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Conformational analysis, intramolecular hydrogen bonding, and vibrational assignment of 4,4-dimethyl-1-phenylpentane-1,3-dione

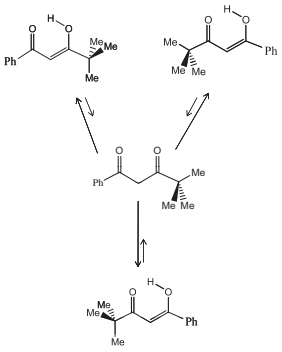
R. Afzali [a], M. Vakili [a,*], S.F. Tayyari [b], H. Eshghi [a], A.-R. Nekoei [c]

[a] Department of Chemistry, Ferdowsi University of Mashhad, Mashhad 91775-1436, Iran
[b] Department of Chemistry, Shahrood Branch, Islamic Azad University, Shahrood, Iran
[c] Department of Chemistry, Shiraz University of Technology, Shiraz 71555-313, Iran

HIGHLIGHTS

- All likely conformers and the structure of stable forms are theoretically studied.
- IHB strength of DMPD has been estimated by using DFT, AIM, and NBO method.
- Complete analysis of vibrational spectra and DFT investigations performed.
- The ^{13}C and ^{1}H chemical shifts are investigated theoretically and experimentally.
- All investigations confirm that DMPD's IHB is stronger than those of BA and DMHD.

GRAPHICAL ABSTRACT



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ABSTRACT

Molecular structure, conformational stabilities, and intramolecular hydrogen bonding (IHB) of 4,4-dimethyl-1-phenylpentane-1,3-dione (DMPD), have been investigated by means of density functional theory (DFT) calculations and experimental results. The geometries and electronic energies of different cis-enol forms of DMPD have been obtained with the *ab initio* (MP2 level) and DFT (B3LYP and TPSSh levels) methods, using various basis sets. The energy differences between three stable E1, E2, and E3 chelated enol forms are negligible. According to the theoretical calculations, DMPD has a hydrogen bond strength of about 16.8 kcal/mol, calculated at the B3LYP/6-311++G** level, which is about 0.7 kcal/mol stronger than that of benzoylacetone (BA). The theoretical and experimental results obtained for stable enol forms of DMPD have been compared with each other and also with those of BA and 5,5-dimethylhexane-2,4-dione (DMHD). The molecular stability and the hydrogen bond strength were investigated by applying the NBO, topological analysis, geometry calculations, and spectroscopic results.

Introduction

Hydrogen bonding is one of the weak forces, which is important in chemical and biological systems. In the intramolecular hydrogen bond (IHB), the proton donor and proton acceptor (the functional groups) belong to the same molecule. The cis-enol forms of β-diketones [1–4], diacylcyclopentadienes [5,6], and tropolones [7,8] form strong IHB which the strength of the hydrogen bond is assisted by π-electron delocalization system.

The β-diketone compounds with at least one α-hydrogen atom are capable to display keto–enol tautomerism. The position of the keto–enol equilibrium in this class of compounds is affected by different parameters such as temperature, nature of substituents, and solvents [9]. The cis-enol forms of β-diketones are engaged in an intramolecular hydrogen bond and are also capable to exist in

* Corresponding author. Tel.: +98 9153215410; fax: +98 511 8795457.
E-mail address: vakili-m@um.ac.ir (M. Vakili).

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different tautomeric forms. It is for several decades that the keto–enol tautomeric equilibrium, the structure of both keto and enol forms, and the nature of the intramolecular hydrogen bond in the enol form of β-diketones have been the subjects of intensive studies [10–13]. Some experimental and theoretical methods such as vibrational spectroscopy, ^{1}H NMR spectroscopy, diffraction methods, and DFT studies have been shown that electron supplying and bulky groups such as phenyl (—C_6H_5) and *t*-But (—$C(CH_3)_3$), respectively, in the β-position make the IHB stronger and increase the enol content [14,15]. However, substitution of these groups in α-position decreases the enol content [16,17]. Whereas electron-withdrawing substitution, such as trifluoromethyl (—CF_3) in the β-position, weakens the IHB, although increases the enol content [18,19]. The theoretical and experimental results confirm the existence equilibrium between the stable cis-enol forms for asymmetric β-diketones such as benzoylacetone (BA) and 5,5-dimethylhexane-2,4-dione (DMHD) [20–22]. However, in 4,4-dimethyl-1-phenylpentane-1,3-dione (DMPD), an asymmetric β-diketone, one terminal group is phenyl and the other is *t*-But group. Simultaneous existing of these two groups may have great effect on the hydrogen bonding in this system. Therefore, the investigation of the nature of intramolecular hydrogen bond in DMPD and comparing with that in BA and DMHD may provide significant insights into understanding the effects of simultaneous existing of these two terminal groups. In addition, the study of tautomerism and conformational analysis of DMPD is also potentially of interest.

