

# Structural transformations of 3-fluoro and 3-fluoro-4-methoxy benzaldehydes under cryogenic conditions: A computational and low temperature infrared spectroscopy investigation

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## ABSTRACT

Structural transformations of 3-fluorobenzaldehyde ( $C_7H_5FO$ ; 3FBA) and 3-fluoro-4-methoxybenzaldehyde ( $C_8H_7FO_2$ ; 3F4MBA), taking place in different solid phase environments and at low temperature, were investigated by infrared spectroscopy, complemented by quantum chemistry calculations undertaken at the DFT(B3LYP)/6–311++G(d,p) level of approximation. The studied compounds were isolated from gas phase into cryogenic inert matrices (Ar, Xe), allowing to characterize their equilibrium conformational composition in gas-phase at room temperature. In both cases, two conformers differing by the orientation of the aldehyde moiety (with the carbonyl aldehyde bond *cis* or *trans* in relation to the aromatic ring fluorine substituent) were found to coexist, with the *cis* conformer being slightly more populated than the *trans* form. *In situ* narrowband UV irradiation of the as-deposited matrices led either to preferential isomerization of the *cis* conformer into the *trans* form or decarbonylation of both conformers, depending on the used excitation wavelength. Deposition of the vapours of 3F4MBA only, onto the cold (15 K) substrate, produced an amorphous solid containing also both the *cis* and *trans* conformers of the compound. Subsequent heating of the amorphous phase up to 268 K led to crystallization of the compound, which is accompanied by conformational selection, the *cis* form being the single species present in the crystal. The experimentally observed transformations of the studied compounds, together with the structural and vibrational results obtained from the performed quantum chemical calculations, allowed a detailed structural and vibrational characterization of the individual conformers.

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## 1. Introduction

Benzaldehydes asymmetrically substituted at the *meta* position are very interesting chemical systems regarding structural modifications. Contrarily to *para* substituted benzaldehydes, they exhibit conformational isomerism, since the aldehyde group may exhibit two non-equivalent stable orientations, with the carbonyl bond being *cis* or *trans* in relation to the *meta* substituent. On the other hand, because the aldehyde group and the *meta* substituent are far apart, and then do not interact directly, the energies of the two types of conformers (*cis* and *trans*) can be expected to be very similar, in opposition to what is generally found in the case of

asymmetrically *ortho* substituted benzaldehydes, where most of times one of the conformers is considerably more stable than the other one and is the only conformer with practical relevance. These facts thus give the asymmetrically substituted *meta* derivatives of benzaldehyde the capability to exhibit *a priori* much richer range of possibilities for structural transformation than their corresponding *ortho* and *para* analogues.

In this article, we report on the structural transformations displayed by fluorobenzaldehyde ( $C_7H_5FO$ ; 3FBA) and 3-fluoro-4-methoxybenzaldehyde ( $C_8H_7FO_2$ ; 3F4MBA) under cryogenic conditions. As described in details below, we consider three different types of processes: (i) conformational isomerization in the isolated molecules of the compounds (in noble gas cryogenic matrices) induced by narrowband UV light, (ii) photoinduced decarbonylation, and (iii) conformational selection upon crystallization (for 3F4MBA).

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In the present study, which follows our previous investigations on structural transformations of other aromatic aldehydes, such as 4-pyridinealdehyde [1], 4-(*N,N*-dimethylamino)benzaldehyde [2], 3-quinolinealdehyde [3], 4-methoxybenzaldehyde [4,5], 3-furaldehyde [6], and 2-hydroxy-benzaldehyde [7], the selected probing technique was infrared spectroscopy, since it is a particularly sensitive experimental approach to subtle structural changes, like conformational transformations, in particular when coupled with matrix isolation sampling [8–10]. To trigger the structural transformations, both temperature and UV-excitation were used, the latter using a tuneable narrowband Laser/MOPO system UV-light source. The experimental studies reported here receive support from quantum chemistry calculations undertaken at the DFT(B3LYP) level of approximation with the polarized and augmented with diffuse functions split-valence triple- $\zeta$  6-311++G(d,p) basis set, for characterization of the relevant regions of the potential energy surfaces of the studied molecules and supporting the assignments of the infrared spectra.

## 2. Experimental and computational methods

Both 3FBA and 3F4MBA were purchased from Sigma-Aldrich (>99%), and further purified using the standard freeze-pump-thaw method. The cryogenic matrices were prepared by room temperature evaporation/sublimation of the compounds using a locally modified Knudsen cell with shut-off possibility, and co-deposition with a large excess of the matrix gas (Ar, Xe; purities: N60, N48) onto a  $T = 15$  K cold CsI substrate mounted on the tip of an APD Cryogenics DE-202A cryostat. The solid amorphous film of neat 3F4MBA was prepared using an identical procedure, but only the vapours of the compound were deposited. Temperature is controlled with a Scientific Instruments, Model 9650-1 digital temperature controller, with an accuracy of 0.1 degrees in the full range of temperatures covered.

The infrared spectra were collected, with  $0.5\text{ cm}^{-1}$  spectral resolution, in a Thermo Nicolet 6700 Fourier transform infrared spectrometer, equipped with a DTGS (deuterated triglycine sulphate) detector, a Globar source, and a KBr beam splitter.

