

# Study of the dehydroacetic acid homolog by IR, Raman spectroscopy, and DFT

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## Research Article

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# Abstract

The IR and Raman spectra of 3-(3,3-Dimethylbutanoyl)-4-hydroxy-6-neopentyl-2H-pyran-2-one (**1**) in the crystalline state have been studied. The tautomerization of **1** was carried out by a quantum-chemical method at the DFT/B3LYP/6-311G\*\* level. The experimental IR and Raman spectra of compound **1** are reproduced by calculations for the 4-hydroxy enol tautomer (*A*). The classification of the bands in the experimental vibrational spectra of **1** has been carried out. The intramolecular H-bond was characterized by IR spectroscopy. The free energies of the tautomers and their populations were calculated for two different solvents.

HOMO and LUMO of molecule **1** are located on the pyran ring. During tautomeric transformations, there is a significant delocalization of charge and a change in the reactivity of the molecule.

The reactivity of the pyrone **1** was characterized using descriptors. The enol form *B* was found to have higher ionization energy, electron affinity, chemical potential, and electrophilic index than the enol *A* form. The dipole moment is higher for form *A*, and the softness of the two molecules is the same.

## Introduction

The study of dehydroacetic acid (DHA) derivatives is interesting and important because they are used in the pharmaceutical, cosmetic and food industries [1 – 5]. DHA and its derivatives are biologically active substances and are used for the manufacture of analgesics, anti-cancer drugs, and to fight against HIV [1 – 5]. DHA is the initial reagent in the synthesis of many organic compounds [1 – 5]. Studies on NMR spectra have shown that among the five tautomeric forms of the acid, two enolic forms predominate [6, 7]. The IR and NMR spectra of DHA and its cinnamoyl derivatives have been studied [8 – 11].

Our work characterized the two low-energy tautomeric forms of the DHA homolog 3-(3,3-dimethylbutanoyl)-4-hydroxy-6-neopentyl-2H-pyran-2-one (**1**) using the methods of IR and Raman spectroscopy and quantum chemistry. The choice of compound **1** is linked to the tautomerism of the central structural fragment of pyrandione, which can modify certain features characteristic of the functional groups. The enamine derivative of synthesized pyrone **1** has an inhibitory activity against the human carcinoma cell line HeLa and the herpes virus VPG. We tried following the evolution of the acid structure, the strength of the H-bond, and its vibrational spectra during tautomeric transformations. The comparison of the free energies of the tautomers makes it possible to estimate their population.

It is interesting to follow the evolution of the geometry, the electronic structure, and the spectra of pyrone **1** during tautomeric transformations. It is important to determine the active sites of the molecule for nucleophilic and electrophilic attacks. The calculation of the charges on the acid atoms made it possible to estimate the capacity of the atoms to form hydrogen bonds and attract ions and metal atoms. The electrophilicity index characterizes the biological activity of compound **1**.

## Experimental

The neopentyl derivative of dehydroacetic acid 3-(3,3-dimethylbutanoyl)-4-hydroxy-6-neopentyl-2H-pyran-2-one (**1**) has been obtained by  $\text{CF}_3\text{SO}_3\text{H}/(\text{CF}_3\text{CO})_2\text{O}$  activated acylation of carboxylic acids according to [12]. The white product has the crystalline powder form (melting point 77 – 78° C). Compound **1** can exist in two tautomeric enol forms, *A* and *B* (Fig. 1).

IR spectra were recorded by accumulating 64 scans in the region of 4000–400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . A Bruker Vector 22 spectrometer was used. The samples were compressed into KBr pellets.

Raman spectra of the acid were recorded in the 3500-50  $\text{cm}^{-1}$  region via the FTIR spectrometer VERTEX 70 and the Bruker FT-Raman RAM II module. The 1064 nm excitation line provided by an Nd: YAG laser with a power of 50 mW was used.

## Computational Methods

The calculation of the vibrational spectra of compound **1** was carried out with the functional B3LYP [13, 14] and the basis set 6-311G\*\*. The calculations were performed using the Gaussian09 program [15]. As a first approximation, we took the experimental coordinates of the atoms obtained using the X-ray diffraction method (Supplementary information S1). Standard optimization methods were used to find minima on the potential surface. Full geometry optimization was performed without any restrictions. The Hessian analysis made it possible to determine the minima of potential energy.

Optimized geometrical parameters of the tautomers were used to calculate the harmonic vibration frequencies. Theoretical structural and spectral data were obtained for both tautomers at 298 K, 1 atm. The potential energy distribution was calculated to attribute the vibrations [16]. Calculated frequencies were scaled using a multiplier of 0.96. The theoretical spectral curves were constructed, taking the Lorentz band shape and a half-width of 10  $\text{cm}^{-1}$ .

The calculation of natural bonding orbitals (NBO) has been performed to characterize the electronic properties of molecules [17]. The chemical potential, hardness, softness, and electrophilicity index are related to the first vertical ionization energy and electron affinity by the following formulas  $\mu \approx -(IE + EA)/2$ ,  $\eta \approx (IE - EA)$ ,  $S = 1/\eta$ , and  $\omega = \mu^2/2\eta$  [18]. The Fukui functions for nucleophilic and electrophilic attacks were calculated using the natural atomic charges on atoms  $q_k$  and the number of electrons  $N$  in a molecule. The local softness of atoms has also been calculated:  $s_k^+ = Sf_k^+$ ,  $s_k^- = Sf_k^-$  [18].

Knowing the difference in free energies of the tautomers, one can calculate their populations at 298.15 K

$$p = \frac{\exp(-\Delta G_i / RT)}{\sum_j \exp(-\Delta G_j / RT)}$$

. A polarizable continuum model was used to assess the influence of the polar environment on the tautomeric equilibrium [19].

## Results And Discussion

As can be seen from the X-ray diffraction data of **1** in the crystalline state at room temperature, the *A* tautomer of compound **1** is realized (Supplementary information S1). The most stable tautomer *A* shows an intramolecular H-bond observed in experimental structure **1** using X-ray diffraction. The measured distance between the O3 and O4 atoms is 2.437 Å. Supplementary information S2 lists the measured bond lengths and angles of tautomer *A* of compound **1**.

The results of optimizing the geometry of tautomers *A* and *B* are shown in Fig. 2 and Supplementary information S2. Gibbs's free energy and Boltzmann weights of tautomers are shown in Table 1. It appears from our data that tautomer *A* dominates. The content of tautomer *B* increases in the non-polar solvent but does not exceed 13%. Vibrational spectra were calculated for tautomers *A* and *B*.

