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Fluorescence excitation spectra, Raman spectra and structure of isochroman in its S_1 (π, π*) state

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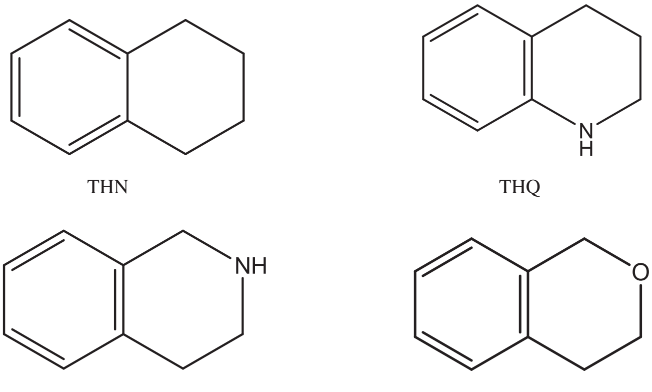
ABSTRACT

The laser induced fluorescence excitation (FE) spectra of jet-cooled isochroman is used along with the theoretical calculations to assign vibronic levels in 0–500 cm^{-1} region in the S_1 (π, π*) state. The origin of $S_0 \rightarrow S_1$ transition appears at 36,989 cm^{-1}. Six low-frequency vibrations are identified in the FE spectrum. These vibrations are compared to the corresponding levels in S_0. The *ab initio* DFT calculations show the molecule to be in the twisted structure in both S_0 and S_1 states with a high barrier to planarity. This barrier is theoretically calculated to be 3572 cm^{-1} in S_0 with the twisting angle as 33° and the corresponding values in S_1 are 3916 cm^{-1} and 31°. Raman spectra are well corroborated by the theoretical calculations. TDDFT calculations are done on the optimized geometries and compared with the experimental results.

1. Introduction

For last few years various groups including our group have been investigating the low-frequency vibrations of saturated ring systems [1–5] to unravel the structure and its conformational landscape. In this regard, the molecule tetrahydronaphthalene (THN), where a six-membered ring is fused to the benzene moiety and some of its derivatives have been extensively studied by our group [5–7] and Yang et al. [8], Autrey et al. [9] and Yang and Laane [10] using laser induced fluorescence excitation (FE) spectroscopy of these jet-cooled molecules. The FE and SVL spectra [6,8] as well as the quantum chemical calculations [9,10] at the *ab initio* level have showed that THN exist in the "twisted" configuration at its global minima of PES in S_0 and S_1. THN showed both twisting and bending vibrational motions associated with the puckering of CH_2–CH_2 groups. The nitrogen substituted derivatives of THN, tetrahydroquinoline [7] (THQ) and tetrahydroisoquinoline [5] (THIQ) were studied earlier. In the former, the nitrogen atom was in conjugation with the benzene moiety, while in the latter case it was non-conjugated. In this work, one of the oxygen substituted derivative of THN, isochroman, is chosen. The structure, conformational landscape and the low-frequency vibrations in S_0 and S_1 (π, π*) states are the main focus of our study.



As the CH_2 group in THN is being replaced by O atom, THN loses its symmetry. The "twisted", "bent" and the "planar" THN belongs respectively to C_2, C_S and C_{2V} point groups. But the reduction in symmetry in isochroman reduces all the corresponding structures (shown in Fig. 1) to C_1.

In THIQ [5], the orientations of the H-atom of the N–H bond have produced a number of conformers. Out of four possible inequivalent conformations, only two inequivalent "twisted" structures were observed. In THQ [7] only the twisted conformer was observed. Comparing THIQ and isochroman, the NH group in the former is replaced here by O atom, which not only has two equivalent lone pairs but also it does not contain any H atom. This

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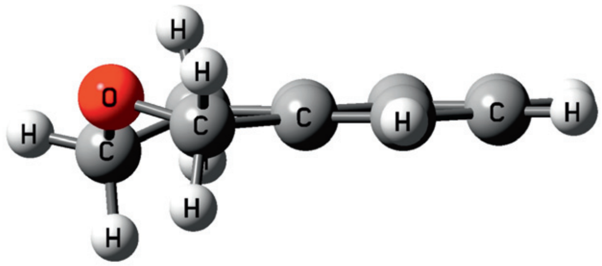
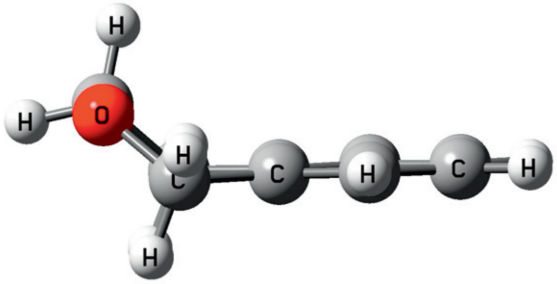
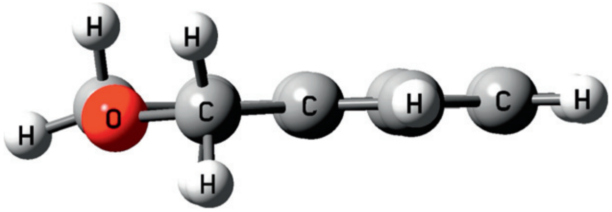


Structure I (TWISTED)



Structure II (BENT)



Structure III (PLANAR)

Fig. 1. The different structures of isochroman.

might simplify the complex conformer picture in it. These also suggest that this molecule might have only two possible conformations. Since the atomic weights of NH group and the O atom are quite close, the low-frequencies in both these molecules should have a close resemblance.

