Spectrochimica Acta Part A 91 (2012) 261–268

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

2-Methoxyphenyl isocyanate and 2-Methoxyphenyl isothiocyanate: Conformers, vibration structure and multiplet Fermi resonance

Jayashree Yenagi*, Anita R. Nandurkar, J. Tonannavar

Department of Physics, Karnatak University, Dharwad 580 003, India

ARTICLE INFO

Article history:
Received 2 November 2011
Received in revised form 4 January 2012
Accepted 16 January 2012

Keywords:
Infrared
Raman, 2-Methoxyphenyl isocyanate
2-Methoxyphenyl isothiocyanate
B3LYP
Fermi resonance

ABSTRACT

IR and Raman spectral measurements in the region 3500–400/50 cm^{-1} have been made for the liquid samples of 2-Methoxyphenyl isocyanate and 2-Methoxyphenyl isothiocyanate. A complete assignment of the measured bands has been proposed as aided by conformational and vibration analyses at B3LYP/6-311++G** level of calculations. Three conformers for 2-Methoxyphenyl isocyanate and two for 2-Methoxyphenyl isothiocyanate have been determined. The tilt of the isocyanate (NCO) and isothiocyanate (NCS) moieties with respect to phenyl ring are in broad agreement with their parents. Stretching mode frequencies of methyl group (–OCH_3) in 2-Methoxyphenyl isocyanate have been lowered in the 2900–2800 cm^{-1}; deformation asymmetric modes are IR strong and symmetric one Raman strong. In 2-Methoxyphenyl isothiocyanate, a similar pattern is true for stretching modes but deformation asymmetric modes are IR strong and symmetric mode has not been observed. Multiplet absorption band system near 2200 cm^{-1} in 2-Methoxyphenyl isocyanate has been interpreted to be caused by Fermi resonance. A similar pattern in absorption near 2100 cm^{-1} in 2-Methoxyphenyl isothiocyanate but more complex Raman band pattern has also been explained through Fermi resonance from *heuristic* stand-point. Many Raman modes in 1300–1100 cm^{-1} are intensified apparently owing to isothiocyanate than isocyanate moiety. Phenyl ring breathing mode is shifted to 1040 cm^{-1} as strong Raman; the symmetric stretching mode of O–CH_3 near 1023 cm^{-1} as strong absorption.

1. Introduction

Study of different derivatives of phenyl isocyanate and isothiocyanate has been of spectroscopic interest. Isothiocyanates are important intermediate and end products in chemical industry. Phenyl isothiocyanate is used as peptide sequencer (Edmen-reagent) [1]. Karol et al. has shown that phenyl isocyanate is a strong inducer of both cellular and humoral immune responses [2]. From spectroscopic stand-point, Caldow et al. [3] has studied absorption in the 2000-2300 cm^{-1} region in aryl isothiocyanates and isocyanates with different substitutions. Vibrational studies of several alkyl isothiocyanates has been done by Kinseley et al. [4]. Williams studied particularly the 2083 cm^{-1} band of phenyl isothiocyanates and similar complexities in nitriles and isonitriles [5]. Ham and Willis [6] have worked on a series of aliphatic and aromatic isothiocyanates and have explained the complex structure of the strong band near 2100 cm^{-1} showing its contour for aliphatic and aromatic isothiocyanates. Infrared intensity measurements on this band are also reported. Systematic study of distinguishing isothiocyanates from thiocyanates based on the structure of 2100 cm^{-1} band has been done by Liber et al. [7]. The vibrational spectrum of phenyl isocyanate has been investigated by Stephenson et al. assuming C_{2v} symmetry [8]. Chantry et al. [9] reassigned the vibrational spectra of the phenyl isocyanate on the basis of C_s symmetry. Low resolution spectra of phenyl isothiocyanate and phenyl isocyanate have been studied in the microwave region by Higgins et al. [10]. The structural determination of phenyl isocyanate based on microwave spectrum was carried out by Bouchy and Roussy[11] giving an evidence of planar C_s gas phase structure with NCO group making an angle of $\sim 140^\circ$ to the C_2 phenyl axis. This was supported by Balfour et al. [12] with their vapor phase electronic absorption spectrum. Electronic spectrum of phenyl isocyanate was reported by Chakravarti et al. [13]. Several studies have been reported on halo and alkyl substituted phenyl isocyanates by our own group [14,15].

