Pioneer: Journal of Advanced Research and Scientific Progress
ISSN: 2751-7551
Volume 04 Number 02 (2025)
https://www.innosci.org/jarsp

Article

"Diketone - Enol" and "Enol - Enol" Tautomerism in Polyfluoroacyl Cycloalkanone Organic Compounds

Kuchkorova Raino Rasulovna*[1], Iskandarov Aybek Yuldashevich[2]

1. Candidate of Chemical Sciences, Associate Professor
2. Tashkent State Pedagogical University named after Nizami

* Correspondence: rano.qochqorova@bk.ru

Abstract: The research investigates tautomers of polyfluoroacyl cycloalkanone structures while exploring how fluorine groups and cyclic ring systems affect their enol and diketone tautomerism. The research field of linear β-diketones has been thoroughly studied but investigational work on fluorinated cyclic analogs stays poorly understood. The analysis of tautomeric equilibria occurred through ^1H and ^{13}C NMR and IR spectroscopy techniques which evaluated solvents such as $CDCl_3$, CCl_4, DMFA-d_7. Computer modeling through MINDO/3, MNDO/H, AM1, RMZ and Sybyl provided structural support. Results show that majority of 2-polyfluoroacyl cycloalkanones exist mainly as enols through strong intramolecular hydrogen bonding but 2-perfluorohexanoylcyclododecanone favors the diketone form because of its macrocyclic effects. IR spectral examinations demonstrated simultaneous existence of tautomers as well as chemical shift data supported electronic modifications from the CF_3 groups. The research discoveries create vital knowledge for understanding fluorinated systems that are utilized in drug design and catalysis applications and material science developments. The investigation of dynamic tautomerism requires more research to be done under physiological conditions while expanding studies to include metal-complexed derivatives and heterocyclic systems.

Keywords: Diketone-enol, Enol-enol, NMR, CCl4, CDCl3, and DMFA-d7, CF3 Groups, Cis-enol, Trans-enol, 1,3-diketones

Citation: Rasulovna, K. R., Yuldashevich, I. A, "Diketone - Enol" and "Enol - Enol" Tautomerism in Polyfluoroacyl Cycloalkanone Organic Compounds. Pioneer: Journal of Advanced Research and Scientific Progress 2025, 4(2), 77-80.

Received: 25th Mar 2025
Revised: 30th Mar 2025
Accepted: 7th Apr 2025
Published: 15th Apr 2025

1. Introduction

Diketone-enol tautomerism is a slow process on the NMR time scale. For 2-polyfluoroacylcycloalkanones, as well as for linear polyfluorinated 1,3-diketones, the tautomeric diketone-enol equilibrium is strongly shifted towards the enol form, both for pure compounds and for solutions in CCl4, CDCl3, and DMFA-d7 [1], [2].

This is confirmed by the presence in the NMR1H spectra of the enol hydroxy group proton signal in the range of δ 11.4-16.3 ppm, while the signal of the diketoform methyl proton is recorded in the range of δ 3.7-4.8 ppm. Either it cannot be detected at all, or its intensity is low [3].

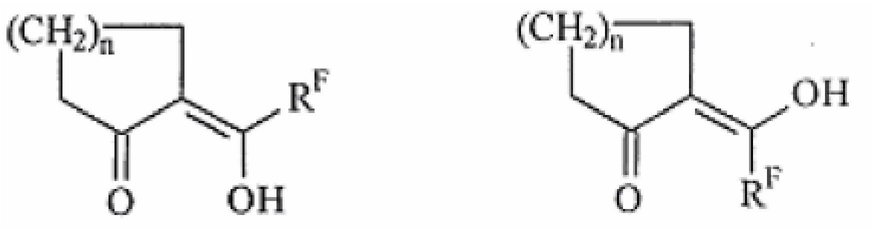
It is known that the introduction of an alkyl substituent into the second position of a linear 1,3-dicarbonyl system shifts the equilibrium towards the diketo-tautomer. Thus, 2-polyfluoroacyl cycloalkanones with ordinary carbocycles can be considered as 2-alkyl substituted 1,3-diketones only in a very rough approximation. At the same time, according to 1H NMR data, 2-perfluorohexanoyl cyclododecanone exists in CDCl3 by 90% as a diketoform [4], [5], [6].

Apparently, in this case, the conformational features of the macrocycle no longer have a noticeable effect on the state of tautomeric equilibrium [7]. Non-fluorinated 2-

alkanoyl cycloalkanones also exist mainly in the form of an enol. Thus, the enol content in 2-acetylcyclopentanone and -hexanone is 95-100%. 2-acetylcycloheptanone and -octanone are enolized by 70% or 95%, respectively [8], [9], [10].

For the tautomeric form of B, cis-trans isomerism is possible with respect to for the tautomeric form of VI B, cis-trans isomerism is possible with respect to Figure 1.