Isochroman bears a special pharmacological as well as biological significance. One of the derivatives [11] of isochroman have been used as a medicine of Alzheimer's disease. The isochroman bears a close resemblance to the basic unit of Vitamin E. It is the most important constituent of the precursors (tocopherols and tocotrienols) of Vitamin E. The earlier studies of isochroman were mainly directed at these orientations. The complete picture of its non-excited and excited configurations might shed more light in understanding the activity and reaction mechanism of this molecule.

2. Experimental

The compound isochroman was purchased from Aldrich Chemical Co. is of 99% purity. The details of the supersonic jet experimental set-up were described elsewhere [5]. In brief, the sample was heated to about 80 °C to increase sample vapor pressure and then expanded with helium carrier gas into a vacuum chamber through a 0.5 mm diameter orifice of a pulsed nozzle valve (General Valve Corp.) with a frequency of about 10 Hz. The background pressure of the chamber during the experiment was maintained at about 10^{-5} Torr by the operation of a 6 in. oil diffusion pump (Varian) backed by a mechanical rotary pump. The output of the Dye laser (PDL 3) pumped by a Nd: YAG laser (Quanta Ray DCR-11) was frequency doubled by a KDP crystal and intensity check was maintained by Autotrackker III (INRAD). The second harmonic output crossed the jet at about 15 mm downstream of the nozzle orifice. The laser induced fluorescence was collected perpendicular to both the laser and the jet directions. The signal was detected by an EMI-9781 R photomultiplier after passing through an optical filter to eliminate the scattered laser light, amplified in a current amplifier and then averaged by a Boxcar Integrator PAR model 264. The normalized output from the Boxcar was then recorded in a PC.

Raman spectra were recorded by a Spex double monochromator (model 1403) fitted with a holographic grating of 1800 grooves/mm and a cooled photomultiplier tube (model R928/115) from Hamamatsu Photonics, Japan. The sample was taken in a quartz cell and was excited by 514.5 nm radiation from a Spectra Physics Ar^+ ion laser (model 2020-05) at a power of 200 mW. Raman scattering was collected at a right angle to the excitation.

3. Method of calculation

All the *ab initio* Density Functional Theory (DFT) calculations were performed with Becke's 3 parameter hybrid exchange functional combined with Lee–Yang–Parr (LYP) gradient corrected correlation functional's with 6-311++G(d,p) basis set. The program package GAUSSIAN 03 [12] is used for geometry optimisations without any constraints. Configuration Interactions singles (CIS) calculations with the above mentioned basis set were performed on the optimized geometries in the ground state configuration without any constraints to have the geometry of isochroman in the excited state. This basis set was also used for calculating the frequencies in S_0 and S_1. The vertical transition energies ($S_1 \leftarrow S_0$) are calculated with TDDFT method. Theoretical Raman spectrum was also obtained with this basis set.

4. Results and discussions

4.1. Theoretical calculations and structure

4.1.1. Ground state (S_0)

Isochroman can exist in two inequivalent conformations. One of them is "twisted" (Structure I in Fig. 1) and the other one "bent" (Structure II in Fig. 1). The globally optimized structure in S_0 was found to be the "twisted" one (Structure I) for all the semi-empirical and *ab initio* calculations with different basis sets. The calculations on "bent" geometry (Structure II) always showed it to be higher in energy than the twisted structure by about 1200 cm^{-1}. This value can be compared to the corresponding values in THN [5], which was shown by Laane et al. to be 850 ± 150 cm^{-1}. The barrier to planarity (structure III) for isochroman was found to be 3572 cm^{-1} high in S_0 and 3916 cm^{-1} in S_1. The calculations regarding possible structures and their energies are enumerated in Table 1. The corresponding values in case of THN [5] were 4500 ± 600 cm^{-1} in S_0 and 5100 cm^{-1} in S_1. So, the barriers to planarity of isochroman in both S_0 and S_1 states are less than that of THN.

Table 1
Calculated relative energies (cm^{-1}) for different structures of isochroman in its ground (S_0) and excited states (S_1).

	S_0	S_1
Structure	B3LYP 6-311G++(d,p)	CIS 6-311G++(d,p)
Planar	3572	3916
Bent	1244	1314
Twisted	0	0