The aim of the present paper is to predict the structure, IHB strength, tautomeric properties, the conformational stabilities, vibrational assignments, and ^{1}H and ^{13}C NMR chemical shifts by means of density functional theory (DFT) calculations. The theoretical results are compared with the experimental data. The obtained theoretical and experimental results will be compared with those for BA and DMHD molecules. Finally, the structure and IHB strength of stable cis-enol forms of DMPD will be compared with the corresponding stable forms of DMHD and BA, using Atoms-In-Molecules (AIM) [23] and Natural Bond Orbital (NBO) methods.

Experimental

DMPD was purchased from Alfa Aesar chemical company. D_2-DMPD was prepared by mixing the DMPD 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 NMR spectra were obtained on Avance Bruker-400 MHz spectrometers. All chemical shifts on NMR experiments are reported as ppm, using 2 mol% solution in $CDCl_3$ at 22 °C, ^{1}H NMR ($CDCl_3$): δ 16.547(b, 1H, OH, enol), 7.926(d, 2H(10, 14), J = 8.0 Hz), 7.551(t, 1H12, J = 6.8 Hz), 7.484(t, 2H(13, 11), J = 8.0 Hz), 6.344(s, 1H7, 97.1% enol), 4.226(s, 2H7, 2.9% keto), 1.293(s, 9H(15a-17c)) and for ^{13}CNMR: δ 202.94 (C2), 184.60(C4), 135.55(C9), 132.15(C12), 128.61 (C(10, 14)), 127.01 (C(11, 13)), 92.14(C3), 39.89(C8), 27.43(C(15-17)).

The observed ^{13}C chemical shifts at 133.48, 128.71, 47.79, and 26.24 ppm are attributed to the existence of trace keto form in the sample. The first two signals are assigned to the carbon atoms of the phenyl group, the signal at 47.79 ppm is assigned to the CH_2 group and the latter is attributed to the carbon atoms of the methyl groups. In contrast to the Nonhebel results [14], our NMR measurement shows 2.9% keto form which its characteristic bond observed at 4.226 ppm.

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

The Far-IR spectra in the 500–200 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 2 cm^{-1} by averaging the results of about 60 scans.

All FT-Raman spectra from 3500 to 200 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.

Method of analysis

All quantum calculations have been done by Gaussian 03 W [24], NBO 5.0 [25], and AIM2000 [26] softwares. The structure of all enol and keto tautomers of DMPD have been optimized at the B3LYP [27,28] level, using 6-31G** basis set. To confirm the relative stability of the cis-enol forms of DMPD, the obtained stable structures were also fully optimized at the B3LYP, using 6-311++G** basis set, the second-order Møller-Plesset (MP2) [29,30] and TPSSh [31], using 6-31G** basis set, levels. The zero point vibrational energy, ZPE, corrections were obtained at the B3LYP/6-311G** level, without applying 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 4.1.2 graphical interface [32] for the Gaussian program, 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 [33].

Orbital populations and Wiberg bond orders [34] were calculated with NBO 3.0 program implemented in Gaussian 03 W. The second order interaction energies (E^2) [35], and steric exchange energies [36] were performed at the B3LYP/6-311G** level using NBO 5.0 program [25], which applied the wave function information file generated by earlier version of NBO (3.0).

The absolute shielding for DMPD and Tetramethylsilane (TMS) have been obtained using the gauge-including atomic orbital (GIAO) method [37,38] at the B3LYP/6-311++G**//B3LYP/6-311++G** level. The predicted ^{1}H and ^{13}C chemical shifts are derived from equation $\delta = \sigma_0 - \sigma$, where δ is the chemical shift, σ is the absolute shielding, and σ_0 is the absolute shielding of TMS.

AIM 2000 software [26] was applied to obtain electron density at the hydrogen bond critical points according to Bader's atoms in molecules (AIM) theory [23] at the B3LYP/6-311G** level.

Results and discussion

Tautomerism and conformational analysis

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*-But group in DMPD, with respect to the plane of the molecule, 32 enol forms and 8 keto forms can be drawn for DMPD molecule (Fig. 1). Among them, only four cis-enol forms (E1-E4) are engaged in a six-member ring by