We report in the present work conformational and vibration analyses of 2-Methoxyphenyl isocyanate and 2-Methoxyphenyl isothiocyanate. The mutual influence of isocyanate (NCO)/isothiocyanate (NCS) and methoxy (OCH_3) groups and theirs on the phenyl ring, as far as we are aware, has not been reported. It has been determined that the methyl stretching and deformation modes (in methoxy) have been affected. The strong asymmetric

---

* Corresponding author. Tel.: +91 9449005426.
E-mail address: jyenagi.phys.kud@gmail.com (J. Yenagi).

1386-1425/$ – see front matter
doi:10.1016/j.saa.2012.01.024

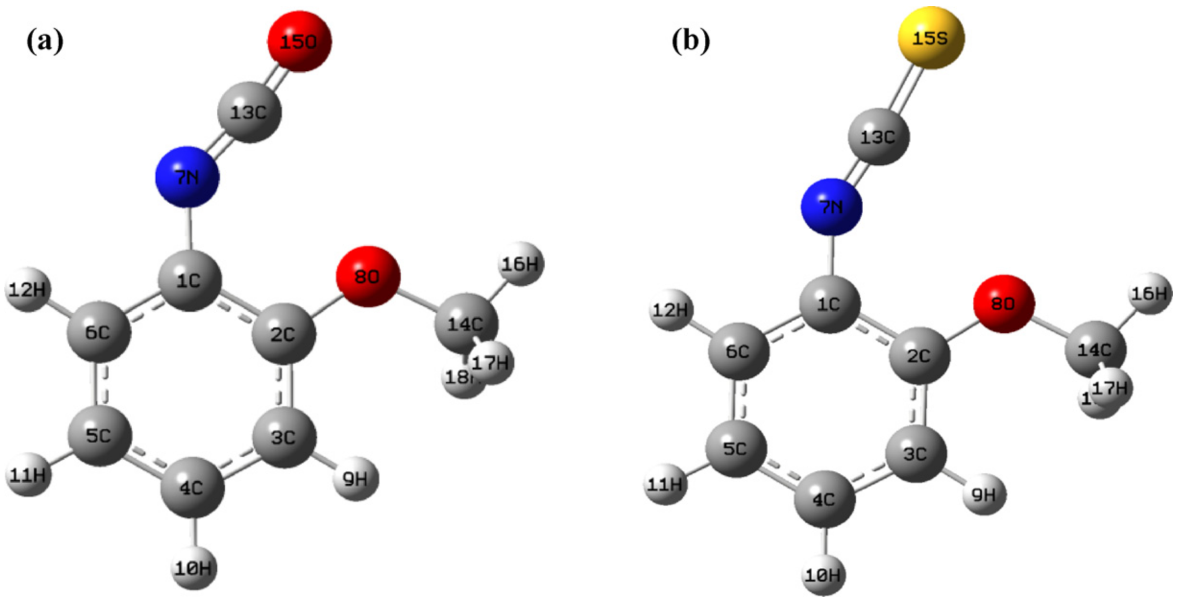

Fig. 1. Optimized structures of 2-Methoxy phenylisocyanate (a) and 2-Methoxy phenylisothiocyanate (b).

stretching mode of isocyanate in 2-Methoxyphenyl isocyanate shows a unique symmetric multiplet structure near 2200 cm^{-1} in absorption. Similar but more complex structure near 2100 cm^{-1} more in Raman than in absorption is shown by 2-Methoxyphenyl isothiocyanate. Both have been interpreted on the basis of Fermi resonance. Modes in the 1300–1100 cm^{-1} are Raman strong in 2-Methoxyphenyl isothiocyanate. The tilt of the NCO and NCS, computed at B3LYP/6-311++G**, are in broad agreement with experimental values reported in the earlier studies [5,6,8,9,11].

