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CRYSTAL STRUCTURE, ENERGY MINIMIZATION AND GEOMETRY OPTIMIZATION STUDIES OF 5-BROMO-1-ETHYL-INDOLINE-2,3-DIONE

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ABSTRACT: Isatin (1H-indole-2,3-dione) is an endogenous compound that has been identified in humans and possesses a wide range of biological activities, such as anxiogenic and sedative activities. A variety of biological activities are associated with isatin, including central nervous system (CNS) activities (Raj, 2012). The single crystal X-ray diffraction study of the title compound has been made and its structure is compared with the optimized structure obtained with MOPAC2016's PM7 algorithm. The title compound, $C_{10}H_8BrNO_2$, containing the isatin moiety crystallized with two independent molecules (A and B) in the triclinic space group *P*-1. The unit cell parameters are a=9.5293 (3) Å, b= 0.0581 (3) Å, c= 1.2138 (3) Å, α=78.921 (1)°, β=75.261 (1)°, γ= 85.151 (1)° with V=982.34 (5) Å^3 and Z=4. The structure is solved by direct methods using SHELXS-97 and refined by full matrix least square on F^2 to an R- value of 0.03 for 2982 reflections (I>2σ(I)) using SHELXL-2014. The total energy and dipole moment of the title molecule are computed as -2335.01 eV and 4.642 Debye respectively. The relative conformation about the bond joining the isatin moiety and the ethyl group of the compound is defined by the C1—N1—C9—C10 torsion angle, 78.9 (4)° and 86.7 (5)° in molecules A and B respectively, decreased to 72.41° in the isolated optimized structure. This indicates a greater twist leading to further separation between the isatin moiety and ethyl group and suggests that the crystal packing is influenced by the collective effect of the intermolecular interactions. The structural stability of the crystal is found mainly to be due to C—H···O interactions.

Chemical Context

Isatin containing compounds (1H-indole-2,3-dione) are found to show a range of biological functions such as anxiogenic and sedative activities. They serve as synthetically useful substrates to prepare wide range heterocyclic compounds including molecules of pharmacological significance [1]. As part of our interest in the identification of bioactive isatin compounds, the crystal structure determination of the title compound has been made. From the literature survey we come to know that the structure of the title compound has already been reported by another research group with similar interest [2]. However, to analyze exhaustively the conformation and packing interactions, we have re-determined the crystal structure at a temperature less by 3K and refined the model to a lesser R factor, weighted R factor and reflections to parameter ratio. The experimental details are given in Table-1. The conformation and geometry of crystalline molecules have been compared with those of that isolated molecule determined by semi-empirical calculations.

Structural Features

The chemical scheme and the molecular structure of the title compound are illustrated in Figure 1 and Figure 2 respectively. It crystallizes with two independent molecules A and B in the asymmetric unit. In each molecule the indoline ring system is nearly planar with the largest deviation from the mean plane being 0.014 (3) Å in molecule A and 0.040 (3) Å in molecule B. In each molecule the ethyl group is nearly perpendicular to the indoline ring system with C8—N1—C9—C10 torsion angles of 95.1 (3)° and 93.0 (3)° in molecules A and B respectively. In the crystal the two molecules are inclined to each other, making a dihedral angle of 6.27 (8)°. The fused rings in the isatin moiety described by the atoms N1A/C1A-C8A and N1B/C1B-C8B is slightly distorted from planarity, evident from the total puckering amplitudes being 0.024 (3) Å (for molecule A) and 0.067 (3) Å (for molecule B) [3].

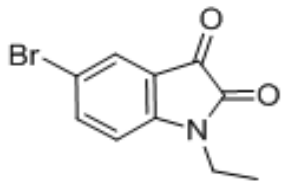

Fig. 1 Chemical scheme

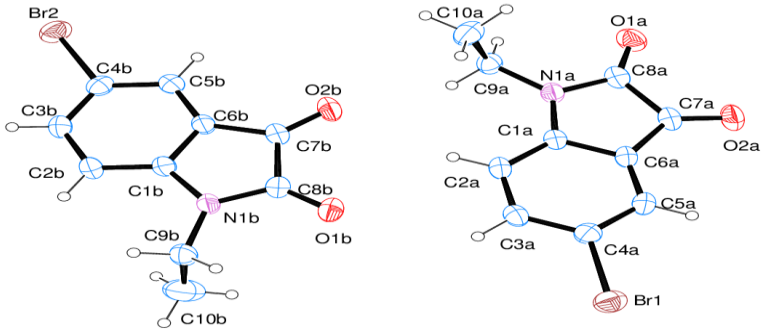

Fig. 2 An ORTEP view of the title compound with displacement ellipsoids drawn at 30% probability level. Hydrogen atoms are shown as small circles of arbitrary radii.

