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Fluorine atom influence on intramolecular hydrogen bonding, isomerization and methyl group rotation in fluorinated acetylacetones

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ABSTRACT

1-Fluoro-pentane-2,4-dione (monofluoroacetylacetone, MFAA) is an asymmetric β-diketone with a strong intramolecular hydrogen bond similar to acetylacetone (AA) and its fluorinated analogs 1,1,1-trifluoro-(TFAA), and 1,1,1,5,5,5-hexafluoroacetylacetone (HFAA). The presence of a fluorine atom in MFAA has the potential to open an HF elimination channel in its gas-phase photochemistry motivating this study of MFAA hydrogen bonding by computer modeling using Density Functional Theory (DFT). As a context, we also report DFT modeling of AA and selected fluorinated acetylacetones: 1,1-difluoro-pentane-2,4-dione (difluoroacetylacetone, DFAA), TFAA, and HFAA. The most stable molecular structure for all three asymmetric β-diketones (MFAA, DFAA and TFAA) is the isomer with the fluoromethyl group proximal to the carbonyl carbon; in comparison to the proton transfer isomer, which has the fluoromethyl group proximal to the hydroxyl carbon, the carbonyl isomer is lower in energy by 5.1–5.5 kJ mol^{-1} (B3LYP/cc-pVTZ) and 2.1–3.7 kJ mol^{-1} (MP2/Aug-cc-pVTZ). We also report hydrogen bond strengths, barriers to proton transfer interconversion and barriers to rotation of the methyl/fluoromethyl groups. Our study, the first to report molecular structure information on MFAA and DFAA, indicates that the most stable chelated isomer of MFAA is not the structure with the strongest hydrogen bond as conventionally determined. Our modeling also reveals a coupling between proton transfer isomerization and methyl group rotation, and an unexpected double-minimum potential for the rotation of the fluoromethyl group of MFAA.

1. Introduction

The group of compounds known as β-diketones are well-known to exist in a keto-enol equilibrium [1,2]. This equilibrium depends on the properties of the substituents on the chelated ring of the enol form [3]. The simplest β-diketone, pentane-2,4-dione (acetylacetone or AA) and its readily available fluorinated analogs, 1,1,1-trifluoro-pentane-2,4-dione (trifluoroacetylacetone, TFAA) and 1,1,1,5,5,5-hexafluoro-pentane-2,4-dione (hexafluoroacetylacetone, HFAA) all favor the enol form, which is known to exhibit a strong intramolecular hydrogen bond [4–7]. In fact the hydrogen bond (HB) in these molecules is on the order of three times stronger than the HB found in water, a phenomenon tied directly to the degree of conjugation in the chelated ring such that it is termed a resonance-assisted hydrogen bond (RAHB) [6]. Although the presence of trifluoromethyl groups on the chelated ring weakens the HB, the enol form remains dominant in the gas phase. Recently Muyskens et al. [8] showed that both TFAA and HFAA undergo gas-phase HF elimination upon UV excitation, whereas the analogous H_2 elimination pathway in AA is not evident. Further understanding of the role that fluorine atoms play in the HB strength and the HF elimination pathway leads to our interest in 1-fluoro-pentane-2,4-dione (monofluoroacetylacetone, MFAA), which is the focus of this paper. A more general question is directed at β-diketones made asymmetric by the addition of fluorine atoms and how that influences the molecular structure and the orientation of the intramolecular hydrogen bond, IHB. We are ultimately curious about whether the molecular structure of MFAA will be poised to undergo the photochemical pathway, since it is possible that the presence of a single fluorine atom in a methyl group is sufficient to open this channel. In the case of an asymmetric acetylacetone, we wonder if the most stable molecular structure will require proton transfer as a necessary first step in the photoelimination mechanism?

Fig. 1 shows the molecular structure of MFAA including the atom numbering scheme and the relevant interconversion of structures due to three adjustments: proton transfer shifting the position of the IHB, rotation about the C—O bond to open the IHB in order to calculate the HB energy, and rotation of the fluoromethyl

