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Vibrational spectra, *ab initio*/DFT electronic structure calculations, and normal coordinate analysis of 2-bromo-5-fluorobenzaldehyde

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ABSTRACT

FT-IR (4000–400 cm^{-1}) and FT-Raman (3500–50 cm^{-1}) spectral measurements of solid samples of 2-bromo-5-fluorobenzaldehyde (BFB) have been done. *Ab initio* (RHF/6-311G*) and DFT (B3LY/6-311G* and B3PW91/6-311G*) calculations have been performed giving energies, optimized structures, harmonic vibrational frequencies, depolarization ratios, infrared intensities, Raman activities and atomic displacements. Furthermore force field calculations have been performed by normal coordinate analysis. Force field calculations showed that several normal modes are mixed in terms of the internal coordinates. A complete assignment of the observed spectra, based on spectral correlations, electronic structure and normal coordinate analysis, has been proposed. Optimization leads to C_S symmetry with O-*trans* and O-*cis* isomers, with respect to aldehydic oxygen and bromine, with O-*trans*-isomer as the low energy stable form. The energy difference between the two isomers is 2.95084 kcal/mol. The results of the calculations have been used to simulate IR and Raman spectra for BFB that showed excellent agreement with the observed spectra. The SQM method, which implies multiple scaling of the *ab initio* and DFT force fields has been shown superior to the uniform scaling approach.

1. Introduction

Several workers have investigated vibrational spectroscopic properties, such as the mutual influence of different types of substituents such as halogens, methyl, methoxy and hydroxyl on benzaldehyde, the interactions between the ring and substituents, by joint experimental and/or theoretical methods [1–4]. The existence of two rotational isomers between phenyl and formyl groups (O-*trans* and O-*cis*) in 2-chlorobenzaldehyde has been investigated by Drakenberg et al. [1] and Akai et al. [2] and they have shown that the O-*trans* isomer is more stable and is the only species existing at room temperature. In another study on the o- and m-substituted benzaldehydes by matrix isolation IR spectroscopy, Bednarek et al. have shown that the relative B3LYP/6-31G* energies of the *cis* and *trans* rotamers between the oxygen of the formyl group and the chlorine in chlorobenzaldehyde decrease significantly from *ortho*- (2.73 kcal/mol) to *meta*- (0.04 kcal/mol) substitution [3]. By investigating the three structural isomers (p-, m- and o-) of fluorobenzaldehyde (FB), Takao Itoh has shown that the formation of the intramolecular C–H···F hydrogen bond for the O-*trans* rotamer of o-FB results in the shortening of the aldehyde C–H bond length. The C–F and C=O bond lengths shortened for the O-*cis* rotamer of o-FB presumably due to the repulsion between the aldehyde O and F atoms [4]. In addition, several vibrational spectroscopic studies on mono-, di- and tri-substituted benzaldehydes have been reported [5–13]. In general, the DFT methods yield sufficiently good and consistent results at moderate computational costs. However, the calculated frequencies usually differ appreciably from the observed frequencies, partly due to the neglect of anharmonicity and partly due to the approximative nature of the quantum mechanical method. To overcome this problem, uniform scaling, i.e. global scaling of the theoretical force field may prove satisfactory for simpler molecules (or when vibrational spectra are unavailable) [14,15]. However, it has been shown, that application of multiple scale factors, i.e. the *selective scaling* of force fields developed by Pulay et al. [16–18], may lead to better results. It appears that only a few halogen-substituted benzaldehydes have been subjected to a systematic investigation of the structure and vibrational assignments and substituent effects using *ab initio*/DFT calculations and normal coordinate analysis. Therefore, as a continuation of our study on the benzaldehyde derivatives [19,20], we have undertaken a systematic structural and vibrational spectroscopic investigation of 2-bromo-5-fluorobenzaldehyde (hereafter, it is referred to as BFB) [21]. The present paper deals with the FT-IR and FT-Raman spectral measurements as well as *ab initio*/DFT electronic structure calculations, normal coordinate analysis, vibrational assignments and a study of the effect of internal rotation of the aldehyde group on the substituents, using solid samples of BFB.

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2. Experimental

A solid sample of BFB was purchased from Aldrich Chemical Co. and used as received. The IR spectral measurement was carried out on a *Nicolet's Model Impact 410 FT-spectrometer*. The FT-spectrometer consisted of a Globar Mid IR source, a deuterated triglycine sulfate (DTGS) solid-state detector and a KBr beam splitter. The absorption spectrum of the title compound was measured in KBr pellet with 100 interferograms at an interval of 1 cm^{-1}. A *Bruker Model FRA 106/RFS 100* FT-spectrometer was employed for the Raman spectral measurement. The spectrometer was provided with a Quartz beam splitter and a high sensitive germanium detector. The detector was cooled to the liquid N_2 temperature. The Raman spectrum was excited in the 180° geometry with 1064 nm laser line from a diode pumped-air cooled-cw Nd:YAG laser. The optical power necessary for the measurement was varied in the range 75–100 mw. The spectrum was obtained by the co-addition of 300 interferograms at the interval of 1 cm^{-1}.

3. Computational

In order to model the structure, geometry optimization was performed by defining two conformational structures, as has been done elsewhere [2–7]: O-*cis* and O-*trans* forms between aldehydic oxygen and bromine. We performed calculations at the RHF/6-311G*, B3LYP/6-311G* and B3PW91/6-311G* levels of theory using the *Gaussian 03W* suite of programs [22]. Molecular electronic energies, equilibrium geometries, IR and Raman spectra have been computed. All the computed harmonic frequencies have been scaled with the factor 0.904 at RHF/6-311G*, with 0.966 at B3LYP/6-311G* and with 0.963 at B3PW91/6-311G* [14]. As an aid in the assignments, potential energy distributions (PEDs) have been calculated in terms of simple internal coordinates from unscaled B3LYP/6-311G* results, using the program MOLVIB [23]. Using the same program, we have also carried out normal coordinate analysis by multiple scaling of the force field in the natural internal coordinate representation to calculate potential energy distributions (PEDs) for the B3LYP/6-311G* results.

