International Journal of Advance Research in Science and Engineering
Volume No 06, Special Issue No. 03, September 2017, AFM-2017
www.ijarse.com
IJARSE
ISSN: 2319-8354

THEORETICAL CALCULATIONS AND EXPERIMENTAL STUDIES OF A SALEN TYPE DERIVATIVE OF SEMICARBAZONE

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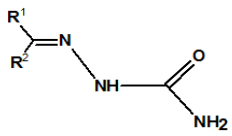
ABSTRACT

Semicarbazones are obtained by the condensation of semicarbazides with suitable aldehydes or ketones. For the preparation of the present organic compound we have selected one salicylaldehyde derivative. After the synthesis of the selected compound we have grown the single crystals of the same and subjected to Single Crystal X-Ray Diffraction Study (SXRD). The spectral studies including elemental analysis, FT-IR, NMR, electronic spectroscopy, NLO activity measurements, thermal studies etc were also done. The DFT studies of the same compound were also done. We have selected this topic due to their wide range of applications that we found from the literature.

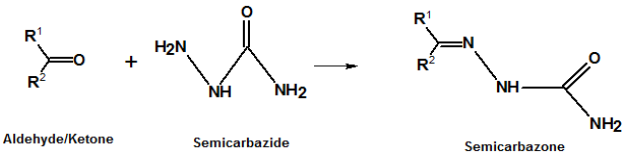
Keywords : Semicarbazone, Single crystal X-ray diffraction, DFT, NLO, Thermogravimetry

I.INTRODUCTION

Semicarbazones are compounds with versatile structural features. It can exist in two tautomeric forms keto and enol. Semicarbazones are compounds having the formula $R_2C{=}N{-}NH{-}(CO){-}NH_2$ (Scheme 1). These compounds are formally derived from aldehyde or ketone by their condensation with semicarbazide (Scheme 2). A great deal of studies have been devoted to the exploration for derivatives of semicarbazides. In recent years there has been considerable interest in semicarbazones due to their wide spectrum of biological applications [1]. Semicarbazones are promising compounds in co-ordination chemistry because of their interesting range of biological properties including antimicrobial [2], antitumour [3], anticonvulsant activities [4,5] etc. Their biological applications also include antihypertensive, hypolipidemic, antineoplastic, and hypnotic activities [6-12].It has been found that the biological activity of these compounds is enhanced by co-ordination with metal ions. An interesting aspect is that semicarbazones show a variety of co-ordination modes with transition metals. The metal complexes of semicarbazones play an essential role in pharmaceutical, agriculture and industrial chemistry. Semicarbazones can be hydrolysed to the original carbonyl compound and hence they are useful for the isolation, purification and characterization of carbonyl compounds [13]. FT-IR, FT-Raman spectra combined with quantum chemical computations have newly been productively employed in the vibrational analysis of drug molecules, biological compounds, natural products and NLO active compounds [14-17].

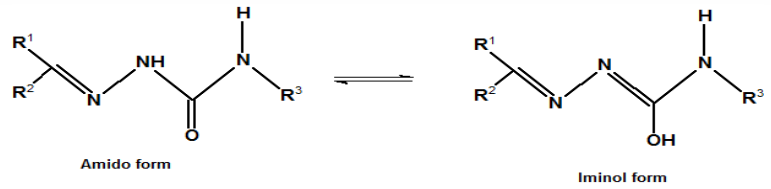


Scheme 1 : Semicarbazone



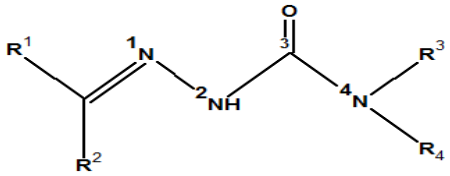
Scheme 2 : Synthesis scheme of semicarbazone

Its very interesting that the semicarbazones exist predominantly in the Amido form in the solid state,whereas exhibit Amido-Iminol tautomerism in solution state due to the interaction of solvent molecules (Scheme 3).



