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STRUCTURAL CHARACTERIZATION AND PHOTOCHEMISTRY OF 2-CHLORO-6-FLUOROBENZOIC ACID ISOLATED IN A XENON MATRIX

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ABSTRACT

2-Chloro-6-fluorobenzoic acid (ClFBA) was studied by low temperature solid state FTIR spectroscopy in a Xe matrix and complemented by DFT(B3LYP)/6-311++G(d,p) calculations. According to the theoretical calculations, the ClFBA molecule exists in three different conformers. Conformers **II** and **III** are *ca.*17 kJ mol^{-1} higher in energy than the most stable conformer (**I**), and possess a *trans* carboxylic acid moiety, while form **I** has this group in the *cis* conformation. According to the energy data predicted theoretically only the conformer **I** was expected to be present in the cryogenic xenon matrix, a result that was confirmed experimentally. Attempts for *in situ* generation and detection of forms **II** and **III** by near-IR (2νOH; 6867 cm^{-1}) excitation of conformer **I** indicated that in solid xenon, once produced, these conformers promptly relax by tunneling to the most stable conformer. Laser UV (λ = 235 nm) excitation of matrix-isolated ClFBA led to prompt decarboxylation of the compound, with production of CO$_2$ and 1-chloro-3-fluorobenzene (ClFB), whose vibrational signatures could be doubtlessly identified in the spectra of the photolysed matrix.

Keywords: 2-Chloro-6-fluorobenzoic acid, Matrix isolation spectra, DFT(B3LYP) calculations, FTIR spectroscopy, 1-Chloro-3-fluorobenzene

1. INTRODUCTION

Benzoic acid (BA; $C_7H_6O_2$) is an aromatic crystalline compound which can be produced by oxidation of toluene with oxygen. It is used as a food preservative and receives also widely application in the treatment of certain diseases, for example, tinea, fungus, and acne [1]. BA crystals were found to be monoclinic [a = 5.393(3) Å, b = 5.003(2) Å, c = 21.689(12) Å, α = 90°, β = 98.51(3)°, γ = 90°], space group P2$_1$/c, with 4 molecules per unit cell (Z = 4) [2]. 2-Chloro-6-fluorobenzoic acid **(**ClFBA) crystals belong to the same space group as those of BA, with a = 3.7655(2) Å, b = 13.9660(7) Å, c = 13.2300(7) Å, α = 90°, β = 98.034(3)°, γ = 90°, and Z = 4 [3].

The dependence on temperature of the hydrogen-bonding disorder within the BA dimers was studied by neutron diffraction [2], and the IR spectra of both BA dimers and monomers were investigated in low temperature argon matrices [4]. Rotamerization of 2-chlorobenzoic acid (and of its OD isotopomer) in low temperature argon and xenon matrices was studied by IR spectroscopy by Nishino and Nakata [5], leading to observation of two low-energy conformers, both bearing a *cis* carboxylic group. *In situ* UV irradiation resulted in the production of the less stable *trans* carboxylic conformers, which were found to convert back by tunneling to the more stable *cis* forms [5].

In the present work, 2-chloro-6-fluorobenzoic acid was investigated by matrix isolation IR spectroscopy and quantum chemical calculations. The theoretical calculations showed that the molecule has 3 conformers, two of them being high-energy forms (**II**, **III**). The most stable conformer (**I**) was successfully isolated in a xenon matrix and characterized structurally and vibrationally. *In situ* irradiation experiments using narrowband near-IR (NIR) light (in an attempt to produce the high-energy

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conformers) or UV (to investigate the photochemistry of the compound) were undertaken, the last allowing for observation of decarboxylation of ClFBA with production of CO_2 and 1-chloro-3-fluorobenzene (ClFB).

