

1-((E)-3-THIOCYNAТОPROP-1-ENYL)BENZENE

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1. Experimental

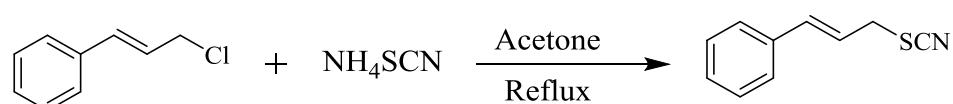
Cinammyl chloride, ammonium thiocyanate, Acetone, n-hexane and Dichloromethane were purchase from sigma Aldrich and were used without further purifications.

1.1.1. NMR and EI-MS data of 1-((E)-3-thiocyanatoprop-1-enyl)benzene

Yield: 84 %; **¹H-NMR** (300 MHz, CDCl₃); δ (ppm) = 3.77 (d, 2H, CH₂, J(¹H,¹H) = 7.49 Hz), 6.23 (dt, 1H, CH, J(¹H,¹H) = 7.49, 15.88 Hz), 6.72 (d, 1H, CH, J(¹H,¹H) = 15.88 Hz), 7.29-7.51 (m, 5H, Aromatic protons); **¹³C-NMR** (75.8 MHz, CDCl₃); δ (ppm) = 36.9, 111.9 (SCN), 121.2, 126.8, 128.6, 128.7, 135.4, 136.4; EI-MS, m/z (% intensity): 175 M⁺ (4), 117 C₉H₉⁺ (100), 91 (24), 82 (20).

2.3. DFT calculations

The geometry of the title compound (**1**) was obtained from X-ray crystallographic data. The molecular structure of (**1**) (C₁₀H₉NS) in ground state was optimized by DFT method including correlation correction using B3LYP-6311G model of theory (Zheng & Musgrave, 2007, Weng *et al.*, 2007, Hagberg *et al.*, 2006, Ahmadi *et al.*, 2010, Jacquemin *et al.*, 2008, Schlegl *et al.*, 2001). Calculations related to other molecular properties i.e., (HOMO-LUMO) Frontier molecular orbital energies, bands gaps (HOMO-LUMO gaps), ionization energy (IE), electron affinity (EA), global hardness and global electrophilicity for the title crystalline compound was calculated with the same level of theory (Taghki *et al.*, 2012, Kaur *et al.*, 2008, Zade *et al.*, 2006, Jagtap *et al.*, 2013, Putz *et al.*, 2003, Ingold, 1935, Soto-Delgado *et al.*, 2010, Khan *et al.*, 2015) All calculations were performed by using Gauss-view molecule visualizer program and GAUSSIAN-03 program package.



Scheme 1. Reaction of cinammyl chloride with ammonium thiocyanate

The molecular structure of compound **1** can be deduced from its characteristic ^1H -NMR and ^{13}C -NMR data set. In ^1H -NMR the doublet peak appears at 3.77 ppm corresponds to $-\text{CH}_2$ protons. The $=\text{CH}$ adjacent to CH_2 appears as doublet at 6.23 ppm, a doublet of triplet (dt) corresponds to $=\text{CH}$ with $^3J(^1\text{H}, ^1\text{H})$ coupling constant 7.49 Hz and 15.88 Hz. All other aromatic hydrogen appear in their characteristic region at 7.26-7.47 ppm as multiplet. In ^{13}C -NMR the olefinic carbon at 135.5 ppm and SCN carbon at 111.9 ppm clearly show the formation of the compound.

Table S1. Selected experimental and theoretical bond lengths (\AA) and bond angles ($^\circ$) of compound

	Experimental	Calculated		Experimental	Calculated
	<u>Bond distances</u>			<u>Bond angles</u>	
S1-C1	1.680(2)	1.7013	C1-S1-C2	99.41(9)	160.036
S1-C2	1.829(2)	1.8858	N1-C1-S1	178.00(2)	178.869
N1-C1	1.134(2)	1.1670	C3-C2-S1	114.20(14)	108.457
C2-C3	1.479(2)	1.4912	C4-C3-C2	123.06(18)	122.960
C3-C4	1.313(2)	1.3440	C3-C4-C5	127.41(16)	127.794
C4-C5	1.463(2)	1.4680	C10-C5-C6	117.75(16)	118.103
C5-C10	1.388(2)	1.4060	C10-C5-C4	119.76(15)	118.579
C5-C6	1.390(2)	1.4077	C6-C5-C4	122.49(15)	123.318

Table S2. Data for hydrogen bonding of compound **1**.

X	H	Y	$d(\text{X-H})$ (\AA)	$d(\text{H-Y})$ (\AA)	$d(\text{X-Y})$ (\AA)	$\angle(\text{XHY})$ ($^\circ$)
C2	H2b	N1	0.970(2)	2.701(3)	3.652(2)	166.70(3)

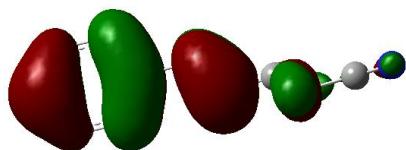
3.2. HOMO-LUMO energy gap of the title compound

HOMO of compound **1** are delocalized on half of the phenyl ring and localized on ethylene and thiocyanate group. The LUMO of the respective molecule are localized on phenyl group and delocalized on ethylene and thiocyanate groups. The energy gap between HOMO-LUMO is 0.158 which shows the stability of LUMO due to the electron accepting properties associated with electron donating properties of HOMO. The low band gap is generally and

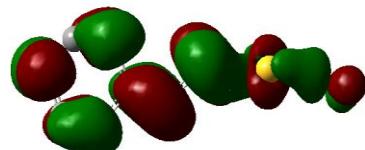
evidence of high reactivity, low stability and charge transfer in a particular molecule (Renuga & Muthu, 2014). The calculated energy parameters of compound **1** are given in **Table 4**.

Table S3. List of HOMO-LUMO energy, ionization energy (IE), electron affinity (EA), global hardness (η), Chemical Potential (μ) and Global Electrophilicity (ω)

E_{HOMO} (eV)	-0.237
E_{LUMO} (eV)	-0.052
$\Delta E = (E_{\text{LUMO}} - E_{\text{HOMO}})$ (eV)	0.185
IE = $-E_{\text{HOMO}}$ (eV)	0.237
EA = $-E_{\text{LUMO}}$ (eV)	0.052
Global Hardness(η) = $1/2 (E_{\text{LUMO}} - E_{\text{HOMO}})$	0.0925
Chemical Potential $\mu = 1/2 (E_{\text{HOMO}} + E_{\text{LUMO}})$	-0.1445
Global Electrophilicity $\omega = \mu^2 / 2\eta$	0.112



$$E_{\text{HOMO}} = -0.237 \text{ eV}$$



$$E_{\text{LUMO}} = -0.052 \text{ eV}$$

Figure S1. Frontier orbitals (HOMO, LUMO) of the compound **1**.

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