



Structural and topological analysis of some isobutyl acetophenone azines sprouting out their asymmetrization effect



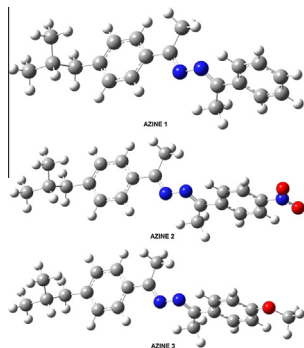
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HIGHLIGHTS

- 3 Asymmetrical p-isobutyl acetophenone azines were prepared and characterized.
- Asymmetrization effect was observed for the three azines from the computational study.
- Comparative analysis of computed structural properties votes for asymmetrization.
- Natural Population & Charge (NBO analysis) study supports the asymmetrization effect.
- The Charge density study (AIM analysis) emphasizes the asymmetrization effect too.

GRAPHICAL ABSTRACT



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ABSTRACT

In this research, three asymmetrical p-isobutyl acetophenone azine 1-3 named 1-(1-(4-isobutylphenyl)ethylidene)-2-(1-phenylethylidene) hydrazine, 1-(1-(4-isobutylphenyl)ethylidene)-2-(1-4-nitrophenylethylidene) hydrazine, 1-(1-(4-isobutylphenyl)ethylidene)-2-(1-4-methoxyphenylethylidene) hydrazine respectively are prepared and characterized by elemental analyses, FT-IR and NMR spectral studies. The stable optimized conformers of the asymmetrical azines (1-3) are predicted using density functional theory (DFT) method. The theoretical IR frequencies are found to be in good agreement with the experimental values. The asymmetrization effect is observed for the three azines 1-3 from their natural population analysis. The comparative analysis of the computed structural properties of the asymmetrical azines (1-3) and symmetrical p-isobutyl acetophenone azine is accomplished. The topological properties of electronic charge density are analyzed employing Atoms In Molecules (AIM) theory. The electron density (ρ) and Laplacian (∇^2_ρ) properties indicates the presence of two C—H...N— intramolecular bridges in the methoxy substituted asymmetrical azine 3 which paves way for the reduction of electron density in the aromatic systems of the azine 3. Nonlinear optical behavior of the asymmetrical azines is also examined by the theoretically predicted values of dipole moment (μ), polarizability (α_0) and first hyperpolarizability (β_{tot}). The α_0 and β_{tot} values clearly depicted that the azine 2 is found to have a good non-linear optical (NLO) property than 1 and 3. The azine 2 is found to be NLO active when it had been subjected to experimental second harmonic generation (SHG) test. The UV-Visible methods are also used to characterize the synthesized azines 1-3.

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1. Introduction

Ibuprofen is the active ingredient in a number of pain relievers, e.g. Advil, Motrin, and Nuprin. p-isobutyl acetophenone (IBAP), the

starting material for the synthesized asymmetrical azines (1–3) in this article has the pharmaceutical importance of synthesizing Ibuprofen. Several articles have been published on the conversion of this IBAP into the corresponding alcohol, ether, acids and hydrocarbons [1a–1c]. These products of IBAP are found to have good biological properties and used as precursors for the synthesis of non-steroidal anti-inflammatory drugs.

Azines are products of condensation between a molecule of hydrazine and two carbonyl compounds. Azines are designated symmetrical or asymmetrical azines, respectively, if the two carbonyl compounds from which the azine derived are the same or different. Azines are receiving increased interest for their ability in bond formation reactions [2–5], their biological properties [6], in the design of liquid crystals [7] and other material applications [8–10]. Azines have been used extensively as ligands for the synthesis of novel organometallic compounds [11–13]. In spite of these synthetic utility, azines have good electronic, linear and non-linear optical properties [14–17]. Asymmetrical azines with acceptor and donor groups in the para positions of the benzene rings on opposing ends of the hyperpolarizable-electron system may be excellent candidates for NLO materials and this is ensured by preliminary experimental and theoretical data [18]. Asymmetrical azines have greater NLO response. Hence such a pharmacologically important compound IBAP is converted to asymmetrical azines which can extend its area of application in material chemistry too. The synthesized asymmetrical azines (1–3) are characterized by elemental analyses, FT-IR, mass and NMR spectral studies. Several theoretical analyses have been carried out for isomeric forms of these azines [19–22].

In this study, the asymmetrization behavior of the azines 1–3 are elicited by the natural populations determined from the Natural bond orbital (NBO) analysis and the comparative analysis of the structural properties of the optimized structure of the asymmetrical azines(1–3) and symmetrical 4-isobutyl acetophenone azine. The AIM analysis of the azines 1–3 reveals the presence of intramolecular hydrogen bonding in the azine 3. The B3LYP level of calculations available in Gaussian 03 software package is used for computational investigation of the synthesized asymmetrical azines (1–3).

