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Synthesis and Structure of Two Isomeric Enaminones

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The reaction of ethyl 2-hydroxy-4-(4-hydroxy-6-methyl-2*H*-pyran-2-on-3-yl)-4-oxo-2-butenoate (**1**) and 1-naphthylamine in ethanol affords two isomeric enaminones: ethyl 4-hydroxy-3-[3-(1-naphthylamino)-2-butenoyl]-2*H*-pyran-2-on-6-carboxylate (**2**) and ethyl 4-(4-hydroxy-6-methyl-2*H*-pyran-2-on-3-yl)-2-(1-naphthylamino)-4-oxo-2-butenoate (**3**).

The structures of both compounds were determined by the single crystal X-ray diffraction. Tautomerism may be involved in two parts of a molecule, in the cyclic part (pyrone ring) and in the side chain, to give a variety of possible tautomeric forms. Attention has been turned to the *endo*-enol enamine and *exo*-enol enamine tautomeric equilibrium, since both tautomers were found in the crystals of compounds with similar structures. The NMR spectroscopic data and X-ray structural analysis confirmed that both compounds exist in the *endo*-enol enamine form in the solution and in the crystalline state. The molecules are characterized by strong, intramolecular hydrogen bonds of N–H···O and O–H···O type reinforced by π-delocalization. The molecules as a whole are not planar, exhibiting planarity only in the central heteroconjugated moiety, while naphthyl rings are almost perpendicular to the central part.

Key words: enaminones, 2*H*-pyran-2-ones, NMR spectra, crystal structures, resonance assisted hydrogen bonds, structure and tautomeric isomerism.

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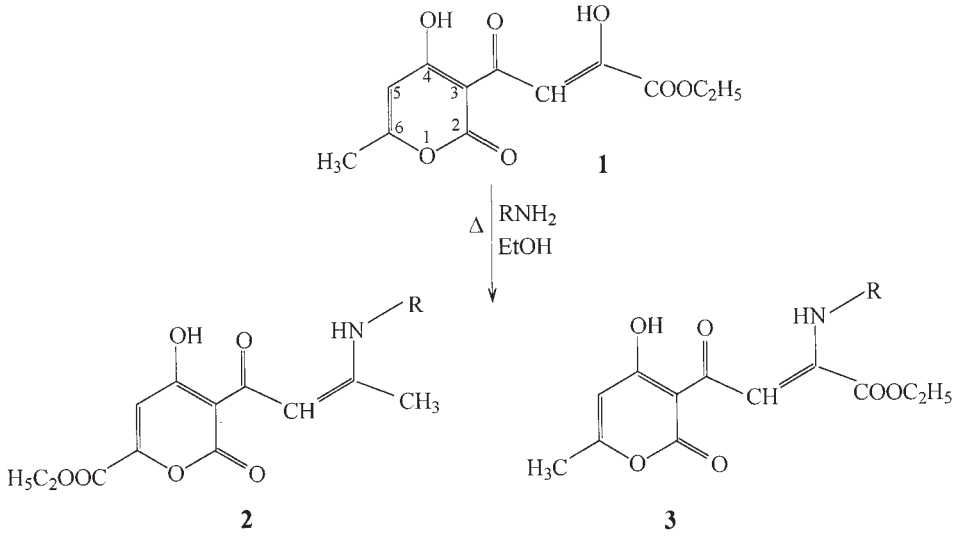
INTRODUCTION

Reaction of **1** with primary amine resulted in a pair of isomeric products: one (isomer **2**) as a result of the nucleophilic attack of the amine at position 6 of the 2-pyrone ring and the other (isomer **3**) as a result of the nucleophilic attack of the amino group at the carbon atom next to the side chain ethoxycarbonyl group. The formation of isomer **2** proceeds by addition of primary amines to C-6, followed by ring opening and by additional cyclization into a new 2-pyrone ring (Scheme 1). In our previous work, this type of enaminone group of compounds was described and structurally characterized on benzyl, phenyl and tyramine derivatives for the first time.[1]



R = 1-naphthyl

Scheme 1

EXPERIMENTAL

The starting compound, ethyl 2-hydroxy-4-(4-hydroxy-6-methyl-2*H*-pyran-2-on-3-yl)-4-oxo-2-butenoate (**1**), was prepared as described in literature.[2]

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrometer at 300 MHz and 75 MHz, respectively, and with TMS as internal standard. The infrared spectra were recorded with a Perkin-Elmer 297 spectrophotometer using KBr pellets. Melting points were determined on a Kofler micro hot stage, and were uncorrected.

