Solid State structure of a novel asymmetric azine: A search for new materials with NLO properties

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A broad analysis of new azine (1E,2E)-1-(4-ethoxybenzylidene)-2-(1-(4-ethoxybenzylidene)-2-(1-(4-nitrophenyl)ethylidene)hydrazine [NPT-HI], $C_{17}H_{17}N_3O_3$, is reported throughout a single crystal X-ray diffraction, spectroscopic investigations and DFT calculations. The results of *ab initio* calculations on (hyper)polarizabilities derived from iterative process confirmed this crystal as a good candidate for photonic devices and optical power applications. The asymmetric azine NPT-HI crystallizes in the centrosymmetric space group $P\bar{1}$ and has an almost planar conformation confirmed by C3-C4-C7-C8 dihedral angle (-18.5°), involving the methyl group. In addition, the non-linearity of the compound is evaluated by the more discrepant dihedral angles that are: C2-C1-N1-O1 (10.3°), C6-C1-N1-O1 (170.2°), C2-C1-N1-O2 (169.59°), C6-C1-N1-O2 (9.9°), C7-N2-N3-C9 (-165.17°), C3-C4-C7-N2 (161.16°), C5-C4-C7-N2 (-19.1°), C3-C4-C7-C8 (-18.5°) and C5-C4-C7-C8 (161.3°). When compared to the bond lengths involved in a conjugated system (≈1.38 Å), the N1-C1 bond has a greater value (1.465 Å) indicating nonexistence of electron transfer between the nitro group and adjacent phenyl ring. The crystal packing is stabilized by C-H···O interactions (Fig. 1) and is constituted of the stack of two-dimensional layer stabilized by such interactions. Each layer is formed of dimers stabilized by C15-H15···O2 and C9-H9···O2 interactions, which are linked by C14-H14···O1. Additionally, the C15-H15···O2 interaction is shorter than C9-H9···O2; it is consistent by the observed difference between the distances of both interactions (2.455 Å and 2.608 Å). Moreover, the analysis of the Hirshfeld surface of indexed form indicates the packing is also stabilized by CH···π interactions on a centrosymmetric dimmer. Such interactions are very important in the structural analysis of NPT-HI since the C-H···O interactions only form a two-dimensional layer that interact throughout C-H···π interactions. The layers are stacked through C17-H17A···Cg2 dimmer interaction, with a distance 2.913 Å between H17A-Cg2. The fingerprint contains different information about the crystal packing of NPT-HI. Being an organic molecule filled with hydrogen atoms, the H···H contacts constitute a high percentage in fingerprints (42.9%). Hydrophobic interactions (C···C and C···H contacts) are also observed; but features in fingerprint indicate that the spatial arrangement is not stabilized by π···π interactions. Added to this, the low contact density N···H (6.8%) and C···O (2,5%) confirms the absence of such interactions in NPT-HI.

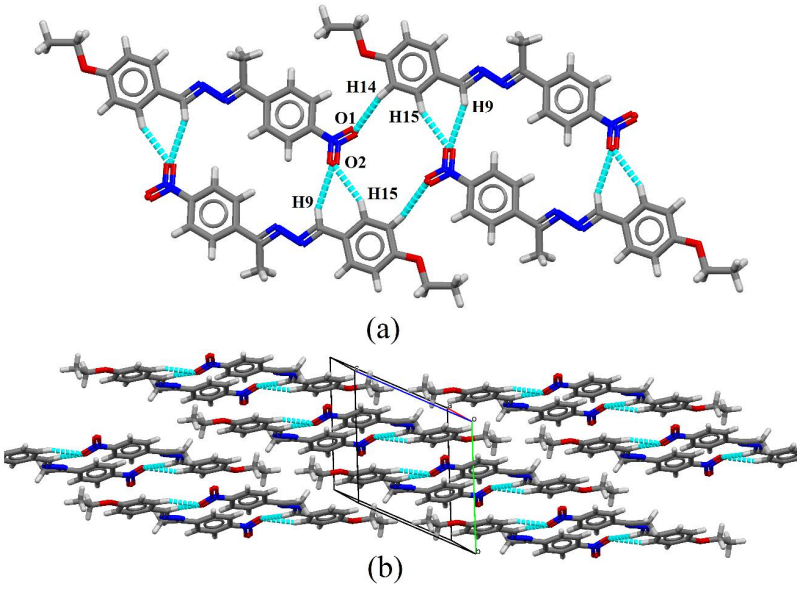

Fig.1: Representation of part of layer formed by C15-H15···O2, C9-H9···O2 and C14-H14···O1 interactions, revealing two dimers stabilized by C14-H14···O1 interaction (a) and crystal packing of NPT-HI (b).