

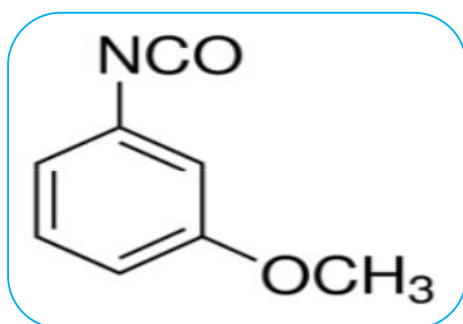


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SPECTROSCOPIC STRUCTURE OF 3-METHOXYPHENYL ISOCYANATE AS STUDIED BY EXPERIMENTAL AND DFT METHODS

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ABSTRACT:

IR absorption spectra in the 4000-400 cm^{-1} has been measured for 3-Methoxy phenylisocyanate $\text{C}_8\text{H}_7\text{NO}_2$. In the present work we report a systematic study and interpretation and vibrational band assignments to identify the type as well as functionality of the chemical functional, the experimental FTIR spectrum of 3-Methoxyphenyl isocyanate with the aid of

density functional theoretical electronic structure calculation at B3LYP/6-311++G level of theory. Electronic structure calculation have been performed using Gaussian 03W software giving optimized structure, energies, harmonic vibrational frequencies. The molecular electronic energy are measured at B3LYP/6-311++G level. Optimized geometrical parameters are found and vibrational frequencies are analyzed and assigned to different normal modes of the molecule. C-H and C-C vibrations are assigned in their normal range. The NCO asymmetric stretching vibrations show dominance in the region around 2272 cm^{-1} overall the geometrical parameters and frequency obtained are in good agreement with the results.

KEYWORDS: IR absorption spectra, theoretical electronic, vibrational frequencies.

1. INTRODUCTION

The derivatives of phenyl isocyanate are of spectroscopic importance due to the role NCO and substituents play in the vibrational structures and spectra. Many studies on vibrational spectroscopy of derivatives of phenyl isocyanates have been reported. Laha et al [1] reported the vibrational assignments of p-chlorophenyl isocyanates and then the work reported on three isomeric fluorophenyl

isocyanates and m- and o-chlorophenyl isocyanates on electronic absorption and infrared spectra followed by work reported on the vibrational spectra, assignments and ad-initio/DFT analysis for 3-chloro,4-chloro and 5-chloro-2 methyl phenyl isocyanates[2,3,4].

Motivations for this study came from the sustained investigations on the structural aspect and vibrational assignments of parent phenyl isocyanate. FT-IR spectral measurements of 3-Methoxyphenyl isocyanate is aided with density functional

theoretical electronic structure calculation. 3-Methoxyphenyl isocyanate having the molecular formula $\text{C}_8\text{H}_7\text{NO}_2$ is used in the synthesis of 1,3-bis(3-methoxyphenyl)-6-methyl-5-(trimethylsilyl)pyrimidine-2,4(1H,3H)-dione.

Electronic structure calculation have been performed using Gaussian 03W software giving optimized structure, energies, harmonic vibrational frequencies. The molecular electronic energy are measured at B3LYP/6-311++G level. Among the DFT levels, the B3LYP/6-311++G(d,p) level was chosen because of its accurate modeling

and low computational cost. Optimized geometrical parameters are found and vibrational frequencies are analyzed and assigned to different normal modes of the molecule. The molecular structure of 3-Methoxy phenyl isocyanate with numbering is shown in the figure 1.

2. EXPERIMENTAL DETAILS:

The liquid sample of the compound 3-Methoxyphenyl isocyanate supplied by Aldrich Chemical Co. and used as received. *Nicolet's Impact 410 FT spectrometer* was used for the infrared spectral measurements at room temperature in the range of 4000-400 cm^{-1} . The instrument was provided with a Global Mid IR source, a deuterated triglycine sulfate (DTGS) solid state detector and a KBr beam splitter. The solid sample was grinded in KBr to form a pellet. The signals were collected for 100 scans with a resolution of 4 cm^{-1} .