*Ethyl 4-hydroxy-3-[3-(1-naphthylamino)-2-butenoyl]-2*H*-pyran-2-on-6-carboxylate (**2**) and ethyl 4-(4-hydroxy-6-methyl-2*H*-pyran-2-on-3-yl)-2-(1-naphthylamino)-4-oxo-2-butenoate (**3**)*

To a solution of compound **1** (1.18 g, 4.4 mmol) in ethanol (50 mL), a solution of 1-naphthylamine (0.63 g, 4.4 mmol) in ethanol (10 mL) was added. The reaction mixture was refluxed for 1 h, then cooled to room temperature to give a yellow precipitate (0.72 g, 42%) of compound **2**, m.p. 182–184 °C (recrystallized from ethanol). Isomer **2** was isolated by filtration and the filtrate was allowed to stand at room temperature. By slow evaporation, orange-red crystals (0.54 g, 31%) of compound **3** were obtained, m.p. 144–146 °C (recrystallized from ethanol).

Compound **2**: IR(KBr) υ_{max}/cm^{-1}: 1740sh, 1728 and 1715 (C=O lactone and ester), 1658, 1600, 1587, 1545sh, 1530 and 1510sh (C=C arom; and C=C and C=O conjugated chelate system); ^{1}H NMR ($CDCl_3$) δ/ppm: 1.41 (t, 3H, J = 7.1 Hz, CH_3 ester), 2.07 (s, 3H, CH_3), 4.41 (q, 2H, J = 7.1 Hz, CH_2 ester), 6.88 (s, 1H, chain), 6.89 (s, 1H, pyrone ring), 7.35–7.97 (m, 7H, naphthyl), 12.30 (s, 1H, NH), 18.72 (s, 1H, OH);

Anal. Calcd. for $C_{22}H_{19}NO_6$ (M_r 393.37): C 67.17, H 4.87, N 3.56%; found C 67.12, H 4.92, N 3.65%.

Compound **3**: IR(KBr) υ_{max}/cm^{-1}: 1730 and 1715sh (C=O lactone and ester), 1645 (C=C 2-pyrone), 1595sh, 1580, 1565 and 1515 (C=C arom. and C=C and C=O conjugated chelate system); ^{1}H NMR ($CDCl_3$) δ/ppm: 0.92 (t, 3H, J = 7.0 Hz, CH_3 ester), 2.27 (s, 3H, CH_3), 4.07 (q, 2H, J = 7.0 Hz, CH_2, ester), 5.93 (s, 1H, pyrone ring), 7.16–8.13 (m, 7H, naphthyl), 7.28 (s, 1H, chain), 11.72 (s, 1H, NH), 17.41 (s, 1H, OH);

Anal. Calcd. for $C_{22}H_{19}NO_6$ (M_r 393.37): C 67.17, H 4.87, N 3.56%; found C 67.37, H 5.05, N 3.41%.

X-ray Diffraction Experiment

Single crystals of good diffraction quality were obtained by slow evaporation from CH_3CN solution for both compounds. The diffraction experiment for compound **2** was controlled by the DENZO program.[3] The crystal to detector distance was 28 mm, with exposure time of 50 s per frame.

Data collection for **3** was controlled by the STADI4 program[4] and corrections for Lorentz and polarization effects were performed by the X-RED program.[5]

The structures of both compounds were solved by direct methods incorporated in the SHELXS-97 program[6] and refined anisotropically for all non-H atoms applying the SHELXL-97 program.[7]

In the isomer **2** structure, all hydrogen atoms were found in difference Fourier maps (C–H distances in the range 0.941(16)–1.00(2) Å, O3–H3O and N–H1N 1.05(2) and 0.918(19) Å, respectively) while in **3**, the H atoms belonging to carbon atoms were generated on idealized geometrical positions and refined applying the riding model (Csp^3–H 0.97 for methylene groups, Csp^3–H 0.96 for methyl groups and Csp^2–H 0.93 Å). Hydrogen atoms in **3**, linked to O3, O4 and N atoms were found in difference Fourier maps at a low R factor value and refined freely with O3··H, O4··H and N–H1N distances of 1.22(5), 1.27(5) and 0.89(3) Å, respectively. The values of positional coordinates and isotropic thermal parameter of H atom in **3** were affected by the reduced accuracy of room temperature data for **3** compared to **2**. All molecular graphics were done by PLATON-98.[8]

Table II lists the general and crystallographic data and details of the data collection procedure and structure refinement.