2. Experimental

The liquid samples of 2-Methoxyphenyl isocyanate and 2-Methoxyphenyl isothiocyanate used in this work were commercial specimen supplied by Aldrich Chemical Co., and was used as received. The FT-infrared spectral measurements were made on Nicolet's *Impact* 410 FT spectrometer equipped with Globar mid-IR source and DTGS detector. The spectra covering 4000–400 cm^{-1} were recorded by smearing the sample on KBr windows. The signals were collected for 100 scans at a resolution of 4 cm^{-1}. The FT-Raman measurements have been done using *Bruker* Ramanscope III FT-Raman spectrometer equipped with diode pumped air-cooled cw Nd-YAG laser operating on 1064 nm as an exciting line and a CaF_2 beam splitter with liquid nitrogen pre-cooled high sensitivity Ge-diode as the detector. The spectrum was recorded for 500 scans with a resolution of 2 cm^{-1} and the samples were excited with power around 300 mW.

3. Computational

All the electronic structure calculations have been performed using quantum chemical Density Functional Theory (DFT) methods using the Gaussian 09W [16] suite of programs. Optimized geometrical parameters, harmonic vibration frequencies, IR intensities, Raman scattering activities, force constants, normal modes were computed following optimization and frequency analysis at B3LYP/6-311++G** level. The harmonic frequencies have been scaled with a scaling factor of 0.9668 [17]. Further, force constants and potential energy distributions (PED) have been deduced from a normal mode analysis [18]; and vibration modes were studied in *GaussView* 5 [19]. Natural atomic charges have been calculated from the NBO version 3.1 available with Gaussian 09W [16] program at the B3LYP/6-311++G** level.

4. Results and discussion

4.1. Geometry optimization

The molecular structures of 2-Methoxyphenyl isocyanate (2-MIC) and 2-Methoxyphenyl isothiocyanate (2-MIT) are shown in Fig. 1(a) and (b) respectively. Potential energy surface scan was performed to determine the exact bending of the respective moieties by varying dihedral angles in steps of 20° from 0° to 360° and all the geometrical parameters were simultaneously relaxed during the scan except the two dihedral angles for both the molecules. The potential energy scan plot of 2-MIC and 2-MIT are shown in Fig. 2. C–N–C–O and C–N–C–S torsional angles for 2-MIC and 2-MIT suggest an orientation of 136° and 148° respectively. Optimization of the 2-MIC yields three conformers with respect to NCO and CH_3, which are shown in Fig. 3(a). The first two conformers with NCO moiety bent on either side of the ring show C_S symmetry on optimization with no any imaginary frequency. However an imaginary frequency was obtained in the third structure. Two conformers obtained for 2-MIT are shown in Fig. 3. (b). First conformer was optimized with C_S symmetry and NCS moiety bent on the OCH_3 substitution side. An imaginary frequency was obtained for the second structure when the dihedral angles were 0° for both moieties. The normal mode corresponding to the imaginary frequency indicated that CH_3 be relaxed. After relaxation the imaginary frequencies became positive for the structures giving rise to C_1 symmetry conformer for both the molecules. For 2-MIC, first conformer is more stable than the second conformer by 2.8 kcal mol^{-1} and 4.98 kcal mol^{-1} from the third conformer; for 2-MIT the energy difference between the two conformers is 3.62 kcal mol^{-1}. All the results of optimization, namely, the energy of the conformers and dihedral angles are shown in Table 1 and geometrical parameters and dipole moments are given in supplementary part.

The optimized parameters show that the C=N bond length to be 1.2089 Å and 1.1953 Å, respectively for 2-MIC and 2-MIT. The C1–N7–C13 angle, when compared between the two, is more in 2-MIT as there is heavy substitution sulphur in place of oxygen.