A superimposed fit of the molecules A and B gives a r.m.s. deviation of 0.078 Å and indicates the identical geometry between them. The corresponding bond lengths and bond angles of the isatin moieties of molecule A and B are almost equivalent and comparable with those in the related reported structures [4] – [8]. The molecules A and B are linked to one another by C—H···O hydrogen bonds forming A—B—A—B — chains along [0 1 -1] direction. The interaction between C2B and O2A via H2B forms a three dimensional network enclosing $R^1_2(7)$ ring motif (Fig.3) [9]. C—H···Br interactions form C3 chain motif along the *b*-axis. The details are given in Table 2. Parallel chains are linked via a weak parallel slipped π-π interactions [Cg1…Cg5^{i} = 3.6087(17) Å, Cg1 and Cg5 are the centroids of rings (N1A/C1A/C6A/C7A/C8A) and (C1B-C6B), respectively, inter-planar dist. = 3.3787 (11) Å, slippage = 1.268 Å]. Also a short Br···O contact [Br1…O1B: 3.177(2) Å) is observed in the three dimensional structure.

Conformational Analysis

In order to explore the conformational changes and effect of packing interactions, a semi-empirical PM7 calculation with MOPAC 2016 [10] have been done on the structure. In the calculations the molecule was assumed to be isolated and in an absolute vacuum, therefore resulting in calculated bond lengths, bond angles and torsion angles that are greater than those observed experimentally. The PM7 method gives the lowest values for the HOMO, LUMO energy levels and the dipole moment. The dihedral angle between the ethyl group and the indoline moiety is 93.3° showing the sustenance of the same conformation even in the isolated molecule. The total puckering amplitude of the isolated molecule is 0.0390 (3) Å, which lie between the values observed for the molecule in the crystalline state. The total energy and the dipole moment of the molecule are 2335.01 eV and 4.642 Debye, the HOMO and LUMO energy levels are −9.199 eV and −1.506 eV respectively. Structure solution and refinement are done using SHELXS-97 [11] and SHELXL-2014 [12] respectively. The thermal ellipsoid plot is made with ORTEP [13]. The packing plot and analysis of structure details have been carried out with PLATON [14].

Table 1: Crystal Data, Data Collection and Refinement

Chemical formula	$C_{10}H_8BrNO_2$	**Radiation type**	Mo Kα	**Temperature (K)**	293	**Z**	4
Crystal system, space group	Triclinic, P -1	**V (Å^3)**	982.34 (5)	**μ (mm^{-1})**	4.16	**M_r**	254.08
a, b, c (Å)	9.5293 (3) 10.0581 (3) 11.2138 (3)	**Crystal size (mm)**	0.18 × 0.15 × 0.11	**θ_{max} (°)**	26.5	**θ_{min} (°)**	2.0
α, β, γ (°)	70.921 (1) 75.261 (1) 85.151 (1)	**Crystal Colour**	Colourless	**Crystal Type**	block	**R_{int}**	0.031
Diffractometer	Bruker AXS kappa apex2 CCD	**No. of restraints**	0	**$\Delta\rho_{max}$ (e Å^{-3})**	0.38	**$\Delta\rho_{min}$ (e Å^{-3})**	−0.41
Absorbtion correction	Multi-scan SADABS	**No. of parameters**	255	**Melting Point (K)**	420	**F(000)**	504
R[$F^2 > 2\sigma(F^2)$], wR(F^2), S	0.030, 0.074, 1.04	**No. of measured, independent and observed [I > 2σ(I)] reflections**	14374, 4035, 2982	**T_{min}**	0.49	**T_{max}**	0.681

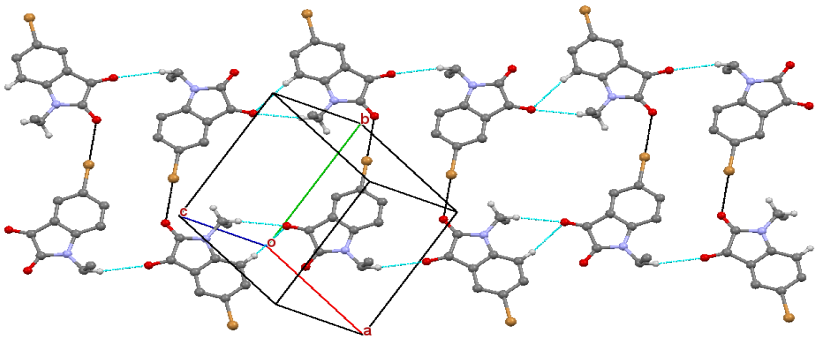

Fig.3 Packing diagram of (I) showing C-H···O hydrogen bonds and Br…O contacts as dashed lines.

Table 2: Hydrogen-bond geometry (Å, °)

D-H…A	D-H	H…A	D…A	D-H…A
C9A --H9A1 ..O2B^{i}	0.97	2.59	3.355(3)	136
C2B --H2B ..O2A^{ii}	0.93	2.59	3.511 (3)	170
C9B --H9B1 ..O2A^{ii}	0.97	2.54	3.368 (4)	143

Conclusion

The single crystal structure determination of the isatin derivative has been made with X-ray diffraction to a good degree of refinement parameter. The geometry of the molecular crystal has been compared with its optimized structure and and its conformation and packing have been analyzed. The relative conformation about the bond joining the isatin moiety and the ethyl group of the compound is defined by the C1—N1—C9—C10 torsion angle, 78.9 (4)° and 86.7 (5)° in molecules A and B respectively, decreased to 72.41° in the isolated optimized structure. The greater twist between the isatin moiety and ethyl group in the solid state suggests that the crystal packing is influenced by the collective effect of the intermolecular interactions. The structural stability of the crystal is found predominantly to be due to C—H···O interactions.

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