Scheme 3: Amido-Iminol tautomerism in semicarbazone

The IUPAC Numbering scheme of Semicarbazones is given in Scheme 4



Scheme 4: IUPAC Numbering scheme of Semicarbazones

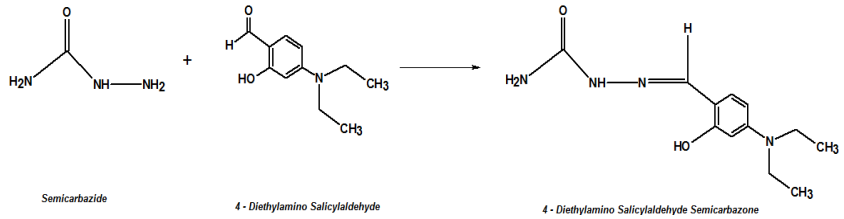
II. EXPERIMENTAL

2.1 Materials used :

N^4-phenylsemicarbazide (Alfa Aesar) and 4-[N,N Diethylamino] Salicylaldehyde (Sigma Aldrich) used were of AR grade. AR ethanol (Merck) for the synthesis of e title compound was used as such without further purification.

2.2 Synthesis of 4 - [N,N Diethylamino] Salicylaldehyde semicarbazone:

The present compound 4-(Diethylamino) Salicylaldehyde Semicarbazone˟ (abbreviated as ˟ SCDS) was prepared by refluxing mixture of Semicarbazide hydrochloride (0.1115g, 1mmol) in 25ml water, Sodium acetate (0.1230g, 1mmol) in 25ml water and 4-(Diethylamino)Salicylaldehyde (0.1932g, 1mmol) in 25ml ethanol for 3-4 hours. The resulting solution was concentrated and cooled to room temperature. A light yellow coloured precipitate of SCDS formed (Scheme: 5) filtered and washed with water and ethanol. The resulting ligand SD was recrystallized from methanol by slow evaporation method in air for few days[18].



Scheme 5: Synthesis of SCDS

III. RESULTS AND DISCUSSIONS

3.1 Elemental analysis

From elemental analysis it is clear that the experimental values are in good agreement with the theoretical values.

Table 1 : Comparison of CHN values

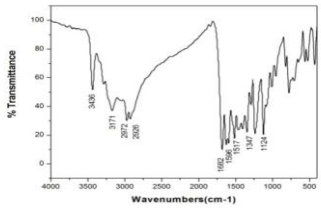
SCDS	C%	N%	H%
OBSERVED	56.69	22.04	22.04
CALCULATED	57.69	22.65	8.07

3.2 FT-IR Study

The peak at 3436 cm^{-1} is assigned to OH stretching frequency. The medium band observed at 3171 cm^{-1} is assignable to ^{4}NH stretching vibration. The ^{2}NH stretching frequency is observed at 2972 cm^{-1}. The =CH

stretching frequency is observed at 2926 cm–^{1}. The strong band at 1682 cm–^{1} is assigned to C=O stretching frequency. This confirms the existence of amido form of the compound in solid state. The IR spectrum shows a medium band at 1517 cm–^{1} which is attributed to C=N stretching mode. A weak band at 1347 cm–^{1} is due to C–N stretching mode. The strong band at 1124 cm–^{1} is assigned to N–N stretching vibrations.

Fig. 1 : FT-IR spectrum of SCDS



3.3 NMR Study

3.3.1 H NMR Study

Triplets at 1.071, 1.089 and 1.106ppm indicates CH_3 protons adjacent to CH_2 group. The quartets around 3.285, 3.303, 3.320 and 3.338ppm indicates CH_2 protons adjacent to CH_3. Multiplet between 6 & 7 ppm indicates phenyl ring protons. A singlet at 7.326ppm indicates protons attached to N=C. A singlet at 9.83ppm shows the presence of hydroxyl proton. A peak at 7.348ppm corresponds to NH proton.