TABLE I

^{13}C Chemical Shifts (ppm) and $^{13}C–^{1}H$ Coupling Constants / Hz in $CDCl_3$

Comp.	Pyrone ring									
	C-2	C-3	C-4	C-5	C-6	C=O	–CH=	=C(NHR)–	C=O (ester)	CH_3
2	159.93	101.16	179.98	109.23	150.92	186.47	95.75	168.97	159.56	21.00
	s	$^{3}J_{OH}$ = 7.1	$^{2}J_{OH}$ = 4.7	^{1}J = 177.0	$^{2}J_{H\text{-}5}$ = 3.1	^{2}J = 4.4	^{1}J = 169.5	$^{2}J_{CH_3}$ = 5.4	^{3}J = 3.1 q	^{1}J = 129.6
		$^{3}J_{H\text{-}5}$ = 4.2	^{2}J = 2.0	$^{3}J_{OH}$ = 5.3			$^{3}J_{NH}$ = 4.0	^{2}J = 3.4		^{3}J = 5.8
							$^{3}J_{CH_3}$ = 4.0	^{2}J = 1.9		^{3}J = 4.3
3	161.34	98.46	180.90	102.17	167.50	192.31	97.67	153.95	163.91	20.47
	s	$^{3}J_{OH}$ = 6.8	$^{2}J_{OH}$ = 5.3	^{1}J = 172.5	$^{2}J_{CH_3}$ = 6.3	^{2}J = 3.0	^{1}J = 172.1	^{2}J = 2.8	^{3}J = 3.2 t	^{1}J = 130.1
		$^{3}J_{H\text{-}5}$ = 4.2	^{2}J = 2.0	$^{3}J_{OH}$ = 6.3	$^{2}J_{H\text{-}5}$ = 6.3		$^{3}J_{NH}$ = 2.9		^{3}J = 4.6 d	^{3}J = 2.8
				$^{3}J_{CH_3}$ = 3.8					^{3}J = 9.2 d	

Comp. **2**: naphthyl carbons (δ/ppm) 134.49, 133.83, 129.74, 128.73, 128.58, 127.72, 127.16, 125.49, 124.10, 122.37; Ester ethyl carbons: 62.84, 14.12.
Comp. **3**: naphthyl carbons (δ/ppm) 135.66, 134.32, 128.44, 128.54, 127.22, 127.14, 126.98, 125.47, 122.28, 120.63; Ester ethyl carbons: 62.26, 13.49.

TABLE II

General and crystal data and details of the data collection and structure refinement procedure for compounds **2** and **3**

Compound	**2**	**3**
Empirical formula	$C_{22}H_{19}NO_6$	$C_{22}H_{19}NO_6$
Molecular weight, M_r	393.37	393.37
Crystal system and space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
Unit cell parameters:[a]		
a / Å	11.809(2)	8.5324(18)
b / Å	10.169(2)	10.956(3)
c / Å	16.102(3)	11.2663(15)
α / °		84.205(1)
β / °	105.03(3)	79.116(1)
γ / °		71.233(1)
V / Å^3	1867.5(7)	978.3(4)
Unit cell contents, Z	4	2
Crystal size / mm^3	0.74 × 0.24 × 0.21	0.52 × 0.44 × 0.15
Crystal habit and colour	prism, yellow	plate, orange
D_{calc} / g cm^{-3}	1.399	1.335
μ / mm^{-1}	0.1	0.1
Diffractometer	Nonius-Kappa CCD	Philips PW 1100
Temperature / K	200	293
λ(Mo-Kα) / Å	0.71073	
2θ range / °	2.4; 25.0	3.4; 27.0
h,k,l range	–14 to 14; –12 to 12; –19 to 19	–10 to 10; –13 to 13; 0 to 14
Number of measured reflections	6325	4347
Number of unique reflections	3269 (R_{int} = 0.019)	4137 (R_{int} = 0.039)
F(000)	824	412
Extinction coefficient	0.0127(15)	–
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001
No. of least-squares parameters	339	272
Final residuals: R, wR, S	0.0352; 0.0934; 0.94	0.0403; 0.1272; 0.75
$\Delta\rho_{min,max}$ / e Å^{-3}	–0.16, 0.18	–0.16, 0.14

[a]The unit cell parameters for **2** were determined from all reliable data, and for **3** by least-squares refinement of 37 reflections in the range $9.1 \leq \theta \leq 16.4$.

RESULTS AND DISCUSSION

^{1}H and ^{13}C NMR Spectra

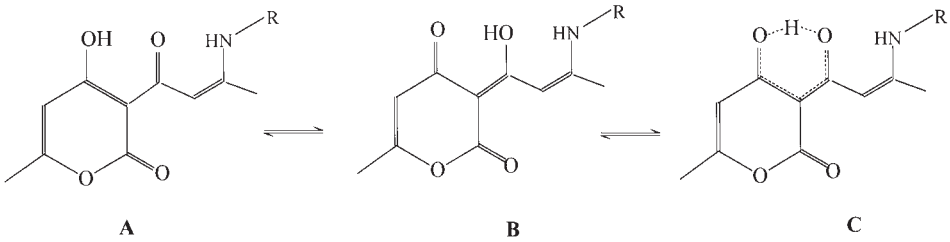
Tautomerism may be involved in two parts of molecules **2** and **3**, in a cyclic part (pyrone ring) and in a side chain, to give a variety of possible tautomeric structures. The unambiguous evidence for the presence of the amino and not imino tautomeric form resulted from the observed coupling of NH hydrogen with *N*-alkyl substituents in ^{1}H spectra of the corresponding analogs derived from compound **1** and benzylamine, butylamine and tyramine.[1]

The ^{1}H NMR spectra of both compounds **2** and **3** in $CDCl_3$ revealed two signals of OH and NH protons, which are shifted downfield due to strong hydrogen bonds. Distinction between two signals assignable to the methine hydrogen (side chain) and H-5 (pyrone ring) was easily achieved because the methine hydrogen signal lost in intensity after addition of D_2O.