This Figure 1 describes the phenomenon of cis-trans isomerism in the enol forms of a β-dicarbonyl compound. The structures illustrate two possible geometric isomers—cis-enol and trans-enol—resulting from the relative positioning of the hydroxyl group (-OH) and the substituent group (R^F) across the double bond. In the cis-enol form (left), both functional groups are on the same side of the double bond, whereas in the trans-enol form (right), they are positioned on opposite sides. This type of stereoisomerism occurs due to restricted rotation around the C=C bond and plays a critical role in the stability and reactivity of tautomeric systems.



Cis-enol **trans -enol**

Figure 1. Cis-Trans Isomerism.

2. Materials and Methods

The studies on tautomeric behavior in 2-polyfluoroacyl cycloalkanones made use of spectroscopic analysis alongside quantum chemical models. Various tautomeric equilibria of pure compounds and their solutions in three different deuterated solvents - $CDCl_3$, CCl_4, and DMFA-d_7 were analyzed. Chemical shift changes between δ 11.4–16.3 ppm in the enol hydroxyl region together with δ 3.7–4.8 ppm changes in the diketone form methyl protons helped analyze the tautomer equilibrium distribution using proton nuclear magnetic resonance (^1H NMR) spectroscopy. The ^{13}C NMR spectroscopic examinations delivered clear understanding about carbonyl environments which were strongly affected by both ring size variation and CF_3 group placement. IR spectroscopy revealed functional group vibrations through broad OH absorption bands and C=O and C=C–C=O characteristic signals which proved both tautomeric forms were present in the studied compounds. The experimental data received support through quantum mechanical calculations executed using the MINDO/3, MNDO/H, AM1, RMZ semi-empirical methods together with molecular mechanics calculations from the Sybyl program. Quantum mechanical calculations through MINDO/3, MNDO/H, AM1, RMZ and Sybyl examined how enol and diketone forms compare in stability within cyclopentanone and cyclohexanone systematics while showing how tension and electronic factors influence the enol–keto tautomerism equilibrium.

3. Results

The most probable form, as for linear polyfluorinated 1,3-diketones, is the cis-enol form, since it can be stabilized by two OH–H type BMVS at once.···OH and OH–H···F. Such a VMVS should shift the enol OH proton signal in the NMR spectrum into a weak field, which is observed in practice [11], [12], [13]. The results of IR spectroscopic studies confirm the fact of the coexistence of diketone and enol forms in 2-polyfluorinated cycloalkanones. In the spectra recorded for pure compounds, solutions in CDCl3 and KBr tablets, a wide absorption band was found in the range of 2300-3500 cm-1, corresponding to fluctuations of the hydroxysi group bound by VMVS. In addition, bands attributed to the vibrations of the v(C = C - C = O) system were found in the region of 1560-1700 cm–1 , and bands of low intensity isolated waves were found in the region of 1670-1780 cm-1 carbonyl groups of the diketoform [14]. By now, it is generally accepted that the enol tautomer of 1,3-diketones is not an average pseudoaromatic structure with an enol OH proton located symmetrically between two oxygen atoms, but an equilibrium mixture of two enol forms A and B. CF3 groups affect different types of electronic environment In this case, the magnitude of the chemical shift of the carbon core of the carbonyl group of polyfluoroacil also indicates. If for the cyclopentanone derivative, the named signal was detected at δ 161.0 ppm, then for 1,3-diketones with a large alicycle size – at δ 170.0-174.3 ppm [15].

4. Discussion

Laboratory results verify that enol tautomers control the chemical structure of most 2-polyfluoroacyl cycloalkanone compounds yet exceptions exist when studying the macrocyclic 2-perfluorohexanoylcyclododecanone since this compound exists primarily in its diketo form. The research results contribute significantly to the study of tautomeric equilibria in fluorinated cyclic diketones because this field lacks extensive exploration despite its importance in organic synthesis and pharmaceutical applications. The united application of NMR, IR spectroscopy and quantum mechanical modeling forms a reliable system to estimate tautomeric reactions within similar chemical substances.

The dynamic behavior of tautomers remains unclear for both physiological conditions and complex reaction environments because these systems exhibit different solvent conditions than inert solutions. Scientists need to conduct comprehensive theoretical investigations regarding how the stereoelectronic properties of different fluorinated substitutions affect cyclic systems. New investigations should analyze tautomerization rates together with the effects that solvent environment and pH and temperature conditions have on tautomeric equilibrium distribution. The development of fluorinated drug candidates with controlled tautomeric forms represents a practical application that improves drug availability and binding specificity to receptors. This analysis should be extended to heterocyclic analogs and metal-complexed derivatives to discover new ways for controlling tautomerism in catalytic applications and material science. Greater knowledge about these systems will produce substantial advancements in structural organic chemistry alongside molecular design.

