



Single stranded helical chains of C–H··· π interactions further connected by halogen–halogen interactions of type I to construct supramolecular structure of (*E*)-5-(diethylamino)-2-[(4-iodophenylimino)methyl]phenol compound

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ABSTRACT

In this study, (*E*)-5-(diethylamino)-2-[(4-iodophenylimino)methyl]phenol compound was investigated from the point of stacking interactions assembling the supramolecular network, conformational isomerism and tautomerism. For this purpose, X-ray diffraction, FT-IR and UV/Vis spectroscopic techniques were used, giving the following structural and spectroscopic properties of the compound: The title compound has two conformers (anti and eclipsed) in the crystal structure resulting from rotation about C–N single bond of ethyl group. Both conformers prefer enol form in the solid state, adopting *E* configuration about the C=N double bond. The supramolecular architecture of the compound is constructed by two non-covalent interactions as C–H··· π and halogen–halogen interactions. The repetition of C–H··· π interactions is resulted in a single-stranded helical structure. The helical structures are further connected by C–I···I–C interactions of Type I to construct the two dimensional supramolecular network defined as (6,3)-net in Wells nomenclature. The title compound adopts both enol and keto forms in EtOH (a polar and protic solvent) while enol form is preferred in the solid state.

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1. Introduction

o-Hydroxy Schiff bases are of interest because of their thermochromism and photochromism in the solid state, which can involve reversible proton transfer from an oxygen atom to the neighboring nitrogen atom. Intramolecular proton transfer mechanism for excited-state and ground-state is still investigated intensively. Based on thermochromic and photochromic Schiff bases, it was proposed that molecules exhibiting thermochromism are planar while molecules exhibiting photochromism are non-planar [1,2]. Photochromic compounds are used as optical switches and optical memories, variable electrical current, ion transport through membranes [3]. In addition, they have widespread usage as ligands in the field of coordination chemistry [4] as well as in diverse fields of chemistry and biochemistry owing to their biological activities [5]. *o*-Hydroxy Schiff bases can exist in two tautomeric structures as enol and keto forms in the solid state [6,7].

In this study, (*E*)-5-(diethylamino)-2-[(4-iodophenylimino)methyl]phenol compound was studied focusing on stacking interactions assembling the supramolecular network,

conformational isomerism and tautomerism. For this purpose, molecular structure and spectroscopic properties of the compound were characterized by X-ray diffraction, FT-IR and UV–vis spectroscopic techniques.

2. Experimental methods

2.1. Synthesis

o-Hydroxy Schiff bases are prepared by the condensation reaction of primary amines with carbonyl compounds [8–10]. The same method was used in the synthesis of (*E*)-5-(diethylamino)-2-[(4-iodophenylimino)methyl]phenol compound. More specifically, the mixture of 5-(diethylamino)-2-hydroxybenzaldehyde (0.5 g, 2.59 mmol, 20 ml ethanol) and 4-iodoaniline (0.57 g, 2.59 mmol, 20 ml ethanol) were stirred for 1 h under reflux. The crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation from acetone (yield 76%; m.p. 384–385 K).

2.2. Instrumentation

The melting point was determined by StuartMP30 apparatus. FT-IR spectrum of the compound was recorded in the 4000–400 cm^{−1} region with a Bruker 2000 spectrometer using KBr

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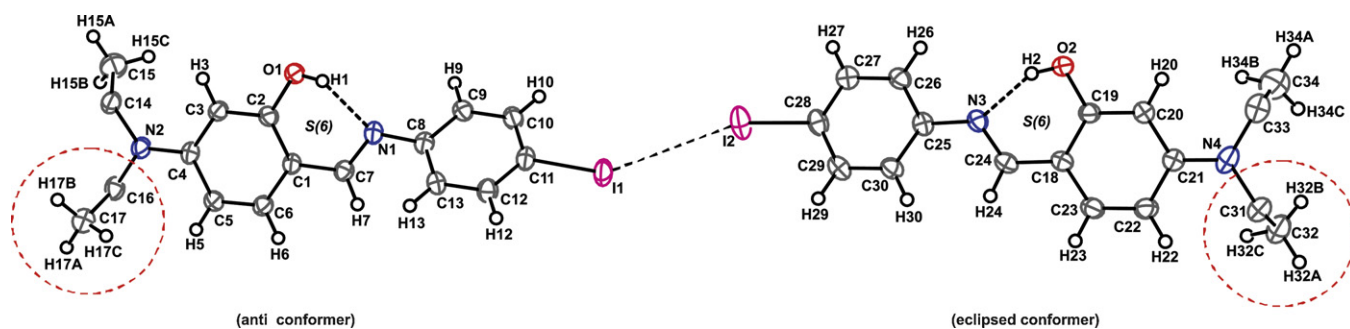


Fig. 1. A view of the title compound, showing anti and eclipsed conformers. H atoms of methylene groups were omitted for clarity.

pellet. UV–vis absorption spectra were recorded on a Thermo scientific BioGenesis UV–vis spectrometer using a 1 cm path length of the cell. Diffraction experiment was carried out at 130 K with an Xcalibur diffractometer using graphite monochromated MoK α radiation. The structure was solved by direct methods using SHELXS-97 [11]. The refinement was carried out by full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically. The H atoms except those bonded to O atoms were placed in geometrically idealized positions and refined by a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}_{\text{methyl}}) = 1.5U_{\text{eq}}(\text{C})$. The relevant crystal data, experimental conditions and final refinement parameters can be obtained from Cambridge Structural Database (CCDC: 801849). WinGX [12], ORTEP-3 for Windows [13] and MERCURY [14] softwares were used for molecular drawings and other materials.