Assignment of the methine and C-5 carbon resonances in the ^{13}C NMR spectra was achieved by comparing their coupling patterns and behaviour of the coupling toward deuteration. For instance, the carbon resonance at 95.75 ppm for methine carbon in spectrum of compound **2** shows splitting due to the proton coupling (^{1}J = 169.5 Hz), and further splitting due to the coupling with NH and CH_3 protons (^{3}J = 4.0 Hz). After addition of D_2O, the multiplicity pattern collapsed into a quartet due to the coupling with CH_3 only, since the coupling with methine and NH hydrogen disappeared upon the deuterium exchange. Similarly, in the ^{13}C spectrum of compound **3**, there are two close carbon resonances (97.67 and 102.17 ppm) assignable to the methine and C-5 carbon, both having the similar one-bond coupling constant (^{1}J = 172 Hz). However, additional long-range C–H splittings are different: the methine carbon resonance (97.67 ppm) shows a doublet due to coupling with amino hydrogen (^{3}J = 2.9 Hz), while the C-5 resonance (102.17 ppm) shows further splitting due to coupling with 4-hydroxy hydrogen (^{3}J = 6.3 Hz) and methyl hydrogens (^{3}J = 3.8 Hz).

The ^{13}C chemical shifts and coupling constants data (Table I) provided evidence of the existence of the *endo*-enol enamine tautomer (form **A** in Scheme 2) in the solution. The *endo*-enol form, *i.e.* 4-hydroxy-2-pyrone structure, was supported by the coupling of C-5 carbon of the pyrone ring with the C-4 hydroxy proton. In the spectrum of compound **2**, the doublet of doublet form of the C-5 resonance at 109.23 ppm became a doublet after addition of D_2O, since the coupling with the C-4 hydroxy proton (^{3}J = 5.3 Hz) dissapeared. Similarly, the three-bond coupling of C-5 at 102.17 ppm with C-4 hydroxy proton (^{3}J = 6.3 Hz) in the spectrum of compound **3** dissappeared after addition of D_2O. The chelated ketoenamine structure in the chain part of compounds **2** and **3** was also inferred from the changes of the long-range coupling patterns of the methyl carbon and ester carbonyl carbon upon

deuteration. The multiplicity pattern of the methyl carbon resonance (21.00 ppm) in the spectrum of compound **2**, as well as of the ester carbonyl carbon resonance (163.91 ppm) in the spectrum of compound **3**, due to three-bond coupling with amino and methine protons, disappeared after addition of D_2O.



Scheme 2

Crystal Structures

Thermal plot drawings of both molecules and their packing in the unit cell are depicted in Figures 1 and 2. Table III contains fractional coordinates and equivalent isotropic thermal displacement parameters for non-H atoms. Bond distances and angles are given in Table IV and hydrogen bond geometry in Table V.

The molecules are not planar. The central part of the molecules containing pyran and two chelate six-membered rings, the heteroconjugated O=C–C=C–OH β-diketone enol fragment and O=C–C=C–NH enamine fragment, are almost planar (dihedral angles defined by best planes calculated through ring atoms of the pyran ring and eight atoms of the heterodienic central part are 4.15(8) and 2.64(17)° for **2** and **3**, respectively). The naphthyl rings are inclined to the central π-delocalized fragment by 88.56(4) and 53.77(7)° for **2** and **3**, respectively. The highest deviation from pyran ring best plane shows C1 (0.028(1) Å) in **2** and C5 (0.014(2) Å) in **3**. The O2 atom is 0.073(2) and –0.017(4) Å apart from the pyran ring plane in **2** and **3**, respectively.

Due to the bond distance values and proton position, both structural isomers exist in the solid state as enamine isomers (C=C–N–H) with C7=C8 bond distance values amounting to 1.392(2) and 1.374(4) Å for **2** and **3**, respectively.