Table 1

Gibbs relative free energy  $\Delta G$  (kcal/mol), Boltzman weighting factor  $p$  (%) of low energy tautomers of **1** calculated in the B3LYP/6-311\*\*G level

Tautomer	Gas		Chloroform		Dimethylsulfoxide	
	$\Delta G$	$p$	$\Delta G$	$p$	$\Delta G$	$p$
<i>A</i>	0	90	0	87	0	90
<i>B</i>	1.35	10	1.12	13	1.32	10

As can be seen from our calculations and experimental X-ray data, the pyran ring of the molecule is flat. A satisfactory agreement is observed between the calculated geometrical parameters of the tautomer *A* and the experimental X-ray data.

It is interesting to estimate the evolution of the bond lengths during the tautomeric transformation. In tautomeric form *A*, the calculated bond lengths are (Å) 1.313 (O(3)–C(7)), 1.250 (O(4)–C(27)), 1.413 (C(6)–C(7)), 1.467 (C(6)–C(27)) and for the *B* tautomer the length of these bonds changes to 1.259, 1.302, 1.458, and 1.411, respectively. Such changes in bond lengths are consistent with the change in their properties during the tautomeric transformation. The H-bond lengths in the *A* and *B* tautomers are also different. The calculated O(3)•••O(4) distances for tautomers *A* and *B* are 2.473 and 2.418 Å, respectively.

The HOMO and LUMO molecular orbitals for the *A* and *B* tautomers are located on the pyran ring (Fig. 3). Conjugation provides a flat structure of this ring. It is interesting to see how the charge distribution changes during tautomeric transformations. In the tautomeric transformation from form *A* to *B*, the negative charge on the O3 atom increases, and that on the O4 atom decreases (Supplementary information S3). In the *B* form, the charges on the atoms C5, C6, C7 increase, and on the C27, H44 atoms decrease. It follows from these data that the chemical properties change during the tautomeric transition.

The pyrone **1** molecule contains several functional groups. Their reactivity can be characterized using descriptors. Form *B* was found to have higher ionization energy, electron affinity, chemical potential, electrophilic index, and energy band gap than form *A* (Table 2). The dipole moment is higher for form *A*, and the softness of both molecules is the same.

Table 2

Calculated ionization energy (*I*), electron affinity (*A*), energy band gap (*|GAP|*), chemical potential (*μ*), global softness (*S*), global electrophilicity index (*ω*), and dipole moment (*M*) for tautomeric forms *A* and *B* of compound **1**.

Tautomer	<i>I</i> , eV	<i>A</i> , eV	<i> GAP </i>	<i>μ</i> , eV	<i>S</i> , eV	<i>ω</i> , eV	<i>M</i> , D
<i>A</i>	8.661	0.803	4.618	-4.732	0.127	2.850	3.414
<i>B</i>	8.795	0.883	4.693	-4.839	0.126	2.960	1.935

The calculation of the local electrophilic indices makes it possible to estimate the reactivity of the atoms for two tautomeric forms (Supplementary information S3). The electrophilic index of oxygen atoms is higher for the *A* form. For the carbon atoms C5, C7, C27, the electrophilicity index is higher for form *A*, and for the atom C6, it is higher for *B* form. The reactivity of the hydroxyl group is higher for the tautomeric form *A*.

The molecular orbitals are similar for the two tautomeric forms, but there is an orbital  $\sigma(2)_{C6-C7} = 0.8137(sp^{1.00}d^{0.00})_{C6} + 0.5812(sp^{1.00}d^{0.00})_{C7}$  in form *A*, which is not in form *B*. In form *B* there is an orbital  $\sigma(2)_{O3-C7} = 0.8605(sp^{1.00}d^{0.00})_{O3} + 0.5095(sp^{1.00}d^{0.00})_{C7}$ , which is not in form *A*. These extra orbitals are of  $\pi$  character and indicate an increase in bond order.

In form *A*, significant interactions of C6–C7, C8–C10 bond orbitals with antibonding orbitals of the O2–C5, O4–C27, C6–C7  $\sigma_2(C6-C7) \rightarrow \sigma_2^*(O2-C5)$ ,  $\sigma_2(C6-C7) \rightarrow \sigma_2^*(O4-C27)$ ,  $\sigma_2(C8-C10) \rightarrow \sigma_2^*(C6-C7)$  with stabilization energies 34.18, 31.20, and 24.96 kcal/mol (Supplementary information S4). Additionally, the molecule has lone electron pairs of oxygen atoms interactions with O2–C5, C5–C6, C6–C7, O3–H44 bonds,  $n(LP_2O1) \rightarrow \sigma_1^*(O2-C5)$ ,  $n(LP_2O2) \rightarrow \sigma_1^*(O1-C5)$ ,  $n(LP_2O2) \rightarrow \sigma_2^*(C5-C6)$ ,  $n(LP_2O4) \rightarrow \sigma_1^*(O3-H44)$  with energies 29.25, 40.10, 15.56, and 42.96 kcal/mol.

In the tautomeric form *B*, the delocalization of electrons is maximal for the C8–C10 bond and is distributed over the antibonding orbitals O3–C7  $\sigma_2(C8-C10) \rightarrow \sigma_2^*(O3-C7)$  with the stabilization energies 27.83 kcal/mol. Additionally, the molecule has lone electron pairs of oxygen atoms interactions  $n(LP_2O1) \rightarrow \sigma_2^*(O2-C5)$ ,  $n(LP_2O1) \rightarrow \sigma_1^*(C8-C10)$ ,  $n(LP_2O2) \rightarrow \sigma_1^*(O1-C5)$ ,  $n(LP_2O2) \rightarrow \sigma_1^*(C5-C6)$ ,  $n(LP_2O3) \rightarrow \sigma_1^*(O4-H44)$  with energies 31.36, 34.08, 37.96, 15.85, and 63.18 kcal/mol.

The determination of the type of vibration in the experimental spectra was carried out by analyzing the potential energy, the atomic displacements, and the comparison with related compounds [20,21]. The

experimental and calculated vibrational spectra for two tautomers *A* and *B* of compound **1** are shown in Figs. 4 and 5 and Table 3.

Table 3

Observed and calculated wavenumbers  $\nu(\text{cm}^{-1})$ , the intensity of the bands in the IR spectra *I* (km/mol) and relative intensity of the bands in the Raman spectra *J* (a.u.) and assignments for the tautomeric forms *A* and *B* of compound **1** in the gas phase by using the B3LYP/6-311++G\*\* method.