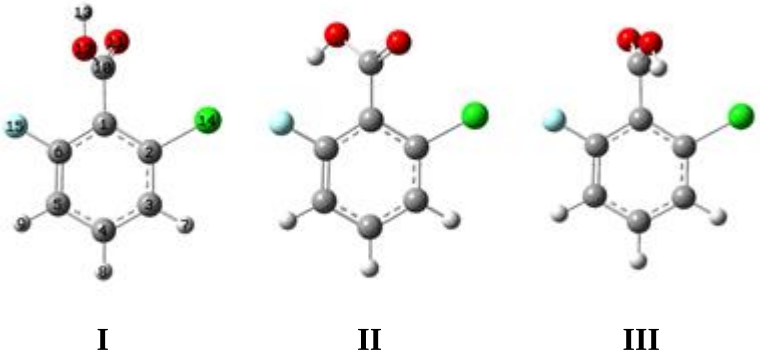
2. EXPERIMENTAL AND THEORETICAL METHODS

Commercial ClFBA, 98.0% purity was sublimated in a homemade furnace mounted inside an APD Cryogenics DE-202A cryostat, and co-deposited with the matrix gas (xenon). The deposition temperature was 20 K. Mid-IR spectra were recorded with a Thermo Nicolet 6700 FTIR spectrometer with 0.5 cm^{-1} resolution. Matrix-isolated ClFBA was irradiated with UV light (λ= 235 nm; fwhm = 0.2 cm^{-1}) provided by a nanosecond OPO/Nd:YAG laser system with 1−3 mJ pulse energy. The irradiation experiments in the NIR region used radiation produced by the idler beam of same OPO/laser system.

All calculations were performed using Gaussian 09 [6]. Geometries were optimized at the DFT(B3LYP)/6-311++G(d,p) level of theory [7-10]. Electronic spectrum was predicted by TD-DFT calculations carried out using same functional and basis function. The harmonic vibrational wavenumbers were calculated using the same theoretical level and, subsequently, scaled by 0.978.

3. RESULTS AND DISCUSSION

The conformational space of the ClFBA was investigated theoretically at the B3LYP/6-311++G(d,p) level of approximation. Three different conformers, all corresponding to doubly-degenerated forms by symmetry, were identified (Figure 1). The more stable conformer (**I**) has the carboxylic acid moiety in its intrinsically most stable configuration (*cis*), with the F···C–C=O dihedral equal to ±110º. In this form, the sterically more relevant acid –O– atom stays closer to the fluorine than to the chlorine atom, while the sterically less significant carbonyl oxygen atom (=O) points to the bigger chlorine atom. The structure of conformer **I** resembles that found in the crystalline state [3]. Conformers **II** and **III** are higher in energy than **I** by 17.1 and 17.3 kJ mol^{-1} with the relative electronic energy (16.0 and 16.5 kJ mol^{-1}, after consideration of zero-point corrected energy), respectively, and have a *trans* carboxylic acid moiety. In form **II**, the OH group is directed towards the fluorine atom, while in conformer **III** it points to the chlorine atom; calculations predict the corresponding F···C–C=O and Cl···C–C=O dihedrals to be ±129.5º and ±106.8º, these values being determined by the relative sizes of the F and Cl atoms. The calculations also indicated that in both conformers, **II** and **III**, no intramolecular H-bonds exist between the carboxylic acid group and the halogen substituents.



I **II** **III**

Figure 1. Conformers of ClFBA with adopted atom numbering used in this study (Color codes for atoms: gray, C; white, H; red, O; green, Cl; blue, F). All conformers have a symmetry-related form, resulting from the structures represented in the figure upon reflexion of the carboxylic moiety in the plane containing the ring.

The B3LYP/6-311++G(d,p) calculated potential energy profiles for rotation about the exocyclic C–C bond, assuming a *cis* and *trans* conformation of the carboxylic group, are shown in Figure 2. The figure shows only half rotation (F···C–C=O varying from 0 to 180º), since the second half of the rotation is related by symmetry with it. When the carboxylic group is *cis* (Figure 2, left panel) a single conformer is observed (**I**), while when the carboxylic group is *trans* two conformers are found (**II** and **III**; Figure 2, right panel), separated by a small energy barrier (0.25 kJ mol^{-1}). The energy barriers located at the planar conformations for a *cis* carboxylic acid conformation are both larger than 10 kJ mol^{-1}, the one corresponding to the structure where the carboxylic –O– atom is closer to the bigger chlorine atom being higher than that corresponding to the structure where that atom is located near the smaller fluorine atom (see Figure 2, left). In turn, for a *trans* carboxylic acid conformation the energies of the two planar structures are significantly different, with that where the OH fragment is near the fluorine *ortho* substituent being only *ca.* 5 kJ mol^{-1}, and the one where that fragment is nearby the chlorine atom amounting to *ca.* 14 kJ mol^{-1} (see Figure 2, right). These energy data allowed one to predict that the most stable conformer **I** should be present in the gas phase prior to deposition in a population close to 100%, so that only this conformer could be expected to be experimentally observed in the low temperature matrix isolation experiments.