3. Results and discussion

3.1. Structure determination

There are two crystallographically independent molecules in the asymmetric unit, which correspond to anti and eclipsed conformers of the title compound (Fig. 1). The two conformers are resulted from rotation about C16–N2 single bond of ethyl group. In conformer I (anti conformer), the ethyl groups are positioned in the opposite directions. On the other hand, the ethyl groups in conformer II (eclipsed conformer) are in the same directions. The torsion angle C4–N2–C16–C17 = 92.1(3) $^\circ$ in anti conformer while its corresponding value in eclipsed conformer is 78.5(4) $^\circ$. The characteristic bond distances and angles related to two conformers are comparatively given in Table 1. The compound prefers enol form in both conformers. The C=N double bond and C–O single bond distances compare well with reported values for similar compounds [15,16]. Both conformers adopt *E* configuration about the C=N double bond (Fig. 1). The strong intramolecular interactions involving phenolic atoms (O1, O2) and nitrogen atoms (N1, N3) constitute six-membered rings defined as *S*(6) in Etter's notation [17]. These hydrogen bonds are characterized by O1...N1 and O2...N3 distances of 2.613(3) Å and 2.595(3) Å (Table 1), being shorter than the sum of the van der Waals' radii for N and O [18]. It is known that there is a strong correlation between the strength of the H-bond and the delocalization of the system of conjugated double bonds, and the effect is qualitatively interpreted by resonance-assisted hydrogen bond (RAHB) model [19]. The observed O...N distances (2.613(3) Å and 2.595(3) Å) for the title compound are shorter than 2.656 Å reported for O–H...N in the class of RAHB [20].

The supramolecular architecture of the title compound is constructed by two non-covalent interactions as C–H... π and halogen–halogen interactions. The C–H... π interactions take place between methyl groups and phenyl rings (Cg). It should be noted that C–H... π interactions only involve the ethyl groups leading

to two conformers in the crystal structure. The repetition of intermolecular C17ⁱ–H17Bⁱ...Cg1ⁱⁱ (i: 5–x, 1.5+y, 2–z; ii: 2–x, 1.5+y, 1–z) and C34ⁱⁱ–H34Aⁱⁱⁱ...Cg2ⁱⁱⁱ (iii: x, 1+y, z) interactions is resulted in C₂²(18) chains (Fig. 2). Interestingly, the extension of these chains through [0 1 0] is resulted in a single-stranded helical structure with a pitch distance of 10.265 Å between iodide atoms (Fig. 2). One another interesting property is that single stranded

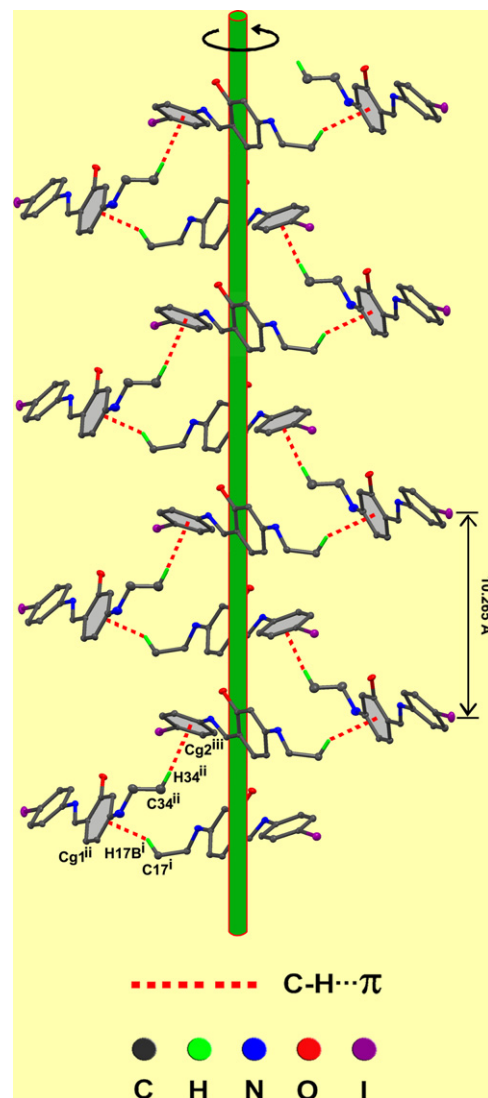


Fig. 2. The formation of a single-stranded helical structure in the crystal packing of the title compound by non-covalent C–H... π interactions [Symmetry codes: (i) 5–x, 1.5+y, 2–z; (ii) 2–x, 1.5+y, 1–z; (iii) x, 1+y, z].

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