Experimental		B3LYP/6-311++G** method						Assignments
IR	Raman	<i>A</i>			<i>B</i>			
n	n	n	l	J	n	l	J	
3427w								
3107w	3108w	3097	1.1	9.2	3092	1.1	8.8	nC8-H9
3004vw	3006w	3018	1.0	2.7	3021	0.6	2.2	nC28-H29 n <sub>as</sub> CH <sub>2</sub>
		2985	30.6	5.7	2984	26.8	5.5	nC19-H20 n <sub>as</sub> CH <sub>3</sub>
		2984	26.3	4.7	2984	33.3	4.8	nC32-H33 n <sub>as</sub> CH <sub>3</sub>
		2980	17.6	4.8	2983	16.2	4.2	nC40-H41 n <sub>as</sub> CH <sub>3</sub>
		2969	64.4	14.8	2969	55.8	10.8	nC23-H24 n <sub>as</sub> CH <sub>3</sub>
		2966	33.2	11.1	2966	43.1	13.4	nC15-H16 n <sub>as</sub> CH <sub>3</sub>
2964s	2967s	2964	43.8	12.8	2965	30.9	7.2	nC11-H12 n <sub>as</sub> CH <sub>2</sub>
		2963	26.0	6.0	2963	45.5	12.3	nC36-H37 n <sub>as</sub> CH <sub>3</sub>
		2961	3.1	2.1	2962	70.0	18.6	nC19-H21 n <sub>as</sub> CH <sub>3</sub>
		2960	79.0	21.3	2961	1.9	1.8	nC32-H34 n <sub>as</sub> CH <sub>3</sub>
2956sh		2957	8.0	1.8	2957	6.7	1.8	nC23-H25 n <sub>as</sub> CH <sub>3</sub>
		2956	3.8	1.5	2956	4.4	1.2	nC15-H17 n <sub>as</sub> CH <sub>3</sub>
		2954	4.7	1.9	2956	22.0	2.7	nC32-H34 n <sub>as</sub> CH <sub>3</sub>
		2953	26.1	2.9	2955	3.2	1.2	nC40-H42 n <sub>as</sub> CH <sub>3</sub>
	2933m	2926	15.8	18.8	2923	14.8	20.7	nC28-H29 n <sub>as</sub> CH <sub>2</sub>
		2916	14.1	37.1	2916	14.2	35.8	nC11-H12 n <sub>as</sub> CH <sub>2</sub>
	2909m	2908	19.5	22.9	2908	20.3	21.8	nC19-H21 n <sub>s</sub> CH <sub>3</sub>
2906m		2905	26.0	50.4	2907	23.9	42.3	nC32-H33 n <sub>s</sub> CH <sub>3</sub>
		2900	25.1	12.2	2901	26.5	1.4	nC23-H24 n <sub>s</sub> CH <sub>3</sub>
		2899	28.5	1.0	2900	26.0	9.6	nC40-H41 n <sub>s</sub> CH <sub>3</sub>
		2897	28.9	2.2	2896	28.7	3.4	nC15-H16 n <sub>s</sub> CH <sub>3</sub>

2868m	2867w	2895	31.1	4.6	2896	29.3	4.5	nC36-H37 n <sub>s</sub> CH <sub>3</sub>
2675vw	2784vw	2682	709.1	3.7	2240	787.7	4.4	nO3-H44
2666vw	2714vw							
2666vw								
2631vw								
2608vw								
2568vw								
2524vw								
2372vw								
2364vw								
2355vw								
2338vw								
1737sh	1738sh							
1719vs	1719m	1726	479.7	10.4	1721	440.3	6.8	nC5=O2
1683w								
1636s	1633vs	1599	394.4	100.0	1617	110.3	100.0	nC3=O7
1615w	1617sh							
1588m	1590m	1576	311.0	78.6	1580	641.7	24.6	βO3-H44
1553vs	1547m	1533	626.8	41.2	1536	775.5	10.3	nC6-C7
1474sh								
1462sh	1467m	1460	18.0	0.7	1460	21.1	0.4	βC32-H33 δ <sub>as</sub> CH <sub>3</sub>
1455m		1458	17.0	0.9	1458	19.6	0.6	βC19-H20 δ <sub>as</sub> CH <sub>3</sub>
		1452	12.7	1.5	1451	19.4	1.6	βC36-H39 δ <sub>as</sub> CH <sub>3</sub>
		1451	4.9	5.1	1450	14.0	3.7	βC15-H16 δ <sub>as</sub> CH <sub>3</sub>
		1449	6.7	1.5	1449	6.6	1.4	βC11-H12 δ <sub>as</sub> CH <sub>2</sub>
1445sh	1448m	1447	11.3	2.6	1447	10.0	3.4	βC28-H29 δ <sub>as</sub> CH <sub>2</sub>
1437sh	1438sh	1433	7.8	11.7	1432	20.9	5.3	βC40-H41 δ <sub>as</sub> CH <sub>3</sub>
		1430	8.7	6.0	1432	15.3	6.1	βC32-H33 δ <sub>as</sub> CH <sub>3</sub>

		1429	3.4	7.4	1429	2.0	7.5	$\beta$ C15-H16 $\delta_{as}$ CH <sub>3</sub>
		1428	6.4	4.2	1428	3.5	5.0	$\beta$ C19-H20 $\delta_{as}$ CH <sub>3</sub>
		1425	0.4	0.2	1425	0.4	0.2	$\beta$ C23-H25 $\delta_{as}$ CH <sub>3</sub>
		1424	2.4	0.3	1424	2.0	0.0	$\beta$ C36-H37 $\delta_{as}$ CH <sub>3</sub>
		1422	77.7	4.5	1422	63.1	1.3	$\beta$ C28-H29 $\delta_s$ CH <sub>2</sub>
		1417	32.8	2.2	1415	6.4	4.6	$\beta$ C11-H12 $\delta_s$ CH <sub>2</sub>
1394vw		1409	64.0	4.0	1400	312.5	7.8	$\beta$ C28-H29 $\delta_s$ CH <sub>2</sub>
1376w	1380m	1379	4.3	1.4	1379	5.8	1.1	$\beta$ C19-H21 $\delta_s$ CH <sub>3</sub>
1365m	1369sh	1376	4.7	0.8	1377	6.8	1.3	$\beta$ C32-H35 $\delta_s$ CH <sub>3</sub>
	1365sh	1351	7.6	1.7	1351	6.2	3.7	$\beta$ C19-H20 $\delta_s$ CH <sub>3</sub>
		1349	6.0	0.3	1350	14.3	0.3	$\beta$ C32-H33 $\delta_s$ CH <sub>3</sub>
		1347	7.3	0.3	1346	8.3	1.2	$\beta$ C23-H24 $\delta_s$ CH <sub>3</sub>
		1344	7.5	0.6	1345	8.6	0.6	$\beta$ C36-H37 $\delta_s$ CH <sub>3</sub>
		1340	44.1	18.9	1341	23.0	43.3	nC5-O1
1315w	1318m	1316	176.4	23.6	1298	30.1	13.8	$\beta$ C28-H29 wag CH <sub>2</sub>
		1289	8.9	29.5	1291	13.8	29.5	$\beta$ C11-H12 wag CH <sub>2</sub>
1282w	1285vw	1278	129.0	57.2	1279	58.2	5.9	nC6-C7
		1261	16.8	2.1	1260	39.7	1.7	$\beta$ C28-H29 wag CH <sub>2</sub>
1251w	1253m	1249	97.4	23.9	1251	63.1	6.6	nC6-C27
1232m	1234vs	1216	34.5	6.1	1215	26.9	28.2	nC6-C27
1203w	1208w	1198	57.3	72.3	1198	60.9	61.8	$\beta$ C23-H24 wag CH <sub>3</sub>
		1192	98.5	21.7	1190	90.7	22.0	$\beta$ C32-H35 wag CH <sub>3</sub>
		1177	4.7	10.8	1184	8.2	49.9	nC5-C6
		1174	2.9	12.4	1176	7.5	3.0	$\beta$ C23-H24 $\tau$ w CH <sub>3</sub>
1161sh	1163w	1170	4.2	3.2	1174	3.4	9.7	nC5-O1
1148m	1151m	1134	2.0	14.2	1128	11.0	8.1	$\beta$ C8-H9