The enamine C–N bond distances are significantly shortened compared to the carbon to nitrogen single bond (1.338(2) and 1.342(4) Å in **2** and **3**, respectively), while the C13–N bond keeps the remarkable single bond charac-

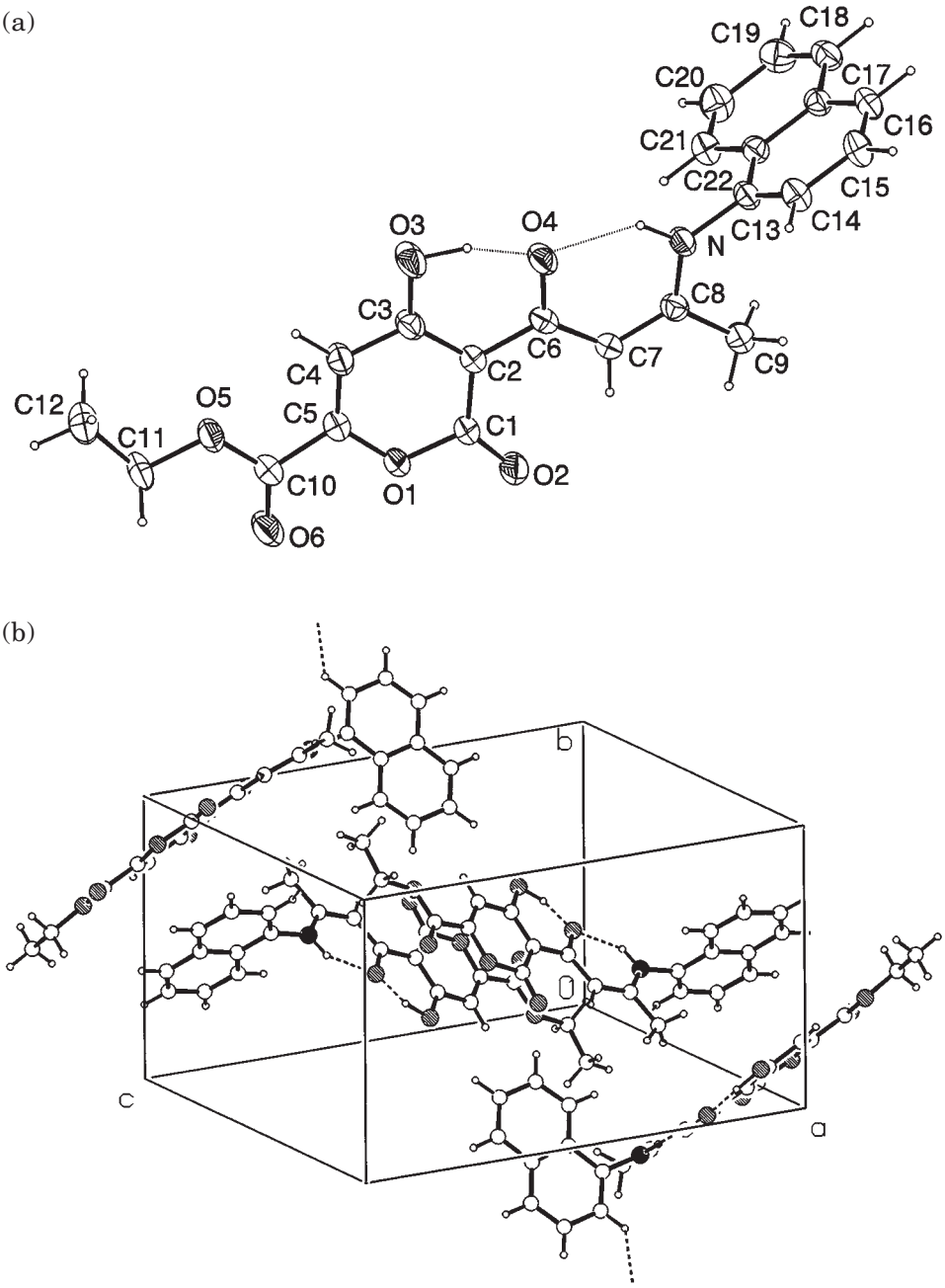


Figure 1. (a) ORTEP drawing of **2** with the atom numbering scheme. Thermal ellipsoids are at the 50% probability level. (b) Packing of the molecules of **2** in the unit cell. Hydrogen bonds are shown by dashed lines.

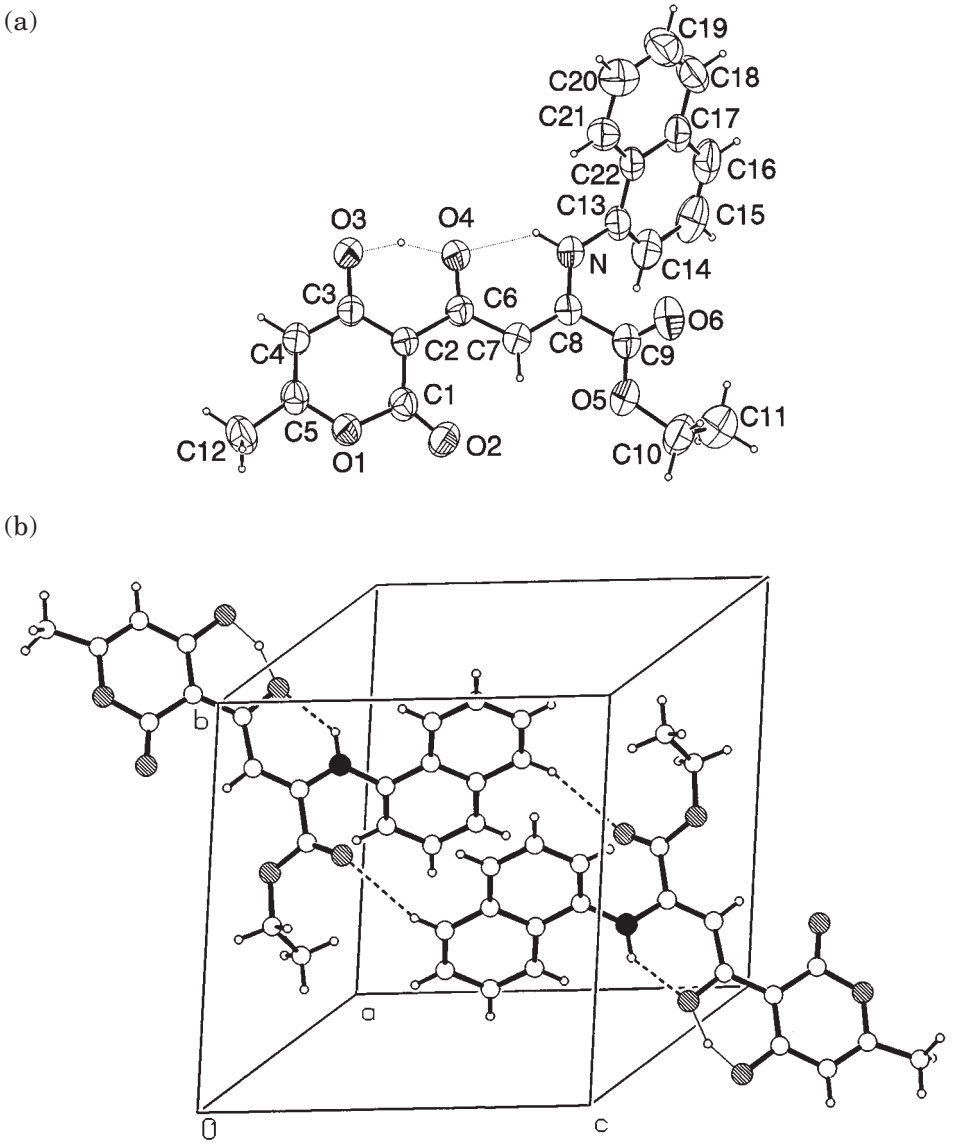


Figure 2. (a) ORTEP drawing of **3** with the atom numbering scheme. Thermal ellipsoids are at the 50% probability level. (b) Packing of the molecules of **3** in the unit cell. Hydrogen bonds are shown by dashed lines.

ter (1.441(2) and 1.427(4) in **2** and **3**, respectively).[9] The valence bond angle sum around N atoms is approx. 360° in both structures, with the largest angle C8–N–C13 of 124.8(1)° in **2** and 127.2(3)° in **3**.

TABLE III

Fractional atomic coordinates and equivalent isotropic thermal parameters / Å^2 for compounds **2** and **3**

Atom	*x*	*y*	*z*	U_{eq}[a]
		Compound **2**		
O1	0.22244(8)	–0.06779(10)	0.07960(6)	0.0347(3)
O2	0.29577(11)	0.07006(12)	0.00291(7)	0.0536(4)
O3	–0.04181(10)	–0.18434(13)	–0.12254(7)	0.0555(4)
O4	0.01584(8)	–0.02571(10)	–0.21646(6)	0.0365(3)
O5	0.09503(8)	–0.30482(10)	0.18456(6)	0.0356(3)
O6	0.25748(10)	–0.18311(12)	0.23285(6)	0.0493(4)
N	0.09391(10)	–0.88802(12)	–0.33000(7)	0.0295(4)
C1	0.21872(13)	–0.00859(14)	0.00014(9)	0.0321(4)
C2	0.12395(11)	–0.04683(13)	–0.07212(8)	0.0268(4)
C3	0.04690(12)	–0.14367(15)	–0.06052(8)	0.0326(4)
C4	0.06160(13)	0.79488(16)	0.02163(9)	0.0350(5)
C5	0.14716(12)	0.20512(13)	0.08736(8)	0.0289(4)
C6	0.10797(12)	0.01094(13)	–0.15881(8)	0.0269(4)
C7	0.18889(12)	0.09780(14)	–0.17949(8)	0.0286(4)
C8	0.18231(12)	0.14294(13)	–0.26222(8)	0.0279(4)
C9	0.27673(15)	0.22962(17)	–0.27795(10)	0.0376(5)
C10	0.17391(12)	–0.21649(14)	0.17688(9)	0.0309(4)
C11	0.11578(15)	–0.36939(18)	0.26825(9)	0.0398(5)
C12	0.01871(17)	–0.4645(2)	0.26256(13)	0.0492(6)
C13	0.08905(12)	0.14510(14)	–0.41786(8)	0.0279(4)
C14	0.02355(13)	0.24922(15)	–0.45585(9)	0.0338(4)
C15	0.01650(13)	0.28050(16)	–0.54259(9)	0.0364(5)
C16	0.07320(12)	0.20605(15)	–0.58899(9)	0.0334(5)
C17	0.14126(11)	0.09613(14)	–0.55184(8)	0.0279(4)
C18	0.20067(13)	0.01602(15)	–0.59878(9)	0.0344(5)
C19	0.26739(14)	–0.08817(16)	–0.56125(10)	0.0405(5)
C20	0.27758(14)	–0.11743(17)	–0.47443(10)	0.0417(5)
C21	0.22074(12)	–0.04321(15)	–0.42707(9)	0.0340(5)
C22	0.15078(11)	0.06492(13)	–0.46384(8)	0.0272(4)

TABLE III (cont.)

Atom	*x*	*y*	*z*	U_{eq}[a]
		Compound **3**		
O1	0.0261(2)	0.01420(17)	–0.30421(16)	0.0559(7)
O2	0.0234(3)	–0.1565(2)	–0.1841(2)	0.0763(9)
O3	0.3205(3)	0.1239(2)	–0.11999(19)	0.0729(9)
O4	0.3387(3)	–0.06221(19)	0.01953(17)	0.0637(8)
O5	0.2114(3)	–0.4769(2)	0.07212(19)	0.0786(9)
O6	0.1800(3)	–0.4291(2)	0.2653(2)	0.0751(8)
N	0.3828(3)	–0.2653(3)	0.1695(2)	0.0592(10)
C1	0.0762(3)	–0.0651(3)	–0.2030(2)	0.0512(10)
C2	0.1823(3)	–0.0287(2)	–0.1369(2)	0.0439(9)
C3	0.2247(3)	0.0837(3)	–0.1760(2)	0.0479(10)
C4	0.1678(3)	0.1582(3)	–0.2778(2)	0.0533(11)
C5	0.0737(3)	0.1221(3)	–0.3410(3)	0.0493(10)
C6	0.2456(3)	–0.1034(3)	–0.0323(2)	0.0488(10)
C7	0.2106(3)	–0.2205(2)	0.0149(2)	0.0524(10)
C8	0.2784(4)	–0.2943(3)	0.1097(2)	0.0508(10)
C9	0.2194(4)	–0.4073(3)	0.1591(3)	0.0578(11)
C10	0.1526(5)	–0.5907(3)	0.1075(4)	0.0890(16)
C11	0.2930(5)	–0.7036(3)	0.1304(4)	0.0959(17)
C12	0.0104(4)	0.1857(3)	–0.4525(3)	0.0706(12)
C13	0.4884(3)	–0.3495(3)	0.2476(2)	0.0509(10)
C14	0.5816(4)	–0.4722(3)	0.2185(3)	0.0672(12)
C15	0.6893(4)	–0.5513(3)	0.2952(4)	0.0788(14)
C16	0.7029(4)	–0.5038(3)	0.3995(4)	0.0762(14)
C17	0.6100(4)	–0.3781(3)	0.4318(3)	0.0593(11)
C18	0.6201(4)	–0.3265(4)	0.5404(3)	0.0775(14)
C19	0.5302(5)	–0.2040(5)	0.5697(3)	0.0872(16)
C20	0.4228(4)	–0.1259(4)	0.4936(3)	0.0754(12)
C21	0.4076(3)	–0.1708(3)	0.3895(3)	0.0576(11)
C22	0.4998(3)	–0.2973(3)	0.3554(2)	0.0472(10)
H	0.348(5)	0.041(5)	–0.039(5)	0.169(16)
H1N	0.398(3)	–0.189(3)	0.147(3)	0.067(9)

[a] U_{eq} = 1/3 of the trace of the orthogonalized U tensor.

TABLE IV

Selected interatomic distances and bond angles for compounds **2** and **3**

	2	**3**
	Interatomic distances / Å	
O2-C1	1.204(2)	1.209(4)
O3-C3	1.313(2)	1.320(4)
O4-C6	1.289(2)	1.279(4)
N-C8	1.338(2)	1.342(4)
N-C13	1.441(2)	1.427(4)
C2-C6	1.481(2)	1.453(3)
C2-C3	1.386(2)	1.399(4)
C6-C7	1.403(2)	1.438(4)
C7-C8	1.392(2)	1.374(4)
	Bond angles / °	
C8-N-C13	124.8(1)	127.2(3)
O3-C3-C2	122.9(1)	121.6(2)
O3-C3-C4	116.5(1)	117.2(3)
C2-C3-C4	120.5(1)	121.2(3)
O4-C6-C7	120.7(1)	118.7(2)
O4-C6-C2	116.2(1)	117.5(2)
C7-C6-C2	123.0(1)	123.8(3)
C8-C7-C6	124.2(1)	123.4(3)
N-C8-C7	122.8(1)	124.3(2)
N-C8-C9	117.4(1)	116.9(3)
C7-C8-C9	119.9(1)	118.5(3)

The O2–C1 2-pyrone bonds of 1.204(2) Å in **2** and 1.209(4) Å in **3** correspond to double C=O bonds and O3–C3 and O4–C6 of β-diketone fragment are 1.313(2) and 1.289(2) Å in **2** and 1.320(4) and 1.279(4) Å in **3**, being in-between C=O keto bond (1.21 Å) and Csp^2–OH single bond (1.36 Å).[9]

Two six-membered chelate rings formed by O–H···O and N–H···O hydrogen bonds are planar with hydrogen atoms H3O and H1N being –0.019(22) and –0.026(18) Å in **2** and H and H1N –0.041(44) and –0.044(27) Å in **3** out of chelate planes.

TABLE V

Hydrogen bonding geometry

D–H···A	D–H / Å	H···A / Å	D···A / Å	∠ D–H···A / °
		Compound **2**		
N–H1N···O4	0.92(2)	1.903(19)	2.651(2)	137(2)
O3–H3O···O4	1.05(2)	1.42(2)	2.426(2)	158(2)
		Compound **3**		
N–H1N···O4	0.89(3)	1.92(3)	2.625(3)	135(3)
O3···H···O4	1.22(5)	1.27(5)	2.428(2)	155(2)

Isomer **2** exists as 4-hydroxy-2*H*-pyran-2-one derivative (tautomeric form **A**, Scheme 2) and isomer **3** shows symmetrically distributed electron density belonging to hydrogen in O3···H···O4 moiety (form **C**, Scheme 2). There is no crystallographic evidence for the existence of hydrogen positional disorder, which could implicate two tautomeric forms of isomer **3** in the crystal.

All available protons participate in O–H···O and N–H···O hydrogen bonds formation (Table V). The O3...O4 distances in **2** and **3** are significantly shorter (≈ 2.43 Å) than in nonresonant systems (≈ 2.6 Å)[10–14] or in ice (2.76 Å). In such a resonance assisted hydrogen bond (RAHB), the H···A distance is extremely short, 1.42(2) Å in **2**, while in **3** the hydrogen atom is situated at almost the same distance from O3 and O4 atoms (O3...H 1.22(5) Å and O4...H 1.27(5) Å). The N–H···O intramolecular hydrogen bonds are somewhat longer since the NH proton is less acidic than the OH one. The crystal structures of both compounds are additionally stabilized by C–H···O weak hydrogen bonds in the range 2.90–3.48 Å. The geometry of naphthyl, methyl and ethoxycarbonyl groups is as expected.[9]

Supplementary Materials. – Atomic coordinates and equivalent isotropic displacement parameters, calculated hydrogen atom parameters, anisotropic thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (deposition numbers 147387 for **2** and 147388 for **3**). Structure factor tables are available from the authors.

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SAŽETAK

Sinteza i struktura dvaju izomernih enaminona

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Reakcijom etil 2-hidroksi-4-(4-hidroksi-6-metil-2*H*-piran-2-on-3-il)-4-okso-2-butenoata (**1**) i 1-naftilamina u etanolu nastaju dva enaminonska izomera: etil 4-hidroksi-3-[3-(1-naftilamino)-2-butenoil]-2*H*-piran-2-on-6-karboksilat (**2**) i etil 4-(4-hidroksi-6-metil-2*H*-piran-2-on-3-il)-2-(1-naftilamino)-4-okso-2-butenoat (**3**).

Strukture obaju spojeva određene su ogibom rentgenskih zraka na monokristalnim uzorcima. Molekule pokazuju više tautomernih oblika, mogućih u dva molekulska fragmenta, tj. u cikličkom (pironski prsten) i u pobočnom lancu. Pozornost je usmjerena na enaminske tautomerne ravnoteže *endo*-enola i *exo*-enola koji mogu postojati u oba tautomerna oblika u kristalnom stanju. Podaci dobiveni NMR spektroskopijom i rentgenskom difrakcijom potvrđuju *endo*-enolnu enaminsku formu kako u otopini tako i u kristalnom stanju.

Molekule karakteriziraju jake, π-delokalizacijom pojačane, intramolekulske vodikove veze N–H...O i O–H...O vrste. Molekule u cjelini nisu planarne, već pokazuju planarnost u središnjem heterokonjugiranom dijelu, dok su naftilni prstenovi gotovo okomiti u odnosu na središnji dio molekule.