3. COMPUTATIONAL DETAILS:

Ab initio density functional theory (DFT) calculations were implemented in the source code Gaussian 03W. Among the DFT levels the B3LYP/6-311++G level was chosen because of its accurate modeling and low computational cost. The electronic structure calculations, giving optimized structure, energies, harmonic vibrational frequencies have been performed using Gaussian 03W software and Gauss view 05(GV5)[5]. All the computed harmonic frequencies have been scaled with suitable scale factor 0.9614.

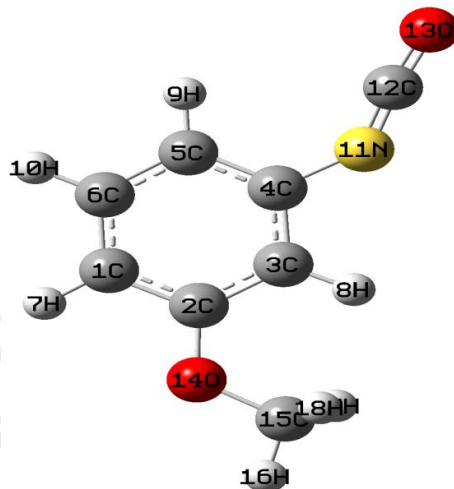


Fig.1: Molecular structure of 3-Methoxyphenylisocyanate.

4. RESULT AND DISCUSSION

Fig 1 shows the structure of 3-Methoxy phenylisocyanate molecule with numbering scheme. 3-Methoxyphenyl isocyanate belongs to C_1 symmetry with 24 normal modes of vibration. The experimental FTIR spectrum is presented in fig 2. The molecular electronic energy is -514.4003447 hartrees at B3LYP/6-311++G level. We presented optimized geometrical parameters as well as experimental FTIR and theoretical fundamental vibrational frequencies with assignments. The geometrical parameters of the most stable conformers of 3-Methoxy phenyl isocyanate are presented in the Table 1,2 and 3. The experimental FTIR and theoretical fundamental vibrational frequencies with assignments are presented in table 4. The observed vibrational frequencies were analyzed and assigned to different normal modes of the molecule. C-H and C-C vibrations are assigned in their normal range. The NCO asymmetric stretching vibrations show dominance in the region around 2272 cm^{-1} overall the geometrical parameters and frequency obtained are in good agreement with the results. The error

obtained between experimental and theoretical frequencies is in general very low. Other general conclusions have also been deduced.

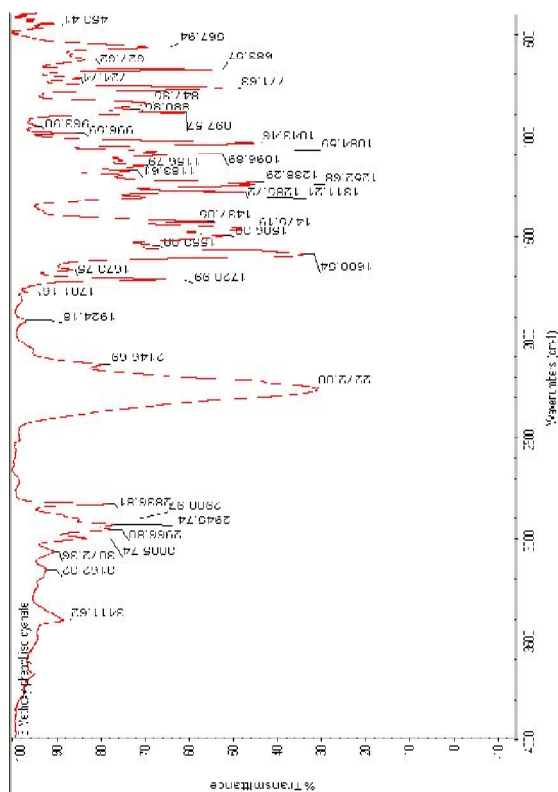


Fig 2: Experimental FTIR spectrum of 3-Methoxyphenyl isocyanate

Table 1: Optimized geometrical parameters: Bond lengths

Name	Bond length	Å
R1	C1-C2	1.401
R2	C1-C6	1.387
R3	C1-H7	1.083
R4	C2-C3	1.395
R5	C2-O14	1.362
R6	C3-C4	1.400
R7	C3-H8	1.080
R8	C4-C5	1.395
R9	C4-N11	1.401
R10	C5-C6	1.395
R11	C5-H9	1.083
R12	C6-H10	1.084
R13	N11-C12	1.203
R14	C12-O13	1.171
R15	O14-c15	1.422
R16	C15-H16	1.088
R17	C15-H17	1.095
R18	C15-H18	1.095