Figure 3 presents the infrared spectrum of C1FBA isolated in a xenon matrix at 20 K, and compares it with the theoretically predicted spectrum for conformer **I**. The calculated data and the experimental wavenumbers are given in Table 1. In the simulated spectrum, the calculated wavenumbers were scaled by 0.978 and bands are Lorentzian functions with a fwhm = 1 cm^{-1}. The analysis of these data confirms the sole presence of conformer **I** in the matrix.

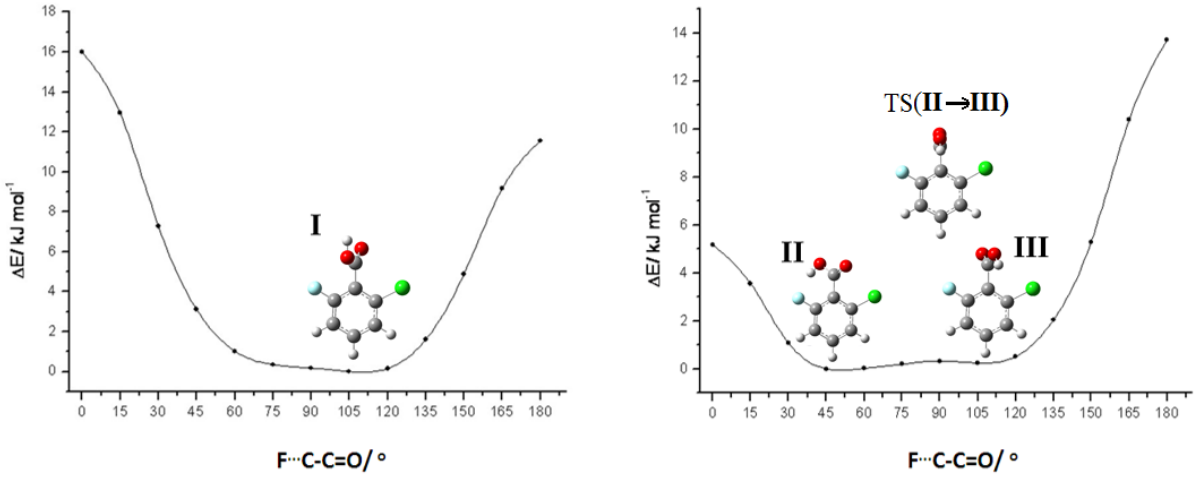


Figure 2. B3LYP/6-311++G(d,p) calculated relaxed potential energy profiles for internal rotation about the exocyclic C–C bond for *cis* (left panel) and *trans* (right panel) arrangements of the carboxylic moiety. Transition state structure (TS) is a maximum in energy connect the conformer **II** with the **III**.

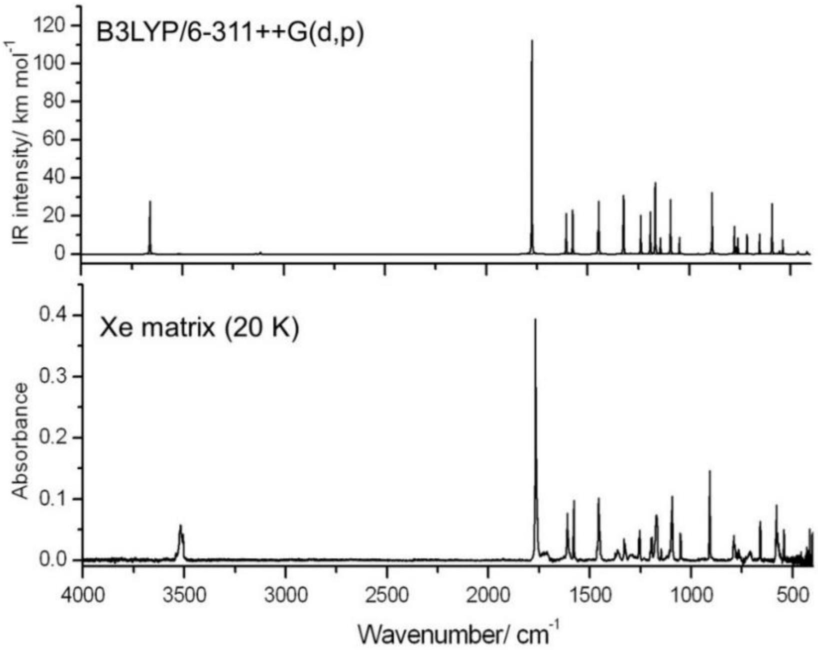
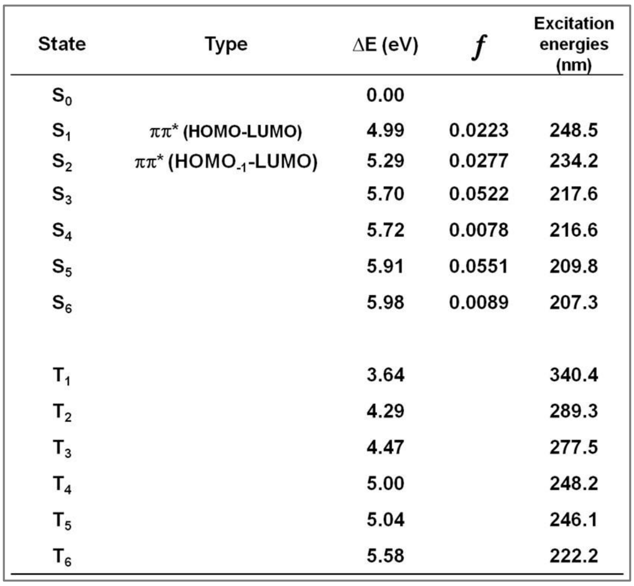


