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Conformational landscape, stability, potential energy curves and vibrations of 1,2,3,4 tetrahydroquinoline

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ABSTRACT

The twisted conformer with the equatorial hydrogen of the NH group is computed to be the most stable conformer of tetrahydroquinoline in S_0 and S_1 states at various levels of quantum chemical computations. The planar structure for equatorial orientation of H atom is found to be higher by 4000 ± 800 cm^{-1} in S_0 and ~3000 cm^{-1} in S_1. For the axial orientation of H atom the barrier is 9500 ± 300 cm^{-1} in S_0 and ~8000 cm^{-1} in S_1. The twisting angle for the optimized conformer is $29^\circ \pm 2^\circ$ in S_0. Observed IR spectra corroborate well with the theoretical calculations. The characteristic low-frequency vibrations appear at 97 cm^{-1} and 154 cm^{-1} in S_0. The excited state structure differs from S_0 and is termed “half-twist”. Potential energy curves corresponding to twisting and bending motions, as well as the one connecting the two motions are found out. Frontier molecular orbital calculations associated with the electron density plots clearly identify the changes on the density on excitation. Molecular electrostatic potential is calculated and the sites of electrophilic interactions are noted. Hardnesses' and electrophilicities are calculated for all the conformers to check their relative stability. The maximum hardness principle and minimum electrophilicity principles are not valid for most of the conformers. Transition state is found to obey the minimum electrophilicity principle.

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1. Introduction

Tetrahydroquinoline (THQ) is found in numerous biologically active natural products and used as pharmacologically relevant therapeutic agents [1]. The nucleus of this molecule possess a wide range of biological activities, including psychotropic activity [2], anti malarial [3], anti-bacterial [4] *etc*. This is also used extensively for the treatment of Alzheimer's disease as platelet aggregation inhibitors [5]. These broad biological and pharmacological activities signify the importance of THQ and its various derivatives for extensive studies. But very few of them are oriented at the structure of this molecule in isolation and consequent changes occurring on excitation. To the best of our knowledge, only Guchhait et al. [6] have studied the structure of the bare molecule (THQ) experimentally through fluorescence excitation spectroscopy and multiphoton ionisation techniques. But, this study provides information only about the excited state only. Chen et al. [7] have studied the structure of THQ dyes for the improved performance of dye sensitized solar cells. The detailed information's about the optimized structures, transition states, potential energy surfaces and the vibrational signatures of THQ in S_0 are still lacking.

From the structural aspects, THQ is the nitrogen substituted derivative of tetrahydronaphthalene (THN). THN [8] and its oxygen and nitrogen substituted derivatives like tetrahydroisoquinoline (THIQ) [9], isochroman [10], chroman [11] etc. have shown interesting features due to their conformational landscapes and associated low frequency vibrations. Amongst these, THQ and THIQ have a complicated conformational behaviour due to the orientation of hydrogen atom associated with the NH group along with the respective orientation of the saturated six member rings. The hydrated clusters of THIQ have also shown cyclic and linear H-bonded structures [12] and a charge transfer band in emission spectra [13] in different solvents. The potential energy surface (PES) has played a key role in these cases. The vibrational frequencies changes with substitution and also vary within the conformational manifold of these molecules.

Quantum chemical calculations at various levels and molecular beam experiments [8] predict the “twisted” configuration to be the

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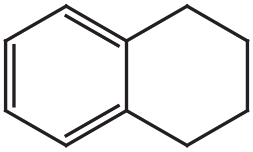
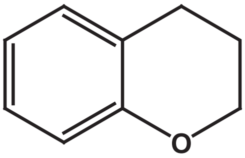
lowest energy conformer for THN in S_0 and S_1 states. The structural change is minimal on excitation. The motion of the CH_2—CH_2 groups yield the low frequency twisting and bending vibrational motions. THQ and chroman can be considered to be structurally similar, regarding the conjugation of the substituent atom to the benzene moiety. The oxygen and nitrogen substituted derivatives of THN are found to be less symmetric than it. The “twisted”, “bent” and the “planar” conformers of THN belong to C_2, C_S and C_{2V} point groups respectively. THQ is less symmetric and the corresponding conformers belong to (Fig. 1) C_1.