Table 2: Optimized geometrical parameters: Bond angles

Name	Bond angle	(°)
A1	C2-C1-C6	119.611
A2	C2-C1-H7	118.8003
A3	C6-C1-H7	121.5887
A4	C1-C2-C3	120.0909
A5	C1-C2-O14	115.8671
A6	C3-C2-O14	124.0421
A7	C2-C3-C4	119.4204
A8	C2-C3-H8	122.1384
A9	C4-C3-H8	118.4412
A10	C3-C4-C5	120.8968
A11	C3-C4-N11	117.2859
A12	C5-C4-N11	121.8173
A13	C4-C5-C6	118.7869
A14	C4-C5-H9	120.3122
A15	C6-C5-H9	120.9009
A16	C1-C6-C5	121.194
A17	C1-C6-H10	119.447
A18	C5-C6-H10	119.3583
A19	C4-N11-C12	140.0347
A20	N11-C12-O13	173.7119
A21	C2-O14-C15	118.7983
A22	O14-C15-H16	105.7652
A23	O14-C15-H17	111.3713
A24	O14-C15-H18	111.3699
A25	H16-C15-H17	109.3431
A26	H16-C15-H18	109.3451
A27	H17-C15-H18	109.554

Table 3: Optimized geometrical parameters: Dihedral angles

Dihedral angle	(°)
C6-C1-C2-C3	0.0014
C6-C1-C2-O14	180.0046
H7-C1-C2-C3	-180.0013
H7-C1-C2-O14	0.0019
C2-C1-C6-C5	-0.0028
C2-C1-C6-H10	-180.0016
H7-C1-C6-C5	179.9999
H7-C1-C6-H10	0.0012
C1-C2-C3-C4	0.0012
C1-C2-C3-H8	180.0017
O14-C2-C3-C4	179.9977
O14-C2-C3-H8	-0.0018
C1-C2-O14-C15	180.0207
C3-C2-O14-C15	0.0241
C2-C3-C4-C5	-0.0025
C2-C3-C4-N11	180.0017
H8-C3-C4-C5	-180.0029
H8-C3-C4-N11	0.0012
C3-C4-C5-C6	0.0011

C3-C4-C5-H9	180.0004
N11-C4-C5-C6	-180.0032
N11-C4-C5-H9	-0.004
C3-C4-N11-C12	179.9806
C5-C4-N11-C12	-0.0152
C4-C5-C6-C1	0.0016
C4-C5-C6-H10	180.0004
H9-C5-C6-C1	-179.9977
H9-C5-C6-H10	0.0011
C4-N11-C12-O13	179.9636
C2-O14-C15-H16	-180.0074
C2-O14-C15-H17	-61.3181
C2-O14-C15-H18	61.3017

Table 4: Experimental and theoretical frequencies (cm⁻¹) with assignments

S.No.	EXPT IR	B3LYP	Assignments
v ₁	3162	3116	vCH
v ₂	3072	3096	vCH
v ₃	3006	3086	vCH
v ₄	2967	2966	vCH
v ₅	2946	2908	vCH
v ₆	2272	2280	v _{as} NCO
v ₇	1600	1583	vCC
v ₈	1554	1569	vCC
v ₉	1506	1495	vCC
v ₁₀	1475	1458	βCH ₃
v ₁₁	1437	1454	βCH
v ₁₂	1311	1309	βCH
v ₁₃	1285	1262	vCO-CH ₃
v ₁₄	1238	1238	vCC
v ₁₅	1096	1098	βCH
v ₁₆	1043	1065	v _{as} O-CH ₃
v ₁₇	897	882	v _{as} CH
v ₁₈	847	851	βCH
v ₁₉	771	757	βCH
v ₂₀	724	706	δCH
v ₂₁	683	671	δCH
v ₂₂	627	627	γNCO
v ₂₃	567	556	γNCO
v ₂₄	453	545	ωNCO

v-stretching, β-in-plane-bending, γ-out-of-plane bending, ρ-rocking, as-asymmetric, s-symmetric, δ-deformation, ω-wagging, τ-torsion

