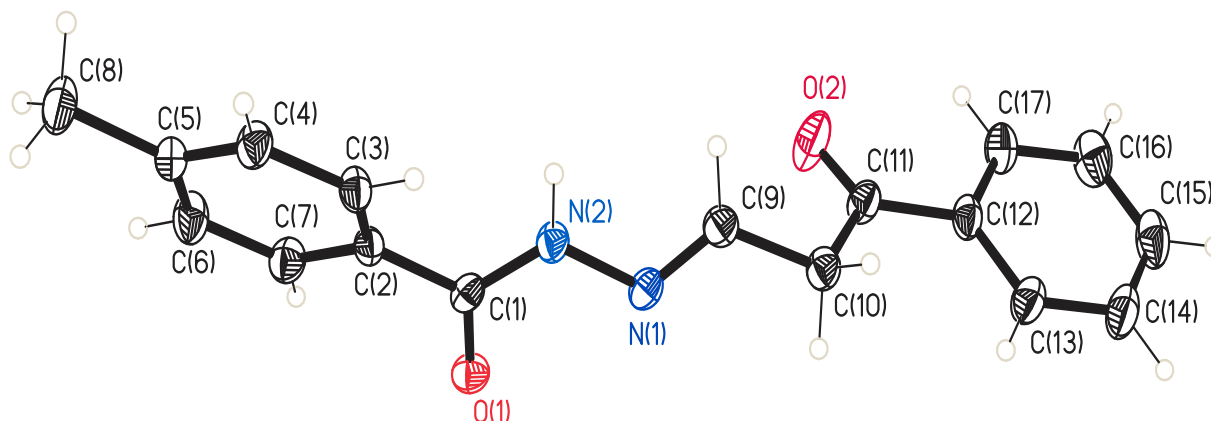


Figure 1. Crystal structure and appearance of hydrogen bonds of 3-phenyl-3-oxopropion aldehyde p-methylbenzene hydrazone (H_2L^8)

O (1) - C (1) (1,230 Å), O (2) - C (11) (1,207 Å), H (1) - C (9) (1,249 Å) depend on the length of the bonds, although they N (2) - C (1) (1,354 Å) are twins, although the length of the bond differs from the rest. This difference in the value of the double bond is explained in our view by the fact that the p-bond in the C = O aldehyde fragment enters the π - π -bond bond with the single π -orbital of the aromatic ring. The C (1) atom has a flat-trigonal configuration (sp^2 -hybrid case), which results in the coplanar arrangement of atoms in space. N (1) N (2) C with values of 173.4 (4)°, -4.3 (6)°, 179.8 (4)°, 177.9 (5)°, respectively. (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 magnitudes of the torsional angles also testify. A similar localized coupling system is formed around the flat-trigonal C (9) atom, which provides the coplanar arrangement of the atoms bound to it in the β -ketoether part of the molecule. Figure 1 shows that the H_2L^2 ligand molecule actually exists in the form of a linear hydrazone (AE). The location of the structural units in the H_2L^2 crystal is shown in Figure 1.

Thus, IR spectroscopy and RSA studies revealed that the ligands are present in the solid state in the form of hydrazone (AE).

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