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Comparison the intramolecular hydrogen bond strength on BA and DBM with AA. A vibrational spectroscopy study

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Abstract:

Effect of phenyl substitution on CH₃ groups of acetylacetone has been studied by vibrational spectroscopy and DFT methods. It has been shown both theoretically and experimentally that this substitutions enhance the hydrogen bond strength.

Introduction:

The cis-enol forms of β -diketones are stabilized by a strong intramolecular hydrogen bond [1]. It has been shown that substitution of methyl groups in AA by phenyl groups increase the hydrogen bond strength [2-3]. By means proton chemical shift of enolated proton, δ OH [4], the following trend in hydrogen bond strength has been obtained:



The aim of the present paper is comparison the intramolecular hydrogen bond strength between BA and DBM with AA by vibrational spectroscopy and by means of DFT levels.

Method of analysis:

B3LYP/6-311++G** level of theory has been used for all calculations. IR and Raman spectra were measured in 50-3200 cm⁻¹ region for all compounds under study.

Results and discussion:

1. Molecular geometry:

According to the calculations, the O...O distance increases in steps by substitution of CH₃ groups by phenyl groups. This result is in excellent agreement with the experimental results, such as OH stretching, OH out-of-plane bending frequency shifts and the proton chemical shifts. The following trend in the hydrogen bond strength is concluded: AA < BA < DBM. This trend suggests that the π -systems, such as phenyl group, the increase intramolecular hydrogen bond strength.

2. The interpretation of the vibrational spectra:

OH stretching mode.

The intensity and broadness of this band are depended on the strength of the intramolecular hydrogen bond. Upon increasing the hydrogen bond strength its intensity decreases while its broadness increases [4].

This band in IR spectrum of DBM and BA is centered at about 2620 and 2650 cm⁻¹. Upon deuteration this band disappears and a new band with considerably narrower band width appears at 1950 and 1960 cm⁻¹, which indicates a ν OH/ ν OD ratio of 1.34 and 1.35. The higher frequencies of ν OH and ν OD and the higher



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ratio of ν_{OH}/ν_{OD} for BA in comparison with the corresponding values for DBM confirms weaker hydrogen bond in BA compared with that in DBM. The ν_{OH} band and ν_{OH}/ν_{OD} ratio in AA appears at 2750 cm^{-1} and 1.36, respectively [5-6].

OH out-of-plane bending

The medium and broad bands at about 965 and 957 (for DBM and BA) cm^{-1} is correlated with the theoretical band at 1000 and 994 cm^{-1} , which has mostly the O-H out-of-plane bending character. Upon deuteration, these bands disappear and a new band appears at about 720 cm^{-1} . The corresponding band in AA/D₂AA appears at about 950/707 cm^{-1} . These frequency shifts also support the following trend in the hydrogen bond strength:



In-plane chelated ring deformation:

The strong Raman bands at 688 cm^{-1} (for DBM) is attributed to one of the in-plane enol ring deformations. The corresponding bands in BA and AA appear at 672 and 640 cm^{-1} , respectively. The position of this band in the enol form of β -diketones has been correlated to the hydrogen bond strength [3, 5-7]. Therefore, the position of this band is also in excellent agreement with the other spectroscopic results.

O...O stretching mode:

The O...O stretching mode in the DBM appears at about 448 cm^{-1} . The corresponding bands in BA and AA occur at 396 and 366 cm^{-1} , respectively. These results also strongly support the aforementioned trend in the hydrogen bond strength.

Conclusion:

Comparison of the vibrational spectra and structural parameters of DBM with those of BA and AA reveals a considerably weaker H-bond in AA than that in BA and DBM. The observed OH/OD stretching and OH/OD out-of-plane bending modes are in good agreement with the calculated O...O distances and observed NMR results.

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