Figure 3. B3LYP/6-311++G(d,p) calculated IR spectrum for ClFBA conformer **I** (top), and spectrum of the compound isolated in a xenon matrix at 20 K (bottom)

It has been shown that vibrational excitation of the first overtone of the OH stretching overtone of a *cis* carboxylic acid fragment, using narrowband NIR light, leads to its conversion to the *trans* conformation, through internal rotation about the carboxylic C–O bond [11-20]. Experiments were then undertaken using this strategy in order to try to generate and detect the higher-energy conformers **II** and/or **III** of ClFBA. *In situ* NIR excitation of the OH stretching overtone of conformer **I** (2νOH; 6867 cm^{-1}), however, proves to be unsuccessful to achieve this goal. This result suggests that in solid xenon, once produced, the high-energy conformers of ClFBA promptly relax by tunneling to the most stable conformer. Since it has been reported [21-23] that isolation of a *cis* carboxylic acid in a nitrogen matrix, followed by its vibrational excitation, allows stabilization of the photogenerated *trans* forms through interactions between these conformers and the nitrogen molecules, we may suggest that an investigation of ClFBA in this matrix media shall be undertaken in order to try to experimentally observe conformers **II** and/or **III**.

The photochemistry of ClFBA resulting from UV excitation of the matrix-isolated compound was also investigated. Irradiations of the deposited compound carried out using different UV light filtered and changes started to occur promptly when the sample was irradiated with $\lambda = 235$ nm. During UV irradiation with $\lambda = 283$ nm, it was not observed any spectral changes in the matrix because of the energy of the UV excitation was below S_2 (5.29 eV), however it was above S_1 state (4.99 eV). This amount of energy (~4.4 eV) was inefficient for transition from the ground state (S_0) to the first excited singlet state (S_1). According to the performed TD-DFT calculations, excitation at this wavelength leads to the S_2 state of the molecule (Table 2), which corresponds to the HOMO$_{-1}$→LUMO ππ* transition (see also Figure 4 for representation of relevant orbitals). This is an additional indication that the observed photochemical changes should be promoted by the excitation to S_2.

Table 2. B3LYP/6-311++G(d,p) TD-DFT calculated excitation energies and oscillators strengths for ClFBA (conformer I)



State	Type	ΔE (eV)	f	Excitation energies (nm)
S_0		0.00		
S_1	$\pi\pi^*$ (HOMO-LUMO)	4.99	0.0223	248.5
S_2	$\pi\pi^*$ (HOMO$_{-1}$-LUMO)	5.29	0.0277	234.2
S_3		5.70	0.0522	217.6
S_4		5.72	0.0078	216.6
S_5		5.91	0.0551	209.8
S_6		5.98	0.0089	207.3
T_1		3.64		340.4
T_2		4.29		289.3
T_3		4.47		277.5
T_4		5.00		248.2
T_5		5.04		246.1
T_6		5.58		222.2

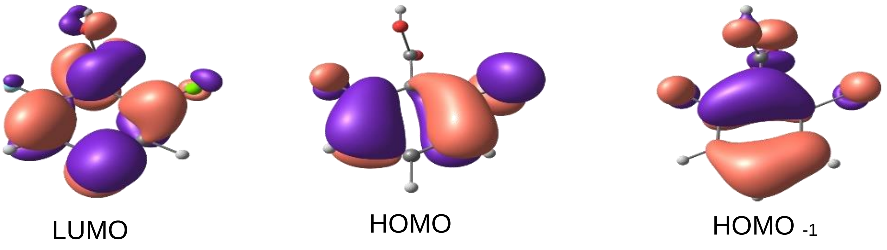


Figure 4. Representation of HOMO-1, HOMO and LUMO orbitals of conformer I of ClFBA, as predicted by the performed B3LYP/6-311++G(d,p) calculations, at isovalues of the electron densities of 0.02 e. Salmon and violet colors correspond to negative and positive wave function signs.

