



# Potassium 3-oxo-2,3-dihydro-1*H*-inden-4-olate: Formation, molecular and electronic structure



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## ARTICLE INFO

### Article history:

Received 26 January 2016

Received in revised form

30 May 2016

Accepted 6 June 2016

Available online 8 June 2016

### Keywords:

7-Hydroxy-1-indanone

Chelation

NMR, IR, UV spectroscopy

X-ray

DFT, MP2 calculations

## ABSTRACT

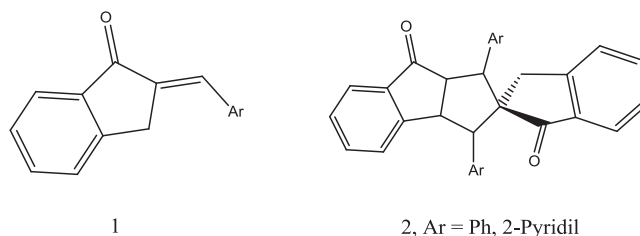
Unlike 1-indanone, 7-hydroxy-1-indanone does not enter the base-catalyzed condensation reaction with 1*H*-pyrrole-2-carbaldehyde but, instead, gives the salt, potassium 3-oxo-2,3-dihydro-1*H*-inden-4-olate dihydrate. X-ray analysis, NMR, IR, UV spectroscopy, DFT and MP2 calculations allowed to prove the chelate structure of the salt and to estimate the effect of chelation on the spectral properties as well as to explain the specific reactivity.

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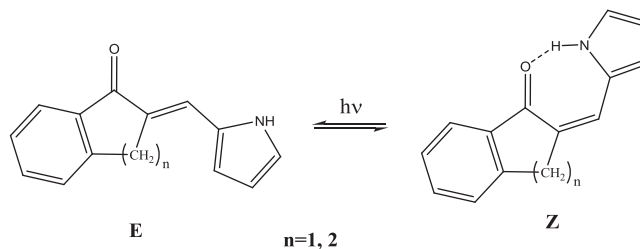
## 1. Introduction

Cyclic chalcones and particularly 2-arylidene-1-indanones (**1**) have a vast field of applications in biology, medicine, optics, rocket engineering and as building blocks in the synthesis of heterocyclic compounds and thermostable polymeric materials [1]. Their synthesis as a rule is straightforward and is carried out in most cases by aldol condensation of the corresponding aldehydes and cyclic ketones in the presence of strong bases like potassium hydroxide [2–6]. In the cases when the use of basic catalysts was inapplicable, the condensation could be achieved in acidic media [7,8].

Among the reactions of cyclic chalcones their dimerization under basic conditions leading to spirocyclic compounds **2** should be noted.



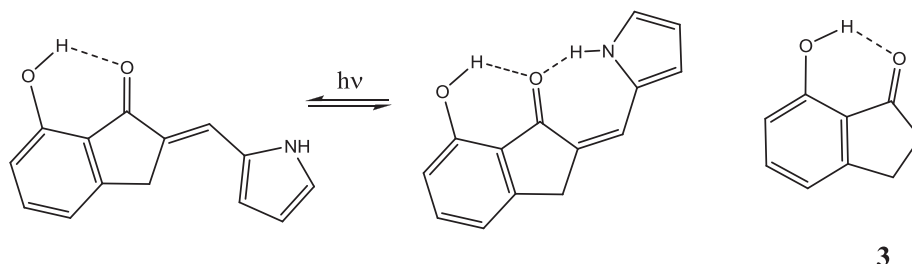
Of special interest is their photochromism, i.e. the ability to isomerize under UV irradiation [9–11]. Recently, we have shown that pyrrolylidene 1-indanone and -1-tetralone, which under normal conditions exist as *E*-isomers, when irradiated, isomerize to the *Z*-isomers possessing intramolecular hydrogen bond [12].



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Introduction of the hydroxy group in the 7-th position of the indanone fragment should result in the formation of a bifurcate hydrogen bond thereby affecting the relative stability of the *Z* and *E* isomers and shifting the equilibrium, assumingly, to the *E*-isomer.



With this in mind, and in order to prepare functionalized derivatives of pyrrolylidene-1-indanone we have tried the reaction of 7-hydroxy-1-indanone (**3**) with 1*H*-pyrrole-2-carbaldehyde. The reaction was carried out under the conditions successfully used for the reaction of 1-*H*-pyrrole-2-carbaldehyde with 1-indanone, that is, by reflux in ethanol in the presence of potassium hydroxide [12]. However, instead of the desired product of condensation, the potassium salt of the starting indanone **3-K** was isolated.

Apparently, the presence of 7-OH group prevents the crotonic condensation since the base abstracts the hydroxyl proton rather than the  $\alpha$ -CH proton to the carbonyl group. An alternative to this method is the reaction under acidic conditions, which we used for condensation of 1,3-indandione with pyrrolcarbaldehyde [13]. However, after overnight stirring at room temperature, the reaction mixture of pyrrolcarbaldehyde with 1-indanone was strongly resinified and contained mainly the reagents and only 5–8% of the product of condensation. Apparently, the difference in the behavior of 1,3-indandione and 1-indanone is due to a much higher reactivity of the former, so that it reacts with pyrrolcarbaldehyde faster (15 min reflux) than the latter is polymerized. Also, the mechanism of the acid-catalyzed condensation requires the attack of the protonated pyrrolcarbaldehyde on the enolized indanone molecule, but for 7-hydroxy-1-indanone the enolization is hindered because of the intramolecular hydrogen bond formation.

Therefore, the synthesis of 7-hydroxy-2-(pyrrolidin-2-ylmethylidene)-2,3-dihydro-1*H*-inden-1-one is a challenging task, which requires pre-protection of the hydroxyl group.<sup>1</sup>

## 2. Results and discussion

However, the unexpectedly isolated salt **3-K** is in itself of interest in view of possible existence in three alternatives forms: the salt of 7-hydroxy-2,3-dihydro-1*H*-inden-1-one (*a*), the salt of 3-hydroxy-1,2-dihydro-4*H*-inden-4-one (*b*), and the salt of chelate structure (*c*). Thus, the goal of the present work is to establish its structure experimentally both in solid state (X-ray) and in solution (NMR, molecular spectroscopy), and theoretically in gas phase (quantum mechanical calculations).

Although form *a* is apparently most aromatic and hence should be preferred over forms *b* and *c*, both the calculations of **3-K** and the X-ray experiment [14] for dihydrate **1-K**·2H<sub>2</sub>O showed the chelate structure (*c*). Note, that the structure and possible tautomerization in 7-hydroxy-1-indanone was studied earlier by laser excitation technique and it was concluded that the enol tautomer (which is similar to salt *b*) exists as a metastable species [15].

The X-ray determined and calculated (DFT, MP2) structures of 7-hydroxy-1-indanone **1** and its potassium salt **3-K** are given in Table 1. The two computational methods reproduce about equally well the experimental geometry (MP2 a little better), except the C1–O1···K···O2–C7 moiety. This discrepancy can be explained by the effect of intermolecular interactions affecting the geometry of a strongly polarized ‘salt part’ of molecule **3-K** but lacking in the calculated isolated molecules.

Interaction of potassium metal with oxygen atom(s) of the neighboring molecule should elongate the O1···K and O2···K distances in the crystal and, indeed, these bond distances, as measured by X-ray diffraction analysis, are 0.18–0.34 Å (MP2) or 0.23–0.37 Å (DFT) longer than those calculated for isolated molecules (Table 1).

In the crystal, potassium is seven-coordinate, like in others similar structures [17,18], being linked to two oxygen atoms of **3**, two water molecules forming the dihydrate molecule **3-K**·2H<sub>2</sub>O, and three water molecules from the neighboring molecules of **3-K**·2H<sub>2</sub>O. The range of the O···K distances (2.729–2.999 Å) is very close to the average distance in potassium complexes [19].

Both the experiment and calculations clearly demonstrate an equalization of the C1–C8 and C7–C8 bonds in going from **3** to **3-K**, which is indicative of extension of conjugation in the salt. This conclusion is supported by UV spectroscopy study. The solution of 7-hydroxy-2,3-dihydro-1*H*-inden-1-one **3** in ethanol is colorless and gives in the UV spectrum two bands at 250 and 315 nm belonging to  $\pi$ – $\pi^*$  transitions [20] (Fig. 1, left). Extension of conjugation of the  $\pi$ -system in salt **3-K** imparts yellow color to its solution in ethanol and results in appearance of a new band at 365 nm in the UV spectrum (Fig. 1, middle), which can be attributed to the charge transfer complex formation [20]. The solution of salt **3-K** in DMSO is red, and the charge transfer absorption band suffers bathochromic shift to 385 nm accompanied by a significant hyperchromic effect due to strong specific solvation of potassium cation by the oxygen atom of DMSO (Fig. 1, right).

<sup>1</sup> Indeed, during the reviewing of this paper, we succeeded in the synthesis of the target product of condensation, whose structural properties are currently being investigated and will be published elsewhere.

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