4. Results and discussions

4.1. Geometry optimization

Table 1
Optimized geometrical parameters for O-*trans* isomer with 6-311G* basis set.

Parameter	Experimental[a]	RHF	B3PW91	B3LYP	B3LYP[b]
Bond lengths (Å)					
C_1–C_2	1.404	1.390	1.399	1.401	1.406
C_1–C_6	1.404	1.391	1.399	1.402	1.403
C_1–C_8	1.482	1.498	1.488	1.492	1.491
C_2–C_3	1.394	1.385	1.391	1.393	1.394
C_2–Br_{11}	1.867	1.905	1.906	1.922	1.909
C_3–C_4	1.394	1.381	1.388	1.391	1.392
C_3–H_{12}	1.094	1.073	1.084	1.083	1.083
C_4–C_5	1.394	1.378	1.388	1.390	1.386
C_4–H_{13}	1.094	1.074	1.085	1.084	1.084
C_5–C_6	1.383	1.371	1.378	1.379	1.381
C_5–F_{14}	1.337	1.323	1.341	1.347	1.348
C_6–H_7	1.094	1.073	1.085	1.084	1.085
C_8–O_9	1.216	1.183	1.207	1.208	1.204
C_8–H_{10}	1.117	1.087	1.105	1.103	1.112
Bond angles (°)					
$C_2C_1C_6$	119.9	118.9	118.8	118.7	118.4
$C_2C_1C_8$	119.7	124.0	124.0	124.1	126.2
$C_6C_1C_8$	120.9	117.1	117.2	117.2	115.4
$C_1C_2C_3$	121.8	120.7	120.7	120.9	120.3
$C_1C_2Br_{11}$	–	122.2	122.0	122.0	123.0
$C_3C_2Br_{11}$	–	117.1	117.3	117.2	116.7
$C_2C_3C_4$	121.0	120.0	120.0	119.9	120.7
$C_2C_3H_{12}$	121.0	120.0	120.0	120.1	119.5
$C_4C_3H_{12}$	119.5	119.9	120.0	120.0	119.8
$C_3C_4C_5$	119.0	119.0	119.1	119.1	118.7
$C_3C_4H_{13}$	121.0	121.1	121.1	121.1	121.2
$C_5C_4H_{13}$	119.5	119.9	119.8	119.8	120.0
$C_4C_5C_6$	121.2	121.7	121.5	121.6	121.3
$C_4C_5F_{14}$	–	119.0	118.9	118.7	119.3
$C_6C_5F_{14}$	–	119.3	119.6	119.5	119.4
$C_1C_6C_5$	118.2	119.8	119.8	119.8	120.5
$C_1C_6H_7$	119.5	119.6	118.8	118.9	120.1
$C_5C_6H_7$	121.0	120.6	121.4	121.3	119.4
$C_1C_8O_9$	125.5	122.6	123.1	123.1	127.2
$C_1C_8H_{10}$	116.0	116.6	116.0	116.0	112.4
$O_9C_8H_{10}$	118.5	120.8	120.9	120.6	120.4

[a] Refs. [9,10,31].
[b] O-*cis* isomer.

The conformers of the molecule-BFB with the numbering scheme for the atoms have been presented in Fig. 1(a and b). We have defined two conformational forms, as has been done elsewhere [2–7]: O-*cis* and O-*trans* forms between aldehydic oxygen and bromine (C_S symmetry). The optimization of the geometry of the O-*cis* and O-*trans*-isomers was performed at the B3LYP/6-311G* level. The computed molecular electronic energies of the two optimized structures, O-*cis* and O-*trans*, are −3018.4510876 and −3018.4557900 hartrees, respectively. The difference in molecular electronic energy between the two optimized structures has been found to be 2.95084 kcal/mol. By referring literature of similar systems of benzaldehyde derivatives [1–3], we may

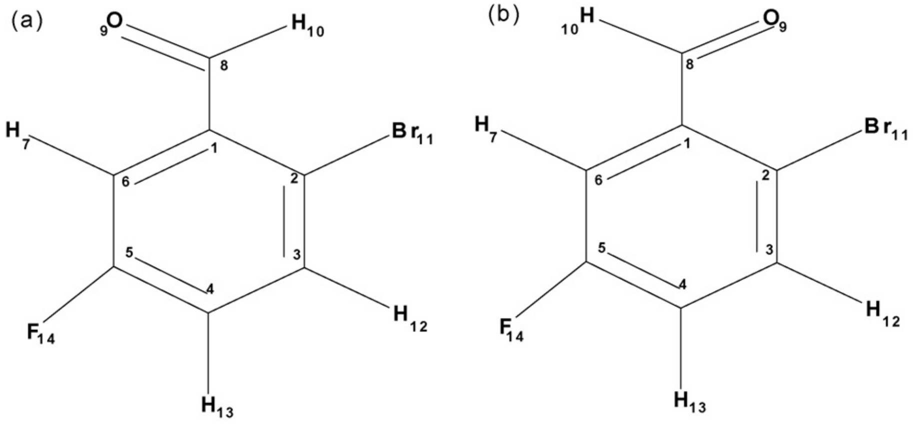

Fig. 1. Molecular structure of 2-bromo-5-fluorobenzaldehyde: (a) O-*trans* and (b) O-*cis*.