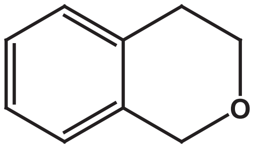
The closeness of atomic weights of NH and O atoms might be reflected in the closeness of low-frequency vibrations in THQ and chroman. The possible number of conformers is expected to be more in THQ, as the orientation of H atom of the NH group might have different orientation with respect to the molecular plane. Comparing chroman and THQ, the O atom in the former is replaced here by NH group, which not only has a lone pair but also it contains H atom, complicating the conformational manifold and reactivity compared to chroman.



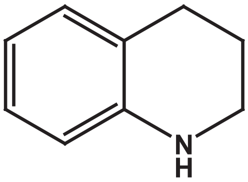
THN



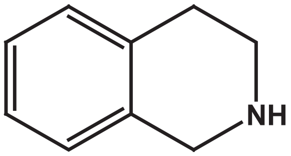
chroman



isochroman



THQ



THIQ

Guchhait et al. [6] has predicted the presence of only the twisted conformer of THQ in S_1 through supersonic jet spectroscopic study and semi empirical calculations done in S_0 only. It was presumed that the structure changes little on excitation as in THN.

We investigate the possible conformers of THQ for S_0 and S_1 states. Subsequently, we also look for the potential energy curves (PEC) connecting possible conformers and the possible transition states. The consistency of our calculations is checked through the comparison of observed and calculated IR spectra. The vibrational modes in S_0 are identified and assigned accordingly. The resemblance of the unsaturated ring vibrations to that of the benzene ring vibrations and the corresponding symmetries are also compared. A few of the vibrational modes in S_1 observed earlier [6] are compared with our calculations. Frontier molecular orbital calculations help in understanding the molecular electrostatic potential (MEP) and its site of nucleophilic and electrophilic attack. These calculations also show how the electron density changes on π-π^* excitation. This study might give some idea on the possible structures of water clusters with THQ.

To have a quantitative assessment on the reactivity and stability of the individual conformers, we calculate the qualitative chemical concepts like, electronegativity [14], hardness [15,16] and electrophilicity [17]. The hardness and electrophilicity are computed by applying Koopman's theorem [18]. In this process, we also check the applicability of maximum hardness principle (MHP) [19] and minimum electrophilicity principle (MEP) [20]. Apart from its enormous success, there are a number of cases where these principles are not valid [21–23] including the case of conformational stability [23,24]. It is also observed [20] that these values have a dependence on the basis sets and level of theory used for calculation. According to Koopman's theorem, operational definition [19] of electronegativity (χ) and chemical hardness (η) are given by $\chi = -\frac{1}{2}(E_{LUMO} + E_{HOMO})$ and $\eta = \frac{1}{2}(E_{LUMO} - E_{HOMO})$ where E_{LUMO} and E_{HOMO} are the energies of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital's (HOMO) respectively. The electrophilicity (ω) is defined as $\omega = \frac{\chi^2}{2\eta}$. Another parameter scaled hardness [20] is calculated as $\tilde{\eta} = \frac{\eta}{|\chi|^{1/3}}$.

2. Computational and experimental methodology

THQ of 98% purity was bought from Sigma Aldrich and used after thorough vacuum distillation to reduce any presence of water. FT-IR spectrum was recorded with a Perkin Elmer (Frontier) FT-IR Spectrophotometer, through KBr pellet (in 400–4000 cm^{-1} range) and polypropylene pellet (in 30-400 cm^{-1} range) through dispersion method. The spectra reported here were recorded with an instrumental resolution of 1 cm^{-1} during the full scan. The sample chamber is purged with dry nitrogen to minimise interferences of atmospheric water vapour.

The geometries of THQ in various conformations in S_0 were performed with Density Functional Theory (DFT), using the popular combination of Becke's three parameter hybrid exchange functional in connection with the Lee-Yang-Parr correlation functional, B3LYP [25,26]. The basis set 6-311++G (2d, 3p) [27] were used for the above calculations.

Additional geometry optimizations were performed using second order Møller-Plesset perturbation theory (MP2) [28] and Coupled Cluster (CC) [29] including single and double excitations, (CCSD) [30]. Various basis sets were used in MP2 calculations including correlated correctional ones like cc-pVQZ [31]. The

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