As result of the performed UV irradiation, ClFBA decarboxylates to CO_2 and 1-chloro-3-fluorobenzene (ClFB), whose vibrational signatures could be doubtlessly identified in the spectra of the photolysed matrix (Figure 5).

Decarbonylation was not a significant process in irradiated compound since yield of carbon monoxide was found to be quite low and observed only after long standing matrix irradiation. Moreover, intensity did not increase during further time irradiation with λ = 235 nm. This means that presence of photoproduct did not undergo during decarbonylation or lower intensity band around 2134 cm^{-1} related with the CO molecule did not diffuse from the original cage where it was formed and interact with ClFB resulting from fragmentation of ClFBA.

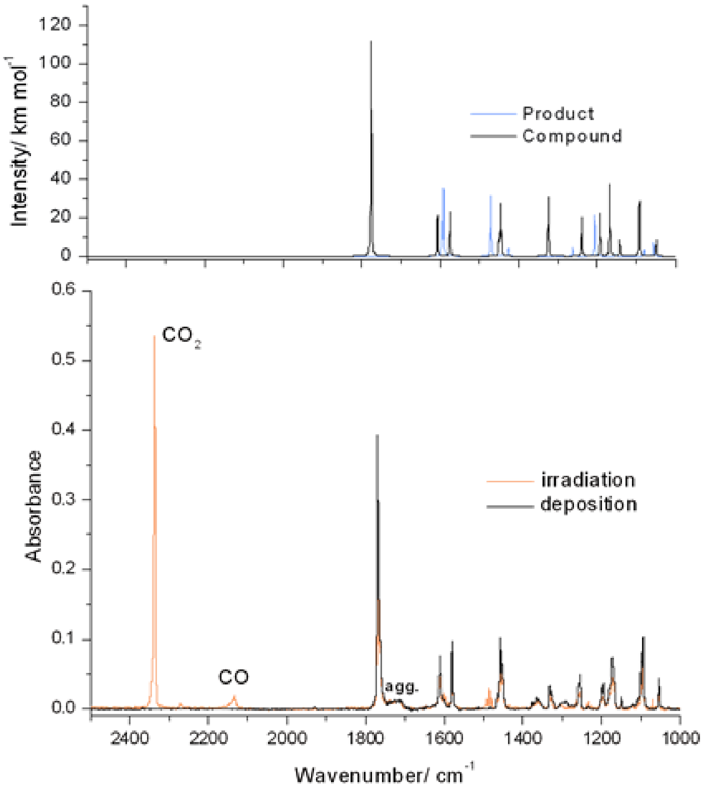


Figure 5. B3LYP/6-311++G(d,p) calculated (top) IR spectra for ClFBA (conformer **I**) and its product of photodecarboxylation (ClFB), and spectra of the as-deposited and photolysed Xe matrix of ClFBA (bottom).

4. CONCLUSION

2-chloro-6-fluorobenzoic acid was studied by matrix isolation IR spectroscopy and DFT(B3LYP) calculations. It was shown that the molecule may exist in 3 conformers. The most stable conformer (**I**) was successfully isolated in a xenon matrix from the gas phase and characterized structurally and vibrationally. The remaining conformers (**II**, **III**) are high-energy forms with negligible populations in the room temperature gas phase equilibrium. *In situ* irradiation experiments using narrowband NIR light tuned at the first OH stretching overtone of conformer **I** were undertaken in an attempt to produce the high-energy conformers. However, it was concluded that the high-energy conformers of ClFBA are unstable in a solid xenon matrix and, assuming its photogeneration from the most stable form upon the NIR excitation, they promptly convert back to this latter form by tunneling.

The UV-induced photochemistry of ClFBA was also investigated, allowing observation of decarboxylation of the compound, with production of CO_2 and 1-chloro-3-fluorobenzene (ClFB).

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