5. Conclusion

Quantum mechanical calculations of the structure of 2-trifluoroacetylcyclopentanone and -hexanone were carried out using semi-empirical methods (MINDO/3, MNDO/H, AMI, and RMZ) and molecular mechanics (Sybyl program). It was found that the exo-enol form is the most stable in cyclopentanone derivatives, whereas for 2-acyl substituted cyclohexanones, both enol forms are comparable in stability. The greater stability of the exo-enol form for acylcyclopentanones (two exocyclic double bonds) and the endo-enol form for acylcyclohexanones (no exocyclic double bonds) can be explained by conformational effects associated with different stresses of five- and six-membered alicycles.

REFERENCES

[1] R. R. Kuchkorova, “IK-i PMR–Spektr-Analiz 1-Benzoil-3-(4-Bromfenil)-5-Gidroksi-5-Triftormetil-2-Pirazolinovogo Liganda,” in *Int. Sci. Res. Conf.*, vol. 3, no. 32, pp. 8–14, Mar. 2025.

[2] B. Umarov and R. Kuchkorova, “Complex Nickel (II) Compounds Based on Acylhydrazones of Aroyltrifluoracetylmethanes,” *Science and Innovation*, vol. 2, no. A12, pp. 236–241, 2023.

[3] B. F. Kurbonov, B. B. Umarov, and N. A. Parpiyev, “Spektroskopicheskoye issledovaniye kompleksov Ni(II), Zn(II), Co(II) s gidrazonami monokarbonilnykh soyedineniy,” *Uzb. Khim. Zhurnal*, no. 3, pp. 3–6, 1996.

[4] Sh. Z. Kadirova and R. R. Kuchkarova, “Preparation of Aliphatic and Aromatic 1,3-Diketones with Polyfluoroalkyl Substitutes,” *Eur. Chem. Bull.*, no. 7, 2023.

[5] R. R. Kuchkarova, “Kompleksnye soyedineniya na osnove asilgidrazonov 1-(2-tenoil)-3,3,3-triftorasetona,” Nov. 2022.

[6] R. R. Kuchkarova, “Kompleksnye soyedineniya proizvodnykh ftorirovannykh β-diketonov s perekhodnymi metallami,” unpublished.

[7] U. B. Bafoevich, R. K. Rasulovna, and K. S. Ziyodulloevna, “Reaction of 1,1,1-Trifluoromethyl-4-Phenylbutanedione-2,4 with Benzoic Acid Hydrazide,” *Inf. Technol. Ind.*, vol. 9, no. 3, pp. 939–944, 2021.

[8] R. R. Kuchkarova, “Kompleksnye soyedineniya sinka(II) na osnove asilgidrazonov 1-(tenoil)-3,3,3-triftorasetona,” *Qo‘qon Davlat Ped. Inst. Ilmiy Xabarlari*, no. 4, pp. 532–539, 2024.

[9] R. R. Kuchkorova, “Complex Nickel(II) Compounds Based on Acylhydrazones of Aroyltrifluoracetylmethanes,” *Science and Innovation Int. Sci. J.*, pp. 236–241, 2023.

[10] R. R. Kuchkorova, “Kolchato-syepnykh peregruppirovkakh ligandov pri kompleksoobrazovanii s ionami perekhodnykh metallov,” *Tafakkur Ziyosi*, no. 1, pp. 158–161, 2024.

[11] B. B. Umarov, *Kompleksnye soyedineniya nekotorykh perekhodnykh metallov s bis-5-oksipirazolinami*, Dr. Sci. diss., Institute of Chemistry, Academy of Sciences of the Republic of Uzbekistan, Tashkent, 1996.

[12] R. R. Kuchkarova, “Asilgidrazony 1-(2-tenoil)-3,3,3-triftorasetona,” *Ta’lim, Fan va Innovatsiya*, no. 1, pp. 39–42, 2024.

[13] R. R. Kuchkorova, B. B. Umarov, and Sh. Z. Kadirova, “Preparation of Aliphatic and Aromatic 1,3-Diketones with Polyfluoroalkyl Substitute,” *Eur. Chem. Bull.*, vol. 12, no. 7, pp. 303–307, 2023.

[14] B. B. Umarov, *Kompleksnye soyedineniya nekotorykh perekhodnykh metallov s bis-5-oksipirazolinami*, Dr. Sci. diss., Institute of Chemistry, Academy of Sciences of the Republic of Uzbekistan, Tashkent, 1996.

[15] R. R. Kuchkorova, B. B. Umarov, and Sh. Z. Kadirova, “Preparation of Aliphatic and Aromatic 1,3-Diketones with Polyfluoroalkyl Substitute,” *Eur. Chem. Bull.*, vol. 12, no. 7, pp. 303–307, 2023.