5. VIBRATIONAL BAND ASSIGNMENTS:

Vibrational assignments have been made based on "Spectra-Structure Correlations", aided by the electronic structure calculations that is, the scaled theoretical vibrational fundamental frequencies. Assignments of vibrational frequencies presented in Table-4 are based on experimental frequencies and calculated B3LYP/6-311++G frequencies. Vibrations are visualized with the aid of Gauss View, that is output of Gaussian is analyzed through GaussView and assignments are made.

1: C-H vibrations.

C-H stretching vibrations:

The benzene derivatives show characteristic medium vibration bands, in the region 3100-3000 cm^{-1} [6,7]. In 3-Methoxyphenyl isocyanate five weak to medium IR bands at 3162,3072,3006,2967 and 2946 cm^{-1} are assigned to the C-H stretching vibrations, for which the computed bands are predicted at 3116,3096,3086,2966 and 2908 cm^{-1} respectively. A medium strong C-H asymmetric stretching is observed at 897 cm^{-1} in IR which is computed at 882 cm^{-1} at B3LYP.

C-H in-plane vibrations:

The CH in-plane bending vibrations are substitution sensitive, normally showing the bands in the region 1300-1000 cm^{-1} [6,7]. In 3-Methoxy phenylisocyanate five medium strong IR bands at 1437,1311,1096,847 and 771 cm^{-1} are assigned to CH in-plane bending vibrations which are computed respectively at 1454,1309,1098,851 and 757 cm^{-1} using B3LYP.

C-H deformation vibrations:

The 3-Methoxy phenyl isocyanate show weak C-H deformation IR vibration band 724 cm^{-1} and a strong C-H deformation vibration IR band at 683 cm^{-1} . The computed C-H deformation bands are respectively observed at 706 and 671 cm^{-1} .

2: C-C vibrations:

C-C stretching vibrations:

The C-C stretching vibrations occur in a wider spectral range covering 1650-650 cm^{-1} [4]. Four medium to strong IR bands at 1600,1554, 1506, and 1238 cm^{-1} are assigned to C-C stretching vibrations which are computed at 1583,1569,1495 and 1238 cm^{-1} respectively.

3: Group vibrations.

NCO vibrations.

There are three vibrations for NCO moiety: asymmetric stretching, out of plane bending and wagging. In our work, two medium strong IR bands at 627 and 567 cm^{-1} are assigned to NCO out of plane bending vibration which are computed respectively at 627 and 556 cm^{-1} respectively. A strong IR band at 2272 cm^{-1} and computed band at 2280 cm^{-1} is assigned to NCO asymmetric stretching vibration and a weak IR band for wagging vibration of the NCO moiety is assigned at 453 cm^{-1} which is computed at 545 cm^{-1} .

CH₃ vibrations.

A medium strong IR band at 1475 cm^{-1} and computed band at 1458 cm^{-1} is assigned to CH₃ in-plane bending vibration.

CO-CH₃ vibrations

In 3-Methoxyphenyl isocyanate a medium strong IR band at 1285 cm^{-1} and the computed band at 1262 cm^{-1} is assigned to the stretching of CO-CH₃ group vibration.

O-CH₃ vibrations

A medium strong IR absorption band at 1043cm^{-1} and computed band at 1065cm^{-1} is assigned to the asymmetric stretching group vibration of O-CH₃ in the molecule of 3- Methoxy phenyl isocyanate

6. CONCLUSIONS.

Vibrational assignments for FTIR spectrum of 3 *methoxy phenylisocyanate* has been proposed, aided by the hybrid density functional method: B3LYP level using 6-31G* basis set. The characteristic NCO asymmetric stretching mode is highly intense and appears at the same frequency as predicted. Characteristic benzene as well as C-H vibrations is in the correlation range. We also note that C-H deformation vibrations show dominance in the region below 750cm^{-1} . All the assignments are in agreement with the similar systems [1-7,14].

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