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Origins of threefold rotational barriers of molecule containing two methyl groups: Ethyl propionate as paradigm

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ABSTRACT

Origins of the rotational barriers of TG^- form of ethyl propionate molecule have been investigated. The barrier heights, as determined from the Raman spectrum, are estimated to be 2.88 and 3.17 kcal/mol for the $-CH_3$ (I) and $-CH_3$ (II) methyl groups of the molecule respectively. The detail analyses suggest that the combined relaxations of the C_2-C_3, C_2-C_4 bond lengths and $H_{10}-C_3-H_{11}$, $C_2-C_4-H_{13}$ angles together play a significant role to control the barrier heights of methyl CH_3 (I), CH_3 (II) groups of the molecule.

1. Introduction

Molecules can exist in various rotameric forms in nature. The different forms can be interconnected exclusively by rotations about the single bond/bonds. Rotations about the single bond/bonds play a pivotal role in drug design and in understanding the enzymatic reactions. The threefold torsional barriers arising due to internal rotation/rotations of methyl functional group/groups of molecules have been an active field of research both from the experimental and theoretical points of views [1–6]. Moreover, the origins of the torsional potential barriers have been an interesting field of research nowadays [7–11]. DFT and ab initio calculations are successfully utilized to understand the origin of the torsional potential barriers [12]. Diverse interpretations on the origin of the barrier have been reported, albeit no unanimous consensus has been arrived till date [13,14].

Ester of propionic acid is ethyl propionate (EP). As common to various other ester molecules, EP has strong odor which smells like that of pineapple. These molecules are the natural constituents of fruits like kiwis and strawberries [15]. EP molecule can exist in various isomeric forms i.e. Trans–Trans (TT), Trans–Antigauche (TG^-) [enantiomeric form Trans–Gauche (TG^+)], Antigauche–Trans (G^-T) [enantiomeric form Gauche–Trans (G^+T)], Antigauche–Antigauche (G^-G^-) [enantiomeric form Gauche–Gauche (G^+G^+)], and Gauche–Antigauche (G^+G^-) [enantiomeric form Antigauche–Gauche(G^-G^+)] forms. Raman and temperature dependent IR studies of the concerned molecule are recently reported by our research group [16]. The study aided by DFT and Car Parrinello Molecular Dynamics (CPMD) simulations reveal the predominant existence of TG^- form of the molecule at room, high and at low temperatures [16]. Considering the preferential existence of the TG^- form, this Letter is primarily focused to understand the origins of the barriers due to internal rotations of the methyl $-CH_3$ (I) and $-CH_3$ (II) containing rotor groups attached to the molecule. The rotational barrier heights of the two methyl tops of the molecule are also estimated from the Raman spectrum. The finale has been drawn on the basis of the unified approach to barrier energetics, natural bond orbitals, nuclear virial and relaxation analyses.

2. Experimental details and theoretical calculations

The Raman spectrum of EP molecule was obtained with a Renishaw Raman Microscope, equipped with a He–Ne laser excitation source emitting at a wavelength of 632.8 nm, and a Peltier cooled (−70 °C) charge coupled device (CCD) camera. A Leica microscope was attached and was fitted with three objectives (5×, 20×, and 50×). For these experiments, the 20× objective was used to focus the laser beam onto a spot of 1–2 μm^2. Laser power at the sample was 20 mW, and the data acquisition time was 30 s. The holographic grating (1800 grooves/mm) and the slit enabled the spectral resolution of 1 cm^{-1}.

The theoretical calculations were carried out using GAUSSION-09 program [17]. Optimization of the TG^- rotameric form of the EP molecule and vibrational frequencies at the pre-optimized geometry were computed by Møllar Plesset (MP2) [18] and Density functional (DFT) levels of theory. Becke's three parameter hybrid exchange (B3) [19] and Lee–Yang–Parr correlation functional (LYP)

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[20] were used for the DFT calculations. Cartesian displacement and the calculated (B3LYP/aug-cc-PVTZ) vibrational modes of the molecule have been displayed using GAUSS VIEW-03 software. The origins of the methyl rotational barriers of EP molecule were also carried out using MP2/6-311++G (2d,p) and B3LYP/aug-cc-PVTZ levels of theory. In this connection it may be firmly mentioned that reasonable barrier heights are reported to be reproducible for many molecules even by HF calculations using a modest 6-31G (d, p) basis set [21–23]. Natural bond orbital (NBO) analyses [24–27] have been carried out using Gen NBO 5.0 suit of software.

3. Results and discussion

The optimized molecular structure of the TG^- form of EP molecule is shown in Figure 1(a). The two methyl ($-CH_3$) groups of the molecule containing the carbon C_3 and C_7 atoms are discerned as I and II respectively. They are also marked in Figure 1(a). The Raman spectra of the EP molecule recorded in liquid state in two separate wave number regions are shown in Figure 2(i) and (ii). The enlarged Raman spectrum in the wave number range 180–350 cm^{-1} is also shown in Figure 2(iii) for visual clarity of the torsional modes involving the methyl $-CH_3$ (I) and $-CH_3$ (II) groups of the molecule. The theoretically simulated Raman spectra in 180–350 cm^{-1} range, as obtained from ab initio and DFT calculations are shown in Figure 2(iv) and (v) respectively. The Raman spectrum of the EP molecule, as shown in Figure 2(iii), is marked by weak humps at ~212 cm^{-1} (calculated at 212//203 cm^{-1} as obtained from MP2/6-311++G(2d,p)//B3LYP/aug-cc-PVTZ levels of theory) and 234 cm^{-1} (calculated at 247//237 cm^{-1} as obtained from MP2/6-311++G(2d,p)//B3LYP/aug-cc-PVTZ levels of theory). These bands are ascribed to the torsional vibrations stemming from the methyl $-CH_3$ (I) and $-CH_3$ (II) tops of the molecule respectively [16]. The cartesian displacement of the above mentioned vibrational signatures are also shown in Figure 1(b) and c. The torsional frequencies of the methyl $-CH_3$ (I) and $-CH_3$ (II) groups are utilized to estimate the threefold (V_3) rotational barrier of the respective methyl groups of the molecule by using the relation we used before [4]