UV excitations were performed through the outer KBr windows of the cryostat, with narrowband ( $<0.2\text{ cm}^{-1}$ ) tuneable UV light provided by the frequency-doubled signal beam of a Spectra Physics Quanta-Ray optical parametric oscillator (MOPO-SL) pumped by a Nd:YAG Spectra Physics Quanta-Ray PRO-230-10 pulsed (10 Hz, 10 ns) laser.

The DFT calculations (optimized geometries, infrared spectra) were performed with Gaussian 09 [11], using the B3LYP functional [12–14] and the 6-311++G(d,p) basis set [15–17]. Potential energy profiles were performed at the same level of theory, and the transition state structures for isomerization located using the STQN (synchronous transit-guided quasi-Newton) method [18,19].

The B3LYP/6-311++G(d,p) calculated vibrational frequencies and infrared intensities for all relevant chemical species were used to help interpreting the experimental spectra. The calculated wavenumbers were scaled by 0.978 (our standard scaling factor for this combination of method and basis set) [1–6], mainly to account for the effects of basis set limitations, neglected part of electron correlation and anharmonicity. Normal coordinate analysis used the optimized geometries and harmonic force constants resulting from the B3LYP/6-311++G(d,p) calculations, and followed the procedure described by Schachtschneider and Mortimer [20] (see Tables S1–S4 in Supporting Information, for definition of the used symmetry coordinates). In the spectra simulation, the bands were represented by convoluting each peak (calculated scaled wavenumber and infrared intensity) with a Lorentzian function with a full-width-at-half-maximum (FWHM) of  $2\text{ cm}^{-1}$ .

## 3. Results and discussion

### 3.1. Conformers and barriers to internal rotation

3-Fluorobenzaldehyde conformational space has been investigated before both experimentally and theoretically. The recent study by Itoh et al. [21] presents a detailed literature reviewing on this subject. In their study, Itoh and coworkers investigated the infrared spectra ( $3000\text{--}700\text{ cm}^{-1}$  region) of the whole series of monofluoro-substituted benzaldehydes (*ortho*, *meta* and *para* isomers) isolated in argon matrices, and paid special attention to conformational matters. The experimental study was accompanied by theoretical calculations undertaken at the DFT(B3LYP)/6-31++G(d,p) level of approximation. In the case of the *meta*-substituted fluorobenzaldehyde (3FBA) Itoh and coworkers [21] concluded on the existence of two conformers differing on the orientation of the aldehyde group (with the carbonyl bond *cis* or *trans* relatively to the fluorosubstituent), whose energy difference was theoretically predicted as  $0.6\text{ kJ mol}^{-1}$  in favour of the *cis* form. From selected experimental relative band intensities (the *cis/trans* pairs of bands at  $1486/1490$  and  $1386/1382\text{ cm}^{-1}$ ), however, the opposite order of stability was estimated, the *trans* conformer appearing to be more stable than the *cis* form by  $1.0\text{ kJ mol}^{-1}$  [21]. A similar study on 3-chlorobenzaldehyde molecule has been reported by Bednarek et al. [22], where the stability of the *cis* and *trans* conformers has also been investigated. Thought no definitive conclusion could be extracted regarding which conformer is the most stable one, the authors concluded that they are practically isoenergetic, with room temperature gas phase populations of ca. 50% each [22].

To the best of our knowledge, no studies on 3-fluoro-4-methoxybenzaldehyde have been reported hitherto.

Figs. 1 and 2 present the optimized structures for the different conformers of 3FBA and 3F4MBA, as calculated in the present study at the DFT(B3LYP)/6-311++G(d,p). The corresponding Cartesian coordinates are provided in Table S5 (Supporting Information).

For 3FBA, the results now obtained using a triple- $\zeta$  basis set essentially replicate those previously reported [21] using the smaller double- $\zeta$  basis set. In particular, the two conformers were found to be planar ( $C_s$  symmetry), with the *cis* form (from now on abbreviated as C) being predicted to be more stable than the *trans* conformer (T) by  $0.6\text{ kJ mol}^{-1}$  [ $\Delta E$  value; both the zero-point energy corrected and standard Gibbs energy (at  $T = 298.15\text{ K}$ ) differences were also estimated as  $0.6\text{ kJ mol}^{-1}$ ]. The dipole moments calculated for the C and T forms are 3.89 and 2.08 D, respectively (exper-

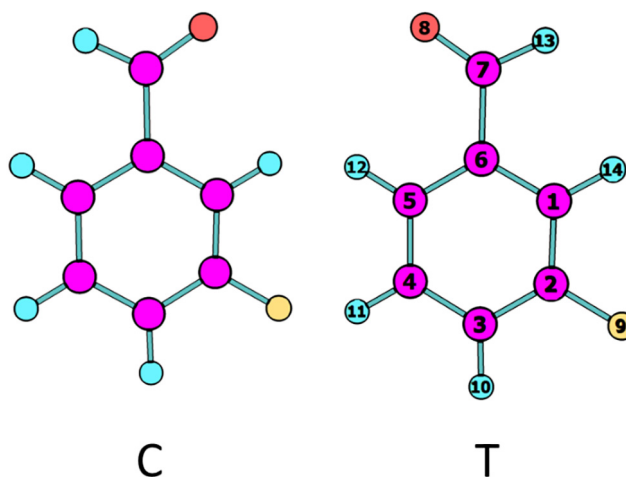


Fig. 1. B3LYP/6-311++G(d,p) optimized structures of the conformers of 3FBA with adopted atom numbering.

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