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Structure, intramolecular hydrogen bonding, and vibrational spectra of 2,2,6,6-tetramethyl-3,5-heptanedione

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ABSTRACT

Molecular structure, intramolecular hydrogen bonding (IHB) and vibrational frequencies of 2,2,6,6-tetramethyl-3,5-heptanedione (TMHD, also known as dipivaloylmethane), have been investigated by means of the density functional theory (DFT) calculations and IR and Raman spectroscopies. In addition, the geometry of the *cis*- and *trans*-enol conformers were also optimized at the MP2/6-31G** level of theory. The results are compared with those of acetylacetone (AA), benzoylacetone (BA), and dibenzoylmethane (DBM). The energy differences between two stable E1 and E2 chelated enol forms, calculated at different levels of theory, are negligible. Comparing the calculated and experimental band frequencies and intensities suggests coexisting of two stable *cis*-enol conformers in comparable proportions in the sample. Also the IR and Raman spectra of TMHD and its deuterated analogue were clearly assigned. According to the theoretical calculations, TMHD has a hydrogen bond strength of about 17.8–18.0 kcal/mol, calculated at the B3LYP/6-311++G** level of theory, which is about 3.0 kcal/mol stronger than that of AA. This enhancement in the IHB strength is also consistent with the experimental results of the band frequency shifts for the modes of OH/OD and O···O stretching and OH/OD out-of-plane bending frequencies. The theoretical calculations and spectroscopic results indicate that the IHB strength of TMHD is between those of AA and DBM.

1. Introduction

It is straightforward to show that a β-dicarbonyl, with at least one α-hydrogen, can transform bidirectionally into two enol forms by keto–enol tautomerism as illustrated in Fig. 1. In the *cis*-enol forms, because of the spatial shape of the molecule, it is possible for hydrogen atom of the hydroxyl groups to lie at a suitable distance and proper orientation for encountering an intramolecular hydrogen bond (IHB) and this stabilizes the *cis*-enol form of β-dicarbonyl [1–4]. Involved hydroxyl, carbonyl, and alkene functional groups of both enol forms contain six atoms that can contribute in a π-electronic resonance conjugation to induce a ring like structure referred to as a chelated ring. The noteworthy aim in ongoing research is to crosscheck the effects of different α or β-substitutions on the stability and IHB strength of the two mentioned enol forms. Malonaldehyde, MA, and acetylacetone, AA, are the simplest β-dicarbonyls and several experimental and theoretical studies have proven their asymmetrical structures due to the strong IHB in their most stable conformers, i.e. their chelated *cis*-enol forms [4–11].

The vibrational spectra of numerous molecules of this category have been investigated, where the existence of a strong IHB has been established in the chelated *cis*-enol tautomers [9–30].

Any factor, which affects on the electronic properties of the chelated ring, can change the IHB strength and the tautomerization equilibrium. It means whenever R_1 and R_3 substitutions in Fig. 1 are electronically and/or spatially different, one of two mentioned enol forms may be more stable. This fact has been established by theoretical and experimental studies such as quantum-mechanical calculations, IR, Raman, microwave, and NMR spectroscopies, X-ray, electron and neutron diffraction measurements on AA and its derivatives [10–15,31–38]. The structure and vibrational spectra of AA has been the subject of a few investigations, which support the existence of a strong IHB of chelating nature [12–15,20].

Additional studies have shown that the IHB strength increases when a bulky group and/or an electron-withdrawing substitution is posited in α position [30,39–43]. On the contrary, several experimental studies suggest that the substitution of electron-withdrawing groups, such as trifluoromethyl ($-CF_3$), in β position,

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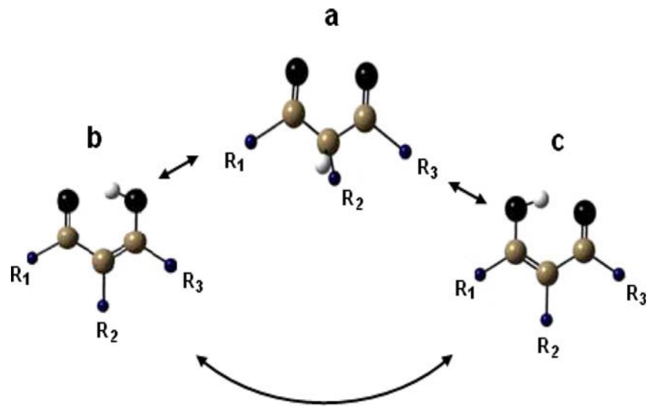

Fig. 1. The keto–enol tautomerism leads to two different chelated enol forms for β-dicarbonyls.

weakens the IHB and that electron supplying and bulky groups such as phenyl ($-C_6H_5$) and *t*-butyl ($-C(CH_3)_3$) make the IHB stronger [18,23,25,44–47].