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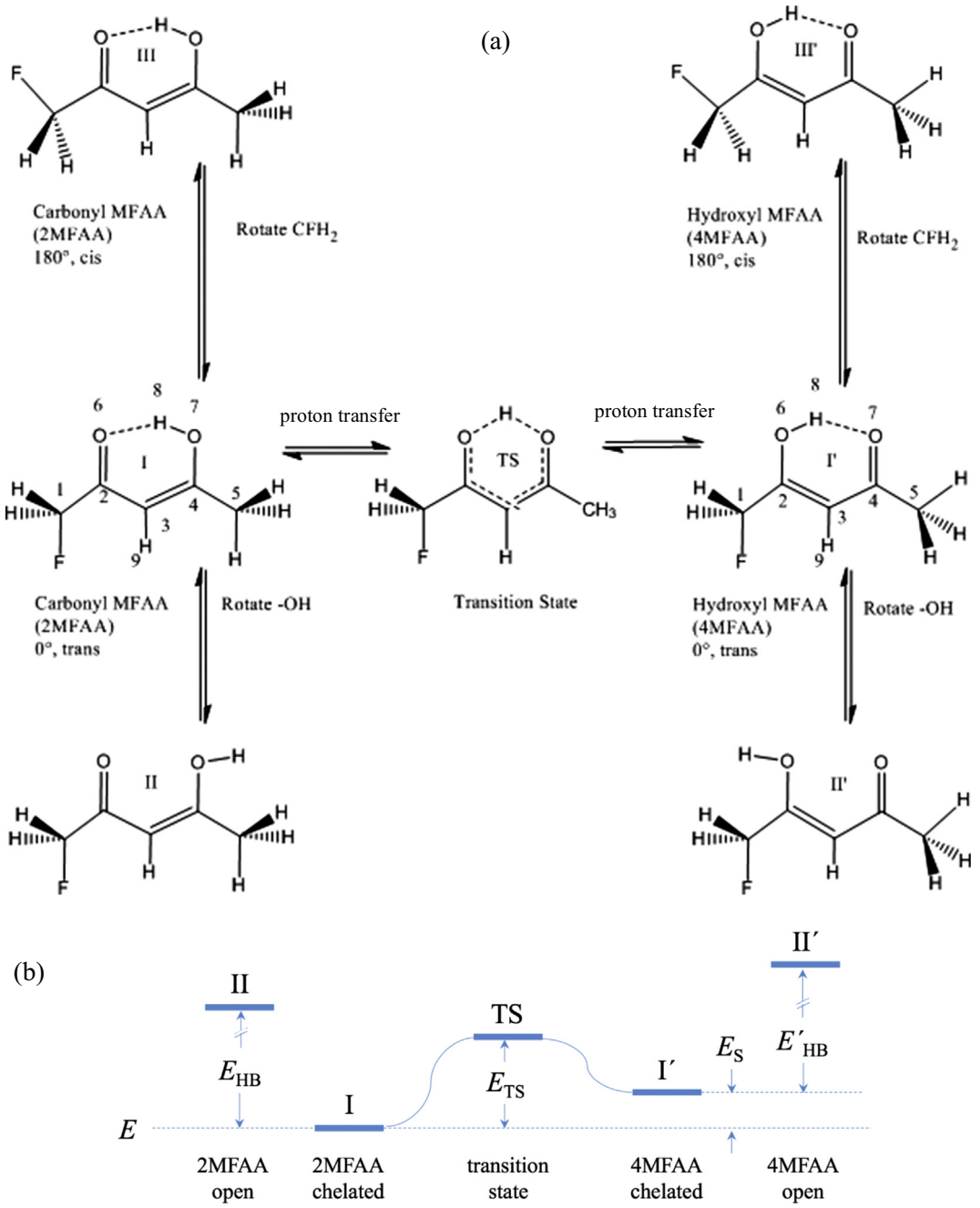

Fig. 1. Diagram illustrating the calculated structures for MFAA as representative for all calculated structures. (a) Molecular structures including the numbering and labeling schemes. In all structures the fluoromethyl group remains attached to C2. The proton shift via the transition state connecting I–I′ results in a shift of the carbonyl group from C2 to C4. The connection between structure I and II is rotating the OH group 180 degrees; the connection between structure I and III is rotating the fluoromethyl group to observe the rotation barrier(s). The prime indicates structures where C4 is the carbonyl carbon – in this case the label for the molecule has a prefix 4, for example 4MFAA. *Trans* refers to the staggered dihedral orientation of F with respect to O across the C1—C2 bond; (b) a scheme representing the relevant energy levels, E_S is the energy by which I is more stable than I′, E_{TS} is the barrier for proton transfer from I to I′, and E_{HB} is the energy of the hydrogen bond ($E_{II} - E_I$).

group. Fig. 1b illustrates the key energy differences that characterize the structures. While the primary focus in this report is on MFAA, we include 1,1-difluoro-pentane-2,4-dione (difluoroacetylacetone, DFAA) in our calculations to further explore the influence of fluorine atoms on the HB strength. For context, we also calculated the structural information for the well-studied AA, TFAA and HFAA. As such, our report describes five molecules, three of which involve an asymmetric fluorine distribution and therefore will have two distinct isomers, one more stable than the other depending on the orientation of the HB; Scheme 1 lists the eight structures reported in this study.

The questions then are which isomer with an asymmetric fluorine distribution will be favored, and is the strength of the HB simply related to the number of fluorine atoms? Scheme 2 shows the proposed mechanism for the gas phase photoelimination reaction of TFAA and HFAA reported by Muyskens et al. [8] adapted for MFAA. In this scheme, the orientation of the IHB is such that proton transfer is not required before C2—C3 rotation brings the fluorine atom into proximity of the proton leading to elimination. We note that in this configuration the fluoromethyl group is bound to the carbonyl carbon; we therefore refer to this as the carbonyl isomer (also labeled 2MFAA or 2DFAA), and proton transfer to the opposite