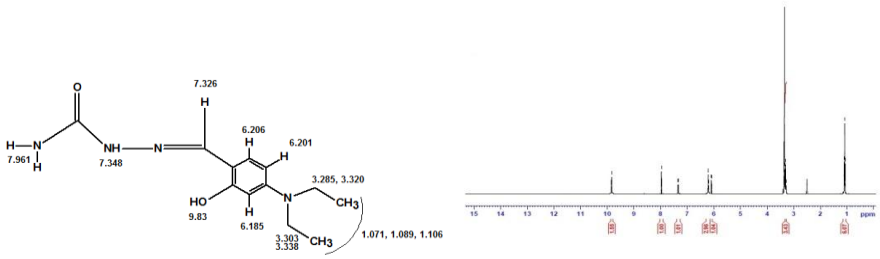


Fig. 2 : ^{1}H NMR spectrum and its interpretations of SCD

3.3.2 ^{13}C NMR Study

The ^{13}C NMR spectrum is shown in Fig.3. The ^{13}C NMR spectrum give 10 different peaks for differentcarbon atoms. Due to conjugation of the semicarbazone skeleton the carbonyl carbon give signal at 157.7 ppm. The azomethine carbon atom signal is shifted to down field at 97.52 ppm due to the presence of the electronegative nitrogen atom and electron delocalization on the azomethine bond. The carbon atom attached to azomethine carbon show signal at a low field, 128.9 ppm due to the presence of azomethine moiety. The carbon atoms nearer to –OH show downshifted signals at 156.48ppm [19] and the carbon bonded to diethylamino group shows signal at 149ppm respectively. The remaining aryl carbons gives signals at 103, 140.5 and 107.79. The methyl groups and methylene groups in the diethylamino group shows signals at 12.520 and 43.72 respectively.

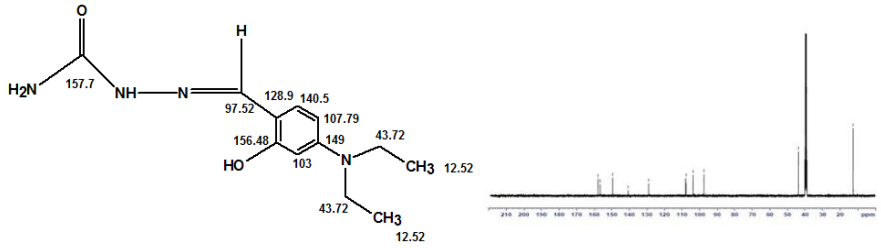


Fig. 3 : ^{13}C NMR spectrum and its interpretation of SCDS.

3.4 Electronic Spectroscopy

The absorption peak at 283 nm corresponds to ***π–π**** transition and the peak at 368 nm is attributed to ***n–π**** transition associated with azomethine linkage. There is no band between 400–800 nm and the compound is a potential candidate for NLO applications.

Table 2 : UV-VIS Values of SCDS

COMPOUND	π–π*	n–π*
SCDS	283	368

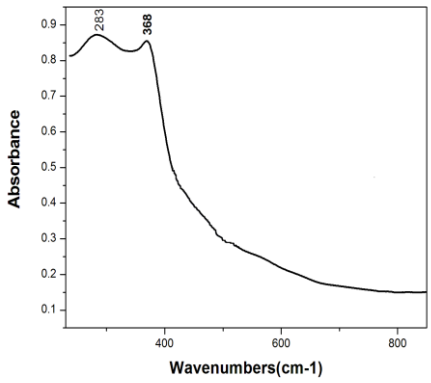


Fig. 4 : UV-VIS Spectrum of SCDS

3.5 Optical activity study

The title compound was subjected to NLO study. SCDS shows NLO activity (NLO value 42mv) and its activity is 76.4% of reference KDP (NLO value 55mv) and 40.7% 0f reference Urea (NLO value 135mv).

Table 3 : NLO Value of SCDS

Sample	SHG Signal(mv)
SD	42
KDP	55
Urea	135

3.6 Thermal study

The thermo gravimetric analysis of the compound SCDS was carried out within the temperature ranges from room temperature to 750°C. The TG/DTG curves of SCDS are shown in Fig. The TG and DTG curve shows that the compound is stable up to 225°C. The analysis shows three stages of decomposition in temperature ranges 227-267 °C, 267-367 °C and 367-765 °C. The first stage decomposition corresponds to a weight loss of 6.8% which could be attributed to the loss of –OH moiety . The second stage decomposition corresponds to a weight loss of 59% which could be attributed to the loss of remaining aldehyde moiety. The third stage decomposition corresponds to a weight loss of 34.2% which could be attributed to the loss of semicarbazone moiety.

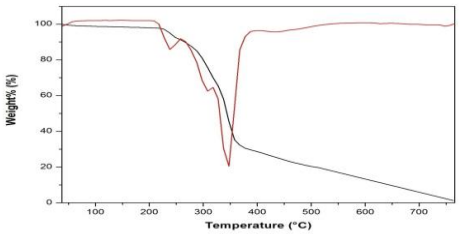


Fig.**5 : TG/DTG curve of SCDS**

3.7 Single Crystal X-Ray Diffraction Study

On crystallization of SCDS we get block shaped colourless crystals. The obtained crystals were subjected to single crystal X-ray diffraction studies. SCDS crystallizes in triclinic space group P-1.

Crystal structure of SCDS:

The photographs of crystalline SCDS is shown in Fig. 8.