Many β-dicarbonyl compounds exist exclusively in an enol structure in the pure and/or solution states [48–52]. The study of TMHD (known as dipivaloylmethane), with very bulky and electron donating characters of *t*-butyl group in both β positions, could be very interesting, since both bulky and electron donation characters of this group are likely to increase the hydrogen bond strength and at the same time favor the keto content of the sample. However, ^{1}H NMR spectroscopy studies indicate that TMHD is completely in the enol form in solution [47]. The NMR proton chemical shift of the enolated proton in TMHD is 16.27 ppm [47], which, as it is expected, is considerably higher than the corresponding value for AA (15.4 ppm) [20]. However, this chemical shift is much lower than that reported for DBM, dibenzoylmethane, (16.7 ppm) [25] but very close to the corresponding value for BA, benzoylacetone, (16.2 ppm) [23]. Furthermore, the X-ray study by Giricheva et al. [48] claimed that TMHD could exist in two enol forms with the symmetries of C_2v and Cs. The concluded $O\cdots O$ distance by these authors for the C_2v and Cs structure are about 2.40 and 2.60 Å. By comparing the NMR chemical shifts for TMHD with other similar compound a bond distance of about 2.50 Å could be concluded (near to that of BA [53]).

To the best of our knowledge, the TMHD vibrational spectra, theoretically or experimentally, have not been described previously. Also the experimental TMHD structure by Giricheva [48] is not consistent with the previous experimental and theoretical studies of similar compounds, which will be discussed later. Therefore, the aim of the present paper is to predict the detailed structure and vibrational spectra (harmonic wavenumbers, and relative intensities for Raman and IR spectra) of TMHD by means of density functional theory (DFT) levels. Then, the calculated stable conformations, geometrical parameters, the IHB energies, ^{1}H NMR shifts and vibrational spectra for TMHD will be compared with AA, BA, and DBM results [23,25]. These comparisons give a clear understanding for the effects of the substitution of the methyl groups of AA and the phenyl rings of BA and DBM by the *t*-butyl groups on the structure and hydrogen bond strength of TMHD. Also, since no vibrational spectroscopic data has been reported for TMHD, a clear vibrational assignment of TMHD is presented by considering the IR and Raman spectra of its deuterated analogue and theoretical calculations.

2. Experimental

TMHD was purchased from Aldrich chemical company. D_2-TMHD was prepared by mixing the non-deuterated sample with D_2O (3:1). After a few hours, the aqueous phase was removed and this procedure was repeated three times. The organic layer was then dried over anhydrous Na_2SO_4.

The FT-Infrared spectra were obtained in the range of 4000–500 cm^{-1} with spectral resolution of 2 cm^{-1} by coadding the results of 10 scans on a Bomem MB-154 Fourier Transform Spectrophotometer.

The Far-Infrared spectra in the 500–50 cm^{-1} region were collected employing a Thermo Nicolet NEXUS 870 FT-IR spectrometer equipped with a DTGS/polyethylene detector and a solid substrate beam splitter. The spectra were collected with a resolution of 4 cm^{-1} by coadding the results of about 60 scans.

All FT-Raman spectra from 3500 to 170 cm^{-1} were recorded using a 180° back-scattering geometry and a Bomem MB-154 Fourier Transform Raman spectrometer. It was equipped with a ZnSe beam splitter and a TE cooled InGaAs detector. Rayleigh filtering was afforded by a set of two holographic technology filters. Laser power at the samples was 500 mW. The spectra were collected with a resolution of 2 cm^{-1} by coadding the results of about 1000 scans.

All spectra were measured at room temperature. The spectra were considered in the neat liquid and CCl_4 solution.

3. Method of analysis

All quantum calculations were performed using Gaussian 03W package [54] program. All possible *cis*-enol conformations of TMHD were fully optimized at hybrid density functional B3LYP [55,56] levels using 6-31G**, 6-311G**, and 6-311++G** basis sets, BLYP [57,56], BPW91 [57,58] and G96LYP [59] levels at 6-31G** basis set. The electronic energies for the *cis*-enol forms were also determined at the second-order Møller–Plesset (MP2) level of theory [60,61] using 6-31G** basis set. The zero point vibrational energy, ZPE, corrections were obtained by using the results of frequency calculations at the B3LYP level with mentioned basis sets, without any scaling.

The vibrational frequencies of the *cis*-enol forms were calculated at the B3LYP/6-311G** level of theory. The assignment of the calculated wavenumbers is aided by the animation option of the GaussView 3.0 graphical interface [62] for the Gaussian program [54], which gives a visual presentation of the shape of the vibrational modes.

The assignments of the experimental frequencies are based on the observed band frequencies and intensities changes in the infrared and Raman spectra of the deuterated species and confirmed by establishing one to one correlation between observed and theoretically calculated frequencies.

Lorentzian function has been utilized for deconvolution of all IR and Raman spectra using Genplot package [63].

4. Results and discussion

4.1. Molecular structure

A β-dicarbonyl compound, with at least one alpha proton, predominantly exists as conjugated *cis*-enol form, stabilized by an intramolecular hydrogen bond. From the theoretical point of view, by considering the conformations of *t*-butyl groups in TMHD, with respect to the plane of the molecule and with respect to each other, 32 enol and 10 keto forms can be drawn for TMHD molecule. The structures of these conformers besides two H-centered transition states for proton transfer, their relative stabilities calculated at the B3LYP/6-31G** level, and the atomic numbering of the system are shown in Fig. 2. The *cis*-enol forms, in which the O–H and C_α=C bonds are in the *cis* arrangement, are designated as I and their cor-