2. Materials and methods

2.1. Synthesis

The Ibuprofen precursor p-isobutyl acetophenone is obtained from Shasun Pharmaceuticals, Puducherry, India. About 1.9 mL of IBAP (0.01 mol L^{-1}) and 4.9 mL of hydrazine hydrate (0.1 mol L^{-1}) is taken in a round bottomed flask. To this mixture 1 mL of glacial acetic acid is added. The mixture is refluxed for about an hour. The refluxed product is cooled and the excess of hydrazine present is removed using separatory funnel method using diethyl ether and distilled water. Hydrazine hydrate goes into the aqueous layer being insoluble in diethyl ether. The ether part is collected. The ether part is evaporated and the product is then refluxed with 1.2 mL of acetophenone (0.01 mol L^{-1}) for about one hour on the same day to avoid the formation of symmetrical azine of p-isobutyl acetophenone. The product is cooled in ice to get yellow precipitate. The whole process is done in a single day. Unsymmetrical azine (1) is obtained by subjecting the yellow precipitate to a column chromatography using benzene/pet-ether (1:1) as solvent. The other two unsymmetrical azines (2, 3) are synthesized in the same manner by using 1.7 g of 4-nitroacetophenone (0.01 mol L^{-1}) and 1.5 mL of 4-methoxyacetophenone (0.01 mol L^{-1}) respectively in the place of acetophenone. The obtained three unsymmetrical azines are recrystallised in ethanol. The yield is calculated by

considering the p-isobutyl acetophenone as the starting material and presented in Table 1. The melting point of the azines is determined and the range is given in Table 1. The synthesized azines are subjected to elemental analysis and the results are given in Table 1. The scheme of preparation is given in Fig. 1.

2.2. Spectral measurements

The 32 scan number IR spectra of the azines with 4 cm^{-1} resolution are recorded in a range of $400\text{--}4000 \text{ cm}^{-1}$ on a NICOLET AVATAR 330 FT-IR spectrometer. The sample has been mixed with KBr and the pellet technique is adopted to record the spectra. NMR spectrum is recorded at 500 MHz on a Bruker NMR at ambient temperature in CDCl_3 . Elemental analyses of the compounds are performed with Vario EL-III instrument. The UV-Visible spectrum of the three azines is recorded in SHIMADSU UV-1800 UV-Visible Spectrometer using N,N-Dimethyl formamide as solvent at ambient room temperature.

3. Computational details

All calculations were done at density functional theory (DFT) level on a personal computer using Gaussian 03 W program package [23]. DFT calculations are less time consuming and include a significant part of the electron correlation leading to good accuracy. The calculations were carried out with the Becke's three-parameter exchange functional with LYP correction (B3LYP) and the basis set 6-311++G(d,p) are used. The computational work has begun with the performance of the potential energy scan for the precursor p-isobutylacetophenone which shed light on the complete geometry optimizations of the synthesized azines and the conformers at minima are characterized for the calculation of the vibrational frequencies, the first hyperpolarizability (β_{tot}), polarizability (α_0) and dipole moment (μ) values. The gauge-independent atomic orbital (GIAO) ^{13}C and ^1H chemical shift calculations for the synthesized azines in CDCl_3 phase are also made by same method. The gauge-independent atomic orbital (GIAO) method has been first adopted for quantum chemical NMR shift calculations by Ditchfield [24]. It has been successfully applied to the calculations of chemical shifts when performed with sufficiently large basis sets that keep electron correlation effects relatively small. The Natural Population analyses of the azines have been made by performing the NBO analysis at DFT level.

The topological properties of the electronic charge density have been also characterized using AIMALL software package.

4. Results and discussion

4.1. Conformational analysis

The main precursor of these new unsymmetrical azines is p-isobutylacetophenone which is subjected to a potential energy surface scan (PES) using B3LYP/6-311++g (d,p) method to find out the geometry at minima. The potential energy surface scan has been performed by rotating the torsional angle C8–C7–C1–C2 from 0° to 180° in steps of 10° . The geometry which had the C8–C7–C1–C2 torsional angle 70° is found to be the most stable conformer of the compound p-isobutylacetophenone. The PES of p-isobutylacetophenone has been summarized in Fig. 2.

This PES of p-isobutyl acetophenone (Table 1S) shed light on the conformation of its derivatives. The E- and Z-isomers of N-p-isobutylacetophenyl hydrazine i.e., the hydrazone derivative of p-isobutylacetophenone are optimized using B3LYP/6-311++g (d,p) method. The E-isomer is found to be the stable isomer.

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