$$V_3 = \frac{8}{9}\pi^2 \nu^2 I_r \tag{1}$$

where ν is the torsional frequency and I_r is the reduced moment of inertia of the respective methyl group [i.e. $-CH_3$ (I) and $-CH_3$ (II)] with respect to the center of gravity as oriented in the TG^- form of the molecule. The threefold barriers to internal rotations for the $-CH_3$ (I) and $-CH_3$ (II) groups of the EP molecule are estimated to be ~2.84 and 3.24 kcal/mol respectively. The rotational barrier heights of the methyl tops of the molecule, as obtained from the Raman spectrum, are in harmony with that reported for other molecules containing the methyl functional group [28].

Figure SI(a) and (b) shows the theoretically estimated shape of the potential energy curves as a function of torsional angle (φ) about the C_2–C_3 and C_6–C_7 bonds of the TG^- form of the EP molecule. The potential parameters for the internal rotation of the methyl groups were obtained by fitting one dimensional torsional potential function $V(\varphi)$ of the form:

$$V(\varphi) = \sum_{i=1}^{6} \left(\frac{V_i}{2}\right)(1 - \cos i\varphi) \tag{2}$$

where φ is the torsional angle and i represents the foldness of the barrier.

Supplementary Figure related to this article can be found, in the online version, at doi:10.1016/j.cplett.2014.07.075.

Table 1 shows the values of V_i ($i = 1, 2, \ldots, 6$) for the internal rotation of the methyl $-CH_3$ (I) and $-CH_3$ (II) groups of the TG^- form of the EP molecule at B3LYP/aug-cc-pvtz and MP2/6-311++G (2d,p) levels of theory. It is seen from Table 1 that both the B3LYP/aug-cc-PVTZ and the MP2/6-311++G (2d,p) levels of theory estimate the threefold barrier potential (V_3) very close to that estimated from the Raman spectrum.

However, apart from this, there exist perturbative instanton approach (PIA), which refers to the multidimensional tunneling

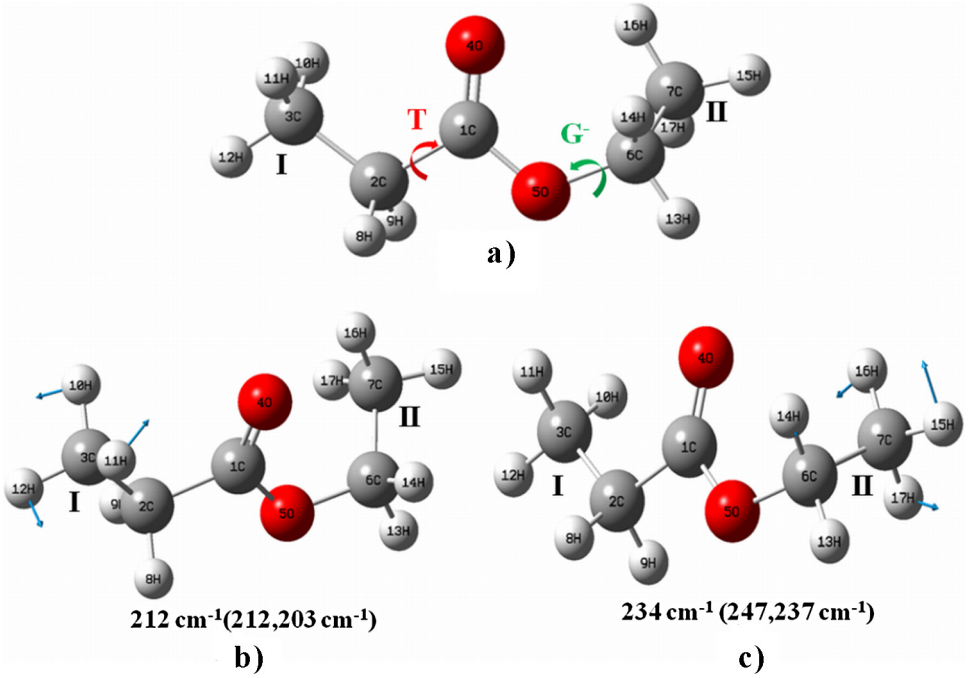

Figure 1. Optimized molecular structure (a) and cartesian displacement of the (b) 212 (calcd. 212 and 203 cm^{-1}) and (c) 234 (calcd. 247 and 237 cm^{-1}) vibrational modes of the TG^- conformer of EP molecule as obtained from MP2/6-311++G(2d,p) and B3LYP/aug-cc-PVTZ levels of theory. Numbers in the parenthesis indicate the calculated vibration frequency of the observed Raman band as obtained from MP2/6-311++G(2d,p), B3LYP/aug-cc-PVTZ levels of theory.