KETO–ENOL TAUTOMERISM IN THE SOLID PHASE. THE CRYSTAL STRUCTURE OF 4-CHLORO-2-(p-DIMETHYLAMINOPHENYL)-1,3-INDANEDIONE


Depending on the pH of the medium, 4-chloro-2-(p-dimethylaminophenyl)-1,3-indanedione may crystallize in three colored modifications. We have carried out an x-ray diffraction structural analysis of the red form. The crystallographic data of the adduct, C₁₇H₁₄NO₂Cl-C₂H₄O₂, are as follows: a = 13.505(5), b = 12.934(4), c = 12.526(4) Å, \( \gamma = 52.30(5)^\circ \), \( d = 1.39 \text{ g/cm}^3 \), \( Z = 4 \), space group \( P2_1/a \). A total of 1539 reflections were measured, \( R = 0.079 \). The molecule has zwitter-ionic structure

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{O} \\
\text{O} \\
\text{NR}_2
\end{array}
\]

The molecules are linked by N—H–O hydrogen bonds to form infinite chains. The other oxygen atom is hydrogen-bonded with acetic acid. Electrochromism was detected, accompanied by a change in color from red to black. Analysis of the crystal structure indicates that the change of color is related to a transition of the zwitter-ion form to a keto–enol form by a cooperative proton transfer.

2-Aryl-1,3-indanediones are organic acids capable of forming several colored modifications depending on the pH of the medium. Yellow and red modifications of 2-(p-aminophenyl)-1,3-indanedione have been isolated. Depending on the pH of the medium, 2-(p-dimethylaminophenyl)-1,3-indanedione crystallizes in yellow, red, or black forms [1]. Three tautomeric forms are possible for 2-arylindanedione in molecular crystals

\[
\begin{array}{ccc}
\text{C} & \text{H} & \text{O} \\
\text{N} & \text{R}_2 & \text{O} \\
& \text{O} & \text{O} \\
& & \text{NR}_2
\end{array}
\]

\[
\begin{array}{ccc}
\text{C} & \text{H} & \text{O} \\
\text{N} & \text{R}_2 & \text{O} \\
& \text{O} & \text{O} \\
& & \text{NR}_2
\end{array}
\]

\[
\begin{array}{ccc}
\text{C} & \text{H} & \text{O} \\
\text{N} & \text{R}_2 & \text{O} \\
& \text{O} & \text{O} \\
& & \text{NR}_2
\end{array}
\]

On the basis of spectral and analytical studies, Neiland and Linaberg [1] concluded that the yellow and red forms have structures \( a \) and \( b \), respectively, while the black form is a complex of internal salt \( b \) and enol form \( c \). However, there has been no direct structural evidence for these conclusions.

A further study of the derivatives of 2-(p-dimethylaminophenyl)-1,3-indanedione indicated that the presence of electron-donor NH₂ and NMe₂ substituents at C5 in the phthaloyl ring leads to disappearance of the polychromic forms in the crystalline state. These compounds are found in only in the diketo form [2]. On the other hand, electron-withdrawing substituents such as Cl, Br, I, and CN lead to the appearance of polychromism.

In order to elucidate the structural features for polychromism, we carried out a structural study of crystals of this interesting class of compounds.
In the present work, we carried out an x-ray diffraction structural analysis for 4-chloro-2-(p-dimethylaminophenyl)-1,3-indanedione (I) obtained in our laboratory in the red form [3].

Our x-ray diffraction structural analysis showed that I crystallizes with an equivalent amount of acetic acid. Figure 1 shows the molecular structure. Table 1 gives the bond lengths and angles.

Fragments A and B are coplanar. The extrusion of the chlorine atom from the $AB$ plane is 0.03 Å. One of the oxygen atoms (O3) in the indane ring lies in the plane, while the other (O2) extrudes by 0.05 Å in the same direction as the chlorine atom. The molecule as a unit is not planar. The plane of the phenyl ring forms an angle of 24.5° with the $AB$ plane. The C7—C15 (1.416 Å) and C14—C15 bond lengths (1.436 Å) indicate that these bonds have significant double bond character. The C15—C16 bond length (1.453 Å) is in good accord with the expected C($sp^2$)–C($sp^2$) bond length [4]. The C7—O2 (1.250 Å) and C14—O3 bonds (1.240 Å) are markedly extended in comparison with the C=O double bonds in indanediones [5]. The existence of an N6—H35 bond (found in the difference map) in conjunction with the bond length distribution noted above serve as evidence that the red form of I has zwitter-ionic structure b. Only one