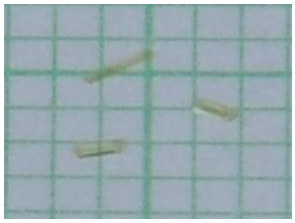


Fig. 6 : Photograph of Crystalline SCDS

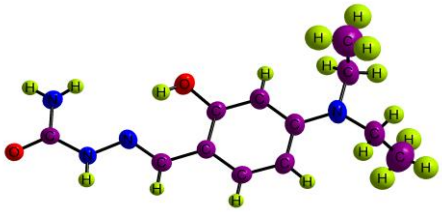


Fig. 7 : A single molecule of SCDS with atom labelling

The packing diagram along the C-axis is in the Fig. 8. The table 4 describes the crystal datas of SCDS from SXRD study.

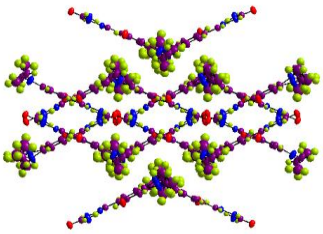


Fig. 8 : The packing diagram of SCDS along C-axis

Table 4 : Crystal data and structure refinement parameters for SCDS

PARAMETERS	SCDS
Space group crystal system	triclinic

Space group IT number	2
Space group name H-M alt	'P -1'
Space group name Hall	'-P 1'
Cell length a	8.7889(9)
Cell length b	12.4948(15)
Cell length c	14.2311(18)
Cell angle alpha	112.873(5)
Cell angle beta	96.085(5)
Cell angle gamma	107.365(5)
Cell volume	1329.8(3)
Cell formula units Z	4
Cell measurement temperature	296(2)
Cell measurement reflns used	3006
Cell measurement theta min	2.509
Cell measurement theta max	21.737
Exptl crystal description	block
Exptl crystal colour	colorless
Exptl crystal density diffrn	1.250
Exptl crystal F 000	536
Exptl crystal size max	0.350
Exptl crystal size mid	0.300
Exptl crystal size min	0.300
Exptl absorpt coefficient mu	0.088
Shelx estimated absorpt T min	0.970
Shelx estimated absorpt T max	0.974
Exptl absorpt correction type	multi-scan
Exptl absorpt correction T min	0.962
Exptl absorpt correction T max	0.972
Exptl absorpt process details	'SADABS (Bruker, 1999)'
Diffrn ambient temperature	296(2)
Diffrn radiation wavelength	0.71073
Diffrn radiation type	MoK\a
Diffrn radiation source	'fine-focus sealed tube'
Diffrn radiation monochromator	graphite

From the Single Crystal X-Ray Diffraction Studies it is clear that two molecules make up the asymmetric unit of the title compound, $C_{12}H_{18}N_4O_2$. i.e. The asymmetric unit consists of two crystallographically independent molecules. I.e. the diethylamino group of one of the molecules is disordered (Fig.11) . The molecular structure of the title compound, showing two crystallographically independent molecules with 30% probability displacement ellipsoids. The intramolecular and hydrogen bonds generate S(6) ring motifs in both molecules in the assymmetric unit of the title compound (Fig.12). Intra and inter molecular hydrogen bonding in SCDS is represented in Fig.13. The existence of amido form of SCDS is confirmed by the azomethine bond of distance 1.285 A° which remain close to the formal bond distances 1.28 A° of C=N and the carbonyl carbon-oxygen bond of distance 1.230A°which remain close to the bond distances 1.220 A° of C=O respectively [20 & 21]. The extended delocalization along the semicarbazone chain can be confirmed by the intermediate bond distance of single and double bonds in N-N, C-N and C-N [22 & 23]. The hydrogen bonding interactions in the compound SCDS is given in table 5.

International Journal of Advance Research in Science and Engineering
Volume No 06, Special Issue No. 03, September 2017, AFM-2017
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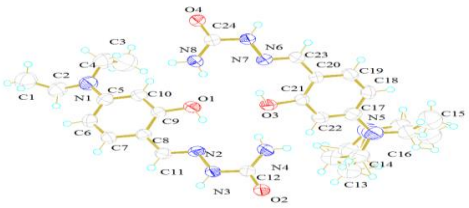

Fig. 9 : Asymmetric unit of SCDS

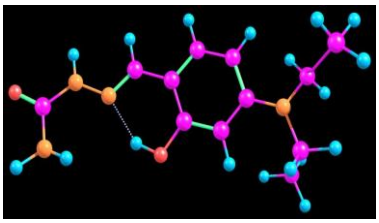

Fig. 10 : intramolecular hