THE STRUCTURE OF MIXED β-ARYL(FURYL)BENZOIN, 2-HYDROXY-2-(4''-CHLOROPHENYL)-1-(5'-*N,N*-DIMETHYLHYDRAZONYLFURYL-2')ETHANONE-1

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The structure of the thermal α→β benzoins isomerization product, 2-hydroxy-2-(4''-chlorophenyl)-1-(5'-*N,N*-dimethylhydrazonofuryl-2')-ethanone-1 has been proved by the XRD study. The possibility of the Me_2NN=CH-substituent conjugation with the carbonyl group via the furane ring take place due to the overall planarity this molecule fragment.

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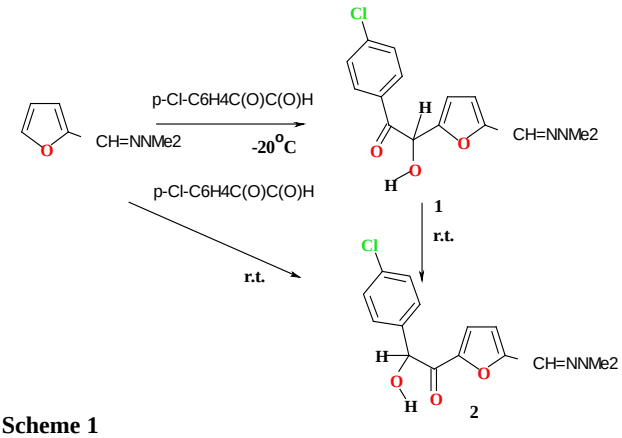
INTRODUCTION

Earlier we had reported that 4-chlorophenylglyoxal reacted with *N,N*-dimethylhydrazone of 2-furanecarbaldehyde yielding at -20 ^{0}C in ether solution the α-benzoin, 2-hydroxy-1-(4''-chlorophenyl)-2-(5'-*N,N*-dimethylhydrazonofuryl-2')-ethanon-1 **1**, which spontaneously isomerized at room temperature in β-benzoin, 2-hydroxy-2-(4''-chlorophenyl)-1-(5'-*N,N*-dimethylhydrazonofuryl-2')-ethanone-1 **2.**[1] The β-benzoin **2** is only product of the 4-chlorophenylglyoxal reaction with *N,N*-dimethylhydrazone of 2-furanecarbaldehyde at room temperature.[1] The letter "α" had been used to indicate the less stable isomer, the letter "β" had been used to indicate the more stable isomer.[2]



Scheme 1

The α-benzoin **1** and β-benzoin **2** structures were established by the data of NMR ^{1}H and MS spectra[1]. But the β-benzoin **2** structure remained unstudied.

EXPERIMENTAL

2-Hydroxy-2-(4''-chlorophenyl)-1-(5'-*N,N*-dimethylhydrazonylfuryl-2')-ethanone-1 (2)

The solution of *N,N*-dimethylhydrazone of 2-furanecarbaldehyde (13.0 mmol, 1.795 g) in PhH (5 ml) was added to the boiling solution of 4-chlorophenylglyoxal hydrate (10.0 mmol, 1.866 g) in PhH (20 ml). The reaction mixture was boiled during 30 min, than it was kept at 20 °C during 2 days, than PhH was evaporated *in vacuo*, the residue was washed hexane (20 ml), PhH (15 ml), yielding 2.168 g (70 %) 2-hydroxy-2-(4''-chlorophenyl)-1-(5'-*N,N*-dimethylhydrazonofuryl-2')-ethanone-1 **2**, orange crystals, mp. 145-146 °C, after crystallization from CH_2Cl_2 mp. 150-151 °C (cf. with mp. 150-151 °C[1]), identify with the sample of **2**[1] by NMR ^{1}H and MS.

The crystals of **1** were grew from CH_2Cl_2, monoclinic, $C_{15}H_{17}N_2O_3Cl \cdot 0.25(CH_2Cl_2)$, at 298 K, a = 26.4863(19) Å, b = 5.7593(5) Å, c = 11.2223(9) Å, β = 103.999(8)°, V = 1661.0(2) Å^3, M_r = 325.01, Z = 4, space group C2, d_{calc} = 1.300 g/cm^3, μ(MoK_α) = 0.245 mm^{-1}, F(000) = 680. Data were measured using Xcalibur 3 diffractometer (T=298 K, graphite-monochromated MoK_α radiation, 2θ/θ scan, $2\theta_{max}$=58.36°).

The structures were solved by direct method using the SHELXTL PLUS program package.[3] Refinement against F^2 in an anisotropic approximation (the hydrogen atoms isotropic in the riding model with U_{iso}=nU_{eq} of worn atom, n=1.5 for HO-group and Me-group, n = 1.2 for other hydrogen atoms) by a full matrix least-squares method for 6445 reflections was carried out to wR_2=0.136 (R_1=0.071for 1887 reflections with F>4σ(F), S=1.07).

RESULTS AND DISCUSSION

The XRD study data are evidence of β-benzoin structure of 2-hydroxy-2-(4''-chlorophenyl)-1-(5'-*N,N*-dimethylhydrazonofuryl-2')-ethanone-1 **2** (Figure 1, Tables1, 2). The Me_2NN=CH moiety conjugates with the benzoin carbonyl group via the furan ring bonds. The Me_2NN=CH moiety, the furan ring and the carbonyl group are oriented in the same plane, whereby this conjugation becomes possible. The middle quadratic deviation of these atoms from the plane of the conjugated bonds is equal 0.036 Å.

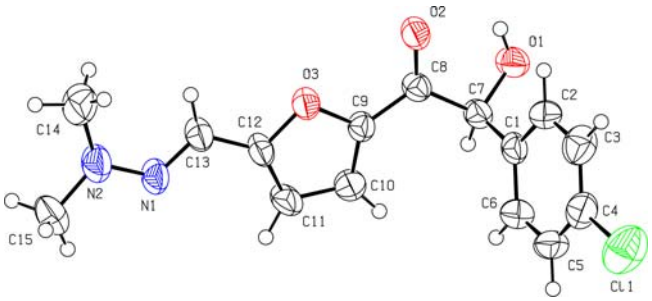
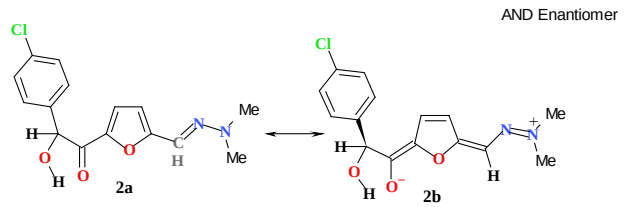


Figure 1. The structure of 2-hydroxy-2-(4''-chlorophenyl)-1-(5'-*N,N*-dimethylhydrazonofuryl-2')-ethanone-1 **2**.

This conjugation chain arises to charge transfer from nitrogen N(2) atom on O(2) oxygen atom. The structure of 2-hydroxy-2-(4''-chlorophenyl)-1-(5'-*N,N*-dimethylhydrazonofuryl-2')-ethanone-1 **2** can be more effectively described by the structure **2b** than the structure **2a** (Scheme 2).



Scheme 2

It was found that in β-benzoin **2** N(2) atom has the nearly planar configuration. The sum of bond angles centered at this nitrogen atom (Σß) is 359°. The N(1)-N(2) bond is shortened to 1.322(4) Å (cf. with N-N bond length 1.45 Å[4]). The O(2)-C(8) bond is some elongated to 1.236 (5) Å (cf. with for C=O bond length 1.21 Å[4]).

The C(8)-C(9) bond and the C(12)-C(13) bond are some shortened to 1.433(5) Å and 1.431(5) Å relatively toward ordinary $C(sp^2)$-$C(sp^2)$ bond (1.47 Å.[4]] All these structure data mean the domination part of the resonance form **2b** in the β-benzoin **2** structure. It may suppose that arising of the long chain of the conjugation between Me_2N- and C=O-moiety is the moving force of the thermal α→β benzoins isomerization yielding β-benzoin **2.**[1]

The *para*-chlorophenyl substituent is perpendicular oriented to this conjugation plane (the C1-C7-C8-C9 torsion angle is -89.7(4)°.

In the resolved crystal of β-benzoin **2** the C(7) atom has absolute *S* configuration.

In the crystals molecules of β-benzoin **2** are linked in the chains along the *b* crystallographic direction due to intermolecular bifunctional hydrogen bonds O(1)-H(1)…O(1^{i}) [i: 3/2-x,-1/2+y,2-z] (H…O 2.33 Å, O-H…O 133°) and O(1)-H(1)…O(2^{i}) (H…O 2.14 Å, O-H…O 150°). Also in the crystal σ-hole bond Cl(1)…O(3^{ii}) [ii: 3/2-x, -1/2+y, 1-z] (Cl…O 3.18, C(4)-Cl(1)…O(3) 167°, C(12)-O(3)…Cl(1) 101°) take place.

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