		1123	25.1	11.1	1122	3.4	16.2	$\beta$ C28-H29 $\tau$ w CH <sub>2</sub>
	1056vw	1119	19.1	3.6	1119	29.0	18.1	$\beta$ C11-H12 $\tau$ w CH <sub>2</sub>
1044m	1041w	1030	0.7	2.7	1106	78.5	0.4	$\beta$ C40-H41
	1014w	1017	0.6	0.8	1027	2.2	1.0	$\beta$ C23-H24
		1011	1.2	1.7	1018	4.0	0.3	$\beta$ C36-H39
		1009	15.2	2.4	1010	1.7	2.7	$\beta$ C23-H24 $\tau$ w CH <sub>3</sub>
1000m	1003w	1007	64.9	1.3	1008	4.1	2.3	$\delta$ O3-H44
		982	22.5	13.9	982	1.2	18.8	nC7-C8
959m	960m	976	41.1	7.2	973	44.3	7.2	nO1-C10
935w	937w	928	0.1	0.1	928	0.5	0.1	$\gamma$ C32-H33 $\rho$ CH <sub>3</sub>
929sh		926	0.0	0.1	926	0.2	0.1	$\gamma$ C23-H24 $\rho$ CH <sub>3</sub>
912vw	914w	910	3.7	2.7	917	135.1	8.4	$\gamma$ C28-H29 $\rho$ CH <sub>3</sub>
	906w	907	4.9	2.2	907	1.4	1.3	$\gamma$ C19-H20 $\rho$ CH <sub>3</sub>
		903	2.1	8.9	903	2.9	7.7	nC14-C23
	899w	902	0.4	4.4	902	3.7	3.1	nC31-C36
888w	891w	887	17.5	9.3	900	35.3	10.5	nC5-C6, nC5-O1
		877	13.4	12.9	876	1.0	6.3	nC14-C19
	861sh	862	3.2	3.9	865	12.8	11.0	nC14-C15
854m	856vw	861	6.9	22.6	857	5.1	14.3	nC10-C11
	844sh	837	57.4	30.0	853	16.6	18.5	nO1-C5
817w	821w	815	26.3	0.3	826	25.0	0.7	$\gamma$ C8-H9
779sh	768m	785	13.7	7.4	779	2.5	4.8	$\rho$ C27-O4
763w	754sh	738	2.6	7.6	742	4.5	2.4	nC8-C10
		729	7.2	5.7	733	2.1	12.5	$\rho$ C7-O3
713w	717w	720	1.4	0.2	721	2.8	1.9	nC10-C11
697sh		686	18.3	21.3	691	7.4	0.6	nC27-C28
686sh	652m	680	6.8	3.9	680	0.3	21.8	$\rho$ C7-O3
650sh	625w	620	1.1	24.4	625	2.2	12.2	nC10-O1

616w	603m	607	12.3	27.0	611	2.8	32.7	$\rho_{C7-03}$
574w	575w	578	0.4	36.4	579	0.8	35.6	$n_{C10-C11}$
544sh		555	17.8	8.0	535	12.8	1.5	$\beta_R$
536sh								
529sh								
505w	507m							
477vw	479w	487	2.6	18.8	489	6.0	17.1	$\beta_R$
453vw	456w	458	4.1	5.4	464	2.0	6.6	$\beta_R$
445vw		438	3.1	4.3	430	10.3	2.6	$\beta_R$
436vs	439vw	426	1.7	1.9	428	0.0	4.8	$\beta_R$
412vw	418vw	419	0.2	3.1	417	8.3	2.4	$\tau_R$
		396	0.1	0.7	400	14.6	5.2	$\tau_R$
	389w	391	3.1	0.5	395	4.8	3.9	$\beta_{C27-04}$
	381sh	375	3.5	2.4	383	11.1	5.5	$\rho_{C5=02}$
		368	0.3	5.3	369	0.4	4.4	$\beta_{C14-C19}$
	359sh	359	0.6	2.9	360	3.0	1.8	$\beta_{C27-C28}$
	347w	340	2.1	1.6	340	0.9	0.8	$\gamma_{C10-C11}$
		326	6.6	6.4	315	3.0	2.1	$\beta_{C27-04}$
	288sh	287	0.4	3.0	288	0.2	1.7	$\tau_{C14-C15}$
	281w	283	1.5	0.6	283	0.2	0.3	$\tau_{C31-C32}$
		280	0.3	0.4	280	0.2	0.2	$\tau_{C14-C15}$
		276	0.1	1.1	277	0.1	0.9	$\tau_{C14-C23}$
	264vw	269	2.2	6.5	265	2.1	2.8	$\tau_R$
		258	1.0	2.6	260	0.3	2.2	$\tau_{C14-C23}$
		254	0.9	6.5	255	0.5	3.5	$\beta_R$
	241vw	235	1.3	4.5	236	0.4	4.3	$\tau_{C14-C23}$
		230	0.2	1.9	230	1.5	3.7	$\tau_{C31-C40}$
		220	0.6	6.0	221	0.3	6.1	$\tau_{C14-C15}$

211vw	219	0.3	1.1	219	0.6	2.0	$\tau_R$
188vw	199	3.6	3.6	195	0.7	5.9	$\tau_R$
178vw	167	0.3	3.1	171	1.0	5.4	$\tau_R$
168vw	157	2.7	6.2	152	2.5	3.0	$\tau_R$
105vw	103	0.2	1.3	105	0.9	2.4	$\tau_R$

Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; v, stretching;  $\beta$ , deformation in plane;  $\gamma$ , deformation out of plane; wag, wagging;  $\tau$ , torsion;  $\beta_R$ , deformation ring;  $\tau_R$ , torsion ring;  $\rho$ , rocking;  $\tau_w$ , twisting;  $\delta$ , deformation; a, antisymmetric; s, symmetric.

The band of free *OH* groups at  $3600\text{ cm}^{-1}$  is absent from the experimental IR spectrum of compound **1**. Therefore, all hydroxyl groups are involved in the formation of H-bonds with bands observed in the region of  $2800\text{--}2400\text{ cm}^{-1}$  (Fig 6). The residual water causes the band at  $3427\text{ cm}^{-1}$  in the experimental IR spectra.

The sharp medium intensity peak in the IR spectrum at  $3107\text{ cm}^{-1}$  and the frequency of  $3108\text{ cm}^{-1}$  in the Raman spectrum refer to *CH* stretching vibrations (C8–H9 bond). Experimental frequencies in the region  $3100\text{--}2960\text{ cm}^{-1}$  in vibrational spectra refer to  $n_{as}(\text{CH}_2)$  and  $n_{as}(\text{CH}_3)$  stretching vibrations. The symmetrical stretching vibrations of the methyl and methylene groups cause frequencies in the range of  $2910\text{--}2860\text{ cm}^{-1}$  in the experimental spectra.

Stretching of carbonyl groups without H-bonds (C5=O bond) causes a band at  $1719\text{ cm}^{-1}$  in the experimental IR and Raman spectra (Figs. 4 and 5). The stretching vibrations of the carbonyl group forming the H-bond (C3=O7 bond) are shifted to the low-frequency region of  $1636\text{ cm}^{-1}$ .

The bands in the region  $1460\text{--}1400\text{ cm}^{-1}$  in the experimental spectra are due to the  $\delta_{as}(\text{CH}_3)$  and  $\delta_{as}(\text{CH}_2)$  bending vibrations. Symmetrical bending vibrations  $\delta_s(\text{CH}_3)$  and  $\delta_s(\text{CH}_2)$  cause bands in the region  $1400\text{--}1340\text{ cm}^{-1}$ . The frequency at  $1315\text{ cm}^{-1}$  in the experimental IR spectrum and the band at  $1318\text{ cm}^{-1}$  in the experimental Raman spectrum is due to the wagging vibrations of the methylene groups.

Stretching vibrations of the *CO* and *CC* bonds of the pyran ring (C5–O1 and C5–C6 bonds) cause frequencies between  $1290$  and  $1150\text{ cm}^{-1}$  in the experimental spectra. The bands in the region of  $1060$  to  $1000\text{ cm}^{-1}$  in the experimental spectra were attributed to the deformation of the *CCH* angles and stretching of the *CC* bonds.

The rocking vibrations of the methyl groups  $\rho(\text{CH}_3)$  cause bands between  $960$  and  $880\text{ cm}^{-1}$  in the experimental IR and Raman spectra. Bands of average intensity in the region of  $860\text{--}760\text{ cm}^{-1}$  in the experimental spectra refer to *CO* and *CC* bonds (C5–O1 and C5–C6 bonds) stretching vibrations.

The band at  $713\text{ cm}^{-1}$  in the experimental spectra refers to the stretching vibrations of the CC bonds (C10–C11 bond). Bending vibrations of the pyran ring cause bands in the  $620\text{--}470\text{ cm}^{-1}$  region in the experimental spectra. Bending and torsional vibrations of the pyran ring cause bands in the  $500\text{--}100\text{ cm}^{-1}$  region of IR and Raman spectra.

It is important to know what changes occur in the vibrational spectra of compound **1** during the tautomeric transformation. The spectra of tautomeric forms *A* and *B* are similar (Figs. 4 and 5). For tautomers *A* and *B*, the frequencies of most bands remain unchanged, but their intensity change. Bands  $1726, 1599, 1576, 1533, 1422, 1315, 1192\text{ cm}^{-1}$  of the form *A* IR spectrum are shifted to frequencies  $1721, 1617, 1580, 1536, 1400, 1341, 1190\text{ cm}^{-1}$  of the form *B* IR spectrum (Fig. 4). Bands  $1726, 1599, 1576, 1533, 1433, 1340, 1316, 1278, 1249, 1198, 837, 686, 607, 578, 487\text{ cm}^{-1}$  in the Raman spectrum of form *A* are shifted to frequencies  $1721, 1617, 1580, 1536, 1429, 1341, 1291, 1198, 853, 680, 579, 489\text{ cm}^{-1}$  in the Raman spectrum of form *B* (Fig. 5).

The theoretical spectra agree with the experimental vibrational spectra of tautomer *A* in a wide frequency range (Figs. 4 and 5). Thus, the use of the DFT approximation for the considered molecular system is correct.

Compound **1** has a strong H-bond with a cyclic chelate structure. The enol form of  $\beta$ -diketones is a well-known case of a 6-membered ring (chelate) with a strong resonance-assisted H-bond [22–25]. The characteristic spectral features observed for such structures are that instead of pronounced carbonyl stretching bands, strong absorption bands are present in the region of  $1580\text{--}1630\text{ cm}^{-1}$  [9]. The stretching of the OH bond band shifts up to  $2200\text{ cm}^{-1}$  [9].

Additionally, due to the resonance of two enol tautomers (both are chelate enol forms), this structural fragment can be considered a quasisymmetric  $\text{O}\cdots\text{H}\cdots\text{O}$  hydrogen bond. This bond has a broad and shallow potential well with two minima, which leads to a series of diffuse absorption bands scattered over a wide wavenumber region.

The analysis of the observed IR spectrum **1** in the region of  $2700\text{--}2000\text{ cm}^{-1}$  shows that there are several weak bands,  $\nu(\text{OH})$  (Fig. 6). The calculated  $\nu(\text{OH})$  frequencies after scaling are  $2682$  and  $2240\text{ cm}^{-1}$  for tautomers *A* and *B*, respectively, and they are in the range between  $2700$  and  $2200\text{ cm}^{-1}$ . An empirical formula is proposed which establishes a correlation between the frequencies  $\nu(\text{OH})$  observed and those calculated in the harmonic approximation:  $\nu_{\text{obs}} = -757 + 1.173 \nu_{\text{harm}}$  [25]. The calculation by this formula yields  $\nu(\text{OH})$  frequencies of  $2520$  and  $1980\text{ cm}^{-1}$  for tautomers *A* and *B*, respectively. In the experimental IR spectrum of compound **1**, the band  $2524\text{ cm}^{-1}$  is observed, which can be attributed to  $\nu(\text{OH})$  vibrations. The shift of this band to low frequencies depends on the strength of the intramolecular H-bond. We see that in the most energy-stable tautomer *A*, the H-bond is weaker.

This conclusion is consistent with the fact that the H-bond length for *A* and *B* tautomers is  $2.473$  and  $2.418\text{ \AA}$ , respectively. The strength of the H-bond can be described using Wiberg bond indices  $0.158$

(tautomer *A*) and 0.204 (tautomer *B*) [26]. These values of the Wiberg indices indicate that strong H-bonds are formed in compound **1** for both tautomers. It appears from our data that there is a correlation between the frequencies  $\nu(OH)$  calculated in the harmonic approximation and the Wiberg indices. The stronger the H-bond, the lower the  $\nu(OH)$  frequency and the higher the Wiberg index.

The strength of the intramolecular H-bond in compound **1** can be estimated as the interaction  $n(LP_2O4) \rightarrow \sigma_1^*(O3-H44)$  with the energy 42.96 kcal/mol of the tautomer *A* and  $n(LP_2O3) \rightarrow \sigma_1^*(O4-H44)$  with energy 63.18 kcal/mol of tautomer *B*. The energy of the donor-acceptor interaction of the H-bond is larger for the *B* tautomer, therefore it is stronger. Interactions  $\sigma_1(O3-H44) \rightarrow \sigma_1^*(C7-C8)$ ,  $\sigma_2(C6-C7) \rightarrow \sigma_2^*(O4-C27)$ ,  $\sigma_2(C6-C7) \rightarrow \sigma_2^*(C8-C10)$ ,  $\sigma_2(C8-C10) \rightarrow \sigma_2^*(C6-C7)$  with energies 5.83, 31.20, 7.49, 24.96 kcal/mol (tautomer *A*), and  $\sigma_2(C8-C10) \rightarrow \sigma_2^*(O3-C7)$  with energy 27.83 kcal/mol (tautomer *B*) are realized due to the conjugation of bonds in a six-membered ring.

## Summary

In conclusion, the study of the IR and Raman spectra, combined with the calculation of the normal vibrations by the DFT method, gives a detailed description of the dynamics of pyrone **1**. The intensities of the bands in the IR spectra show a high sensitivity to the H-bond in compound **1**.

The homolog of dehydroacetic acid has been studied by the methods of vibrational spectroscopy and quantum chemistry. The bands belonging to different fragments of the acid were determined.

The HOMO and LUMO orbitals of the acid molecule are located on the pyran ring. During tautomeric transformations, there is a significant delocalization of the charge, which modifies the reactivity of the molecule.

The reactivity of compound **1** was characterized using descriptors. Form *B* was found to have higher ionization energy, electron affinity, chemical potential, and electrophilic index than form *A*. The dipole moment is higher for form *A*, and the softness of the two molecules is the same.

## Declarations

### Author contribution

Victor Furer: Conceptualization, Methodology, Software, Writing- Original draft preparation and Editing

Alexandr Vandyukov: Investigation of IR and Raman spectra

Ekaterina Nomerotskaya: Synthesis of 3-(3,3-Dimethylbutanoyl)-4-hydroxy-6-neopentyl-2H-pyran-2-one

Mariyam Mukhtarova: Synthesis of 3-(3,3-Dimethylbutanoyl)-4-hydroxy-6-neopentyl-2H-pyran-2-one

Vladimir Kovalev: Conceptualization, Methodology, Reviewing and Editing

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## Data availability

We allow the journal to review all the data, and we confirm the validity of results.

## Code availability

NA.

## Ethics approval

The authors agree with ethical standards. This work was not published previously, and is not submitted to more than one journal. No data have been fabricated or manipulated.

## Consent to participate

The authors agree to participate in the article.

## Consent for publication

The authors agree to participate in the publication of the article.

## Conflict of interest

The authors declare no competing interests.

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## Figures

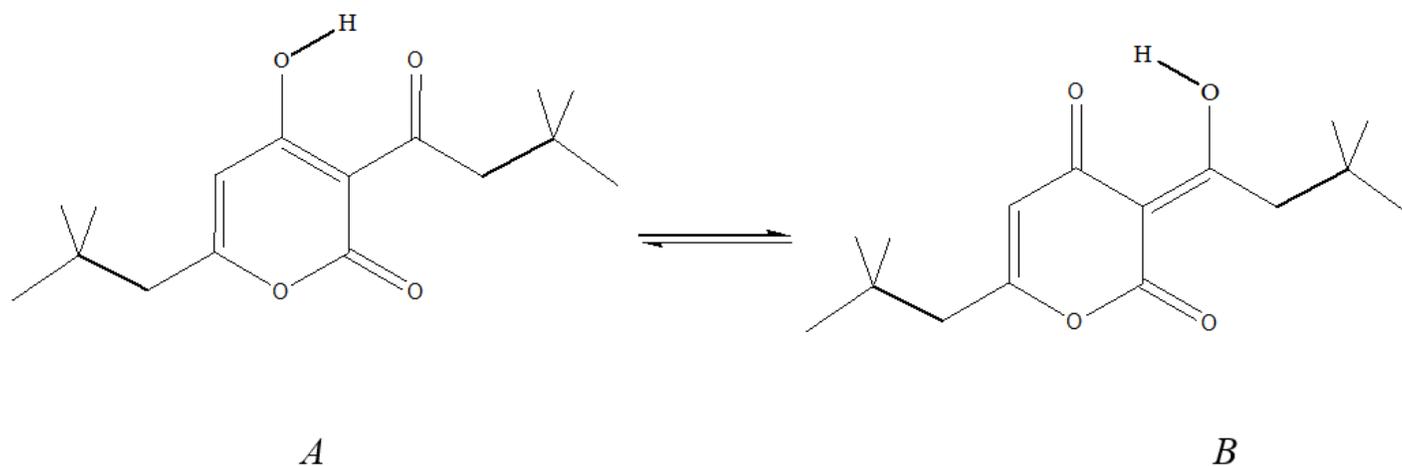
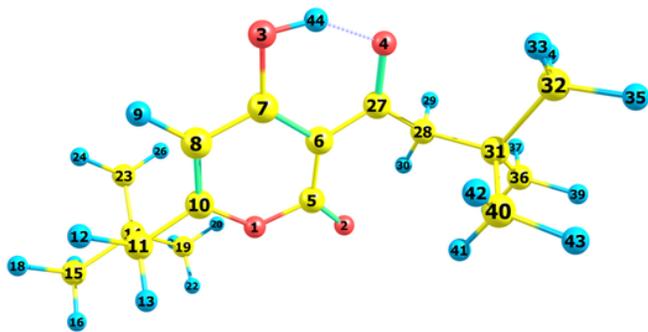
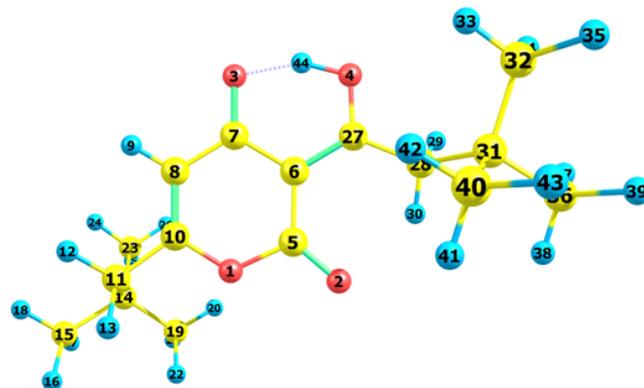


Figure 1

The structure of tautomeric forms A and B of compound 1



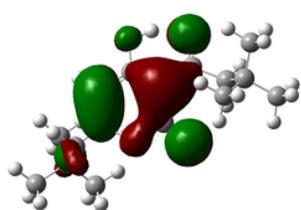
(1)



(2)

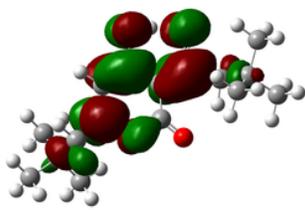
**Figure 2**

Geometry and atom numbering for tautomeric forms *A* (1) and *B* (2) of compound 1

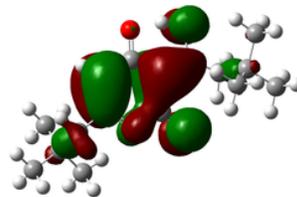


HOMO

1

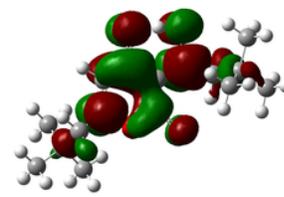


LUMO



HOMO

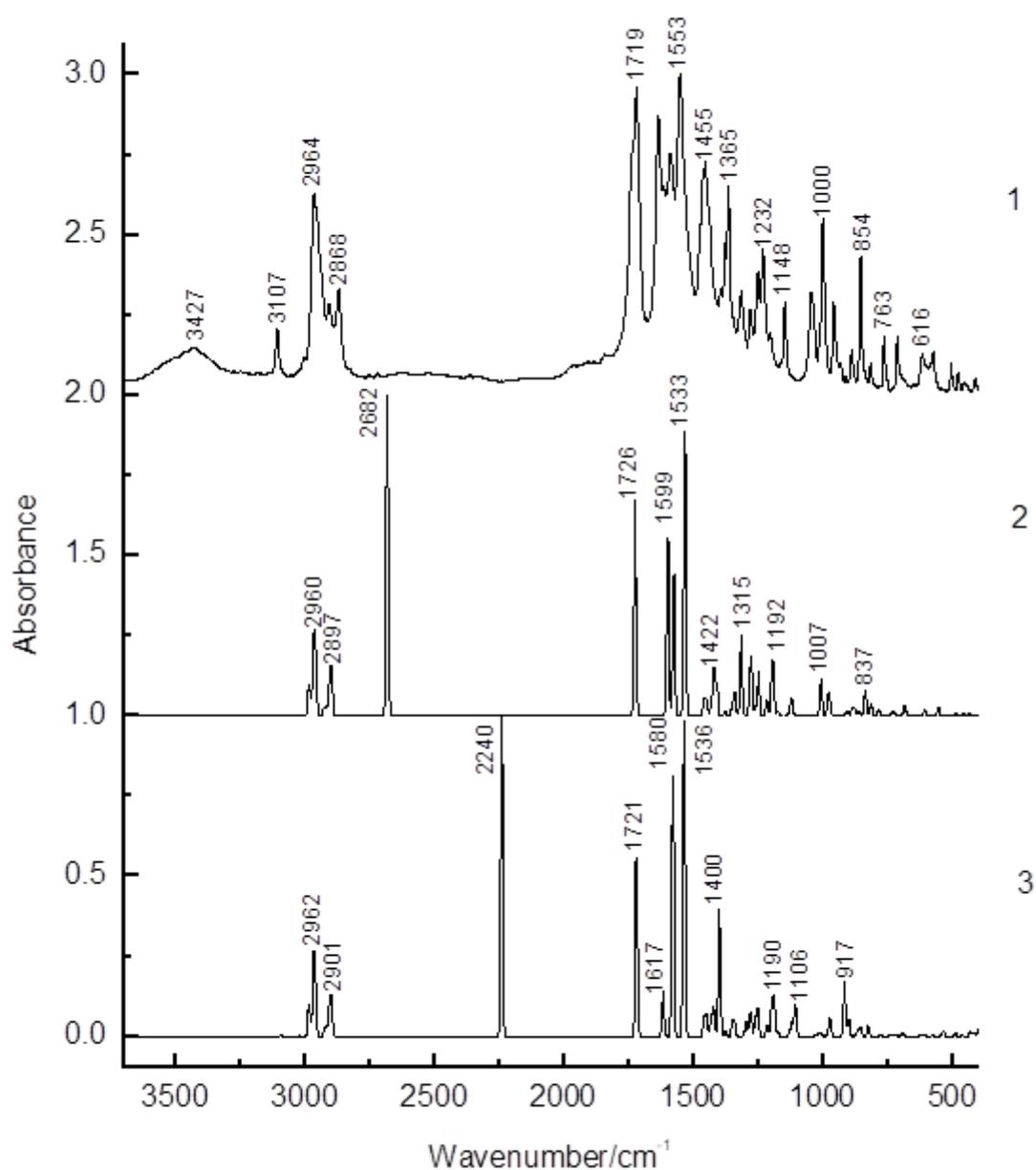
2



LUMO

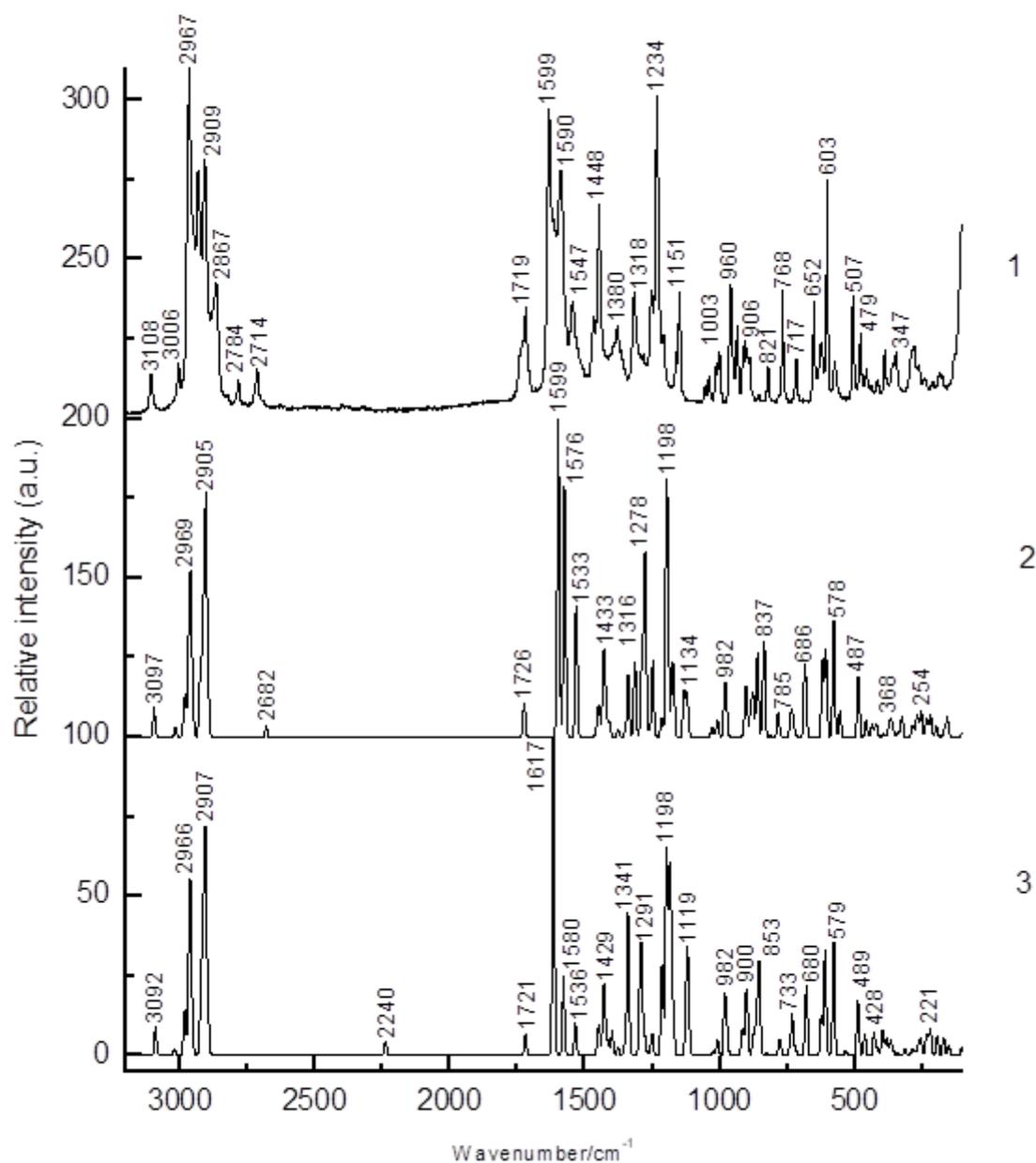
**Figure 3**

Molecular orbital surfaces for tautomeric forms *A* (1) and *B* (2) of compound 1



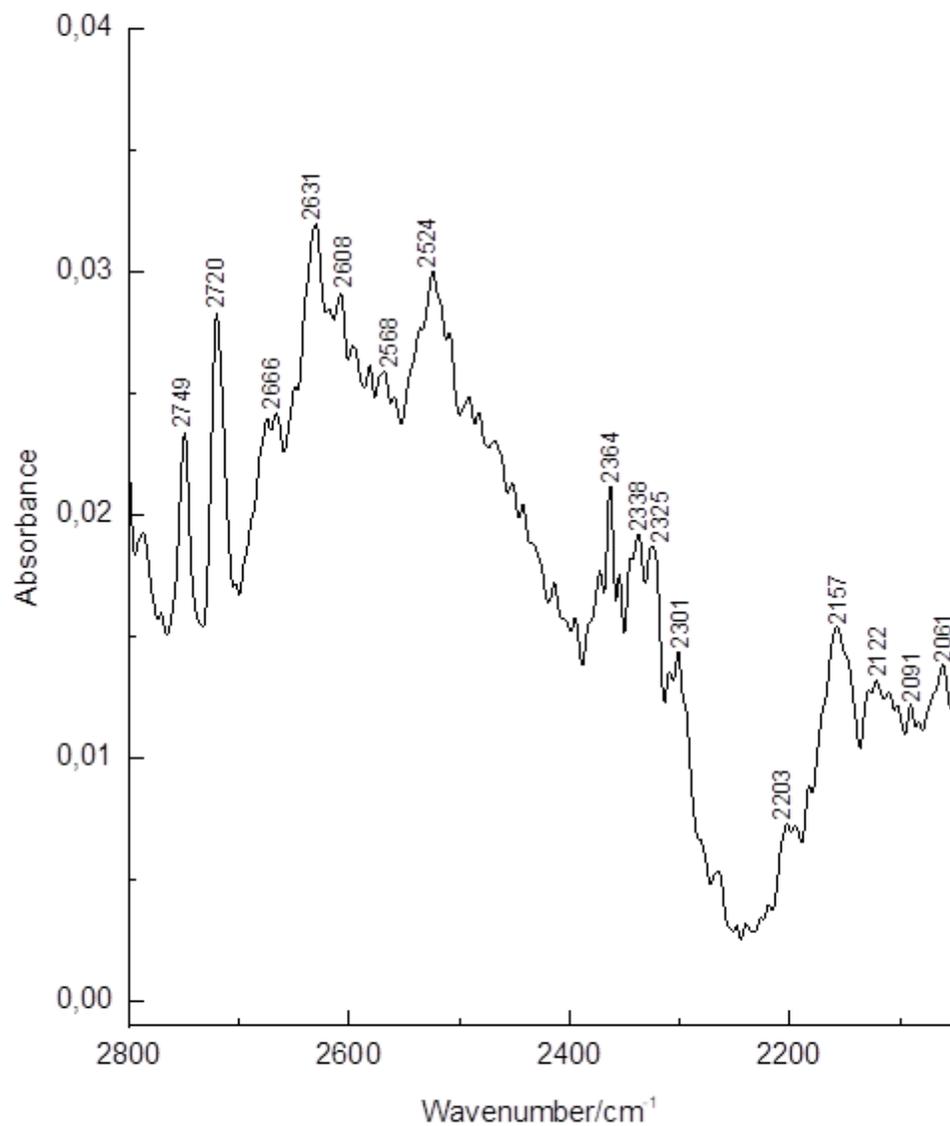
**Figure 4**

Experimental IR spectra of crystalline compound **1** (**1**) and calculated IR spectra of tautomeric forms A (**2**) and B (**3**). The theoretical spectra were modeled using Lorentz functions centered on the calculated frequencies, scaled by a factor of 0.96 and an FWHM of 10 cm<sup>-1</sup>



**Figure 5**

Experimental Raman spectra of crystalline compound **1** (**1**) and theoretical Raman spectra of tautomeric forms *A* (**2**) and *B* (**3**). The theoretical spectra were modeled using Lorentz functions centered on the calculated frequencies, scaled by a factor of 0.96 and an FWHM of  $10\text{ cm}^{-1}$



**Figure 6**

The experimental IR spectrum of compound **1** in the region 3600–2700 cm<sup>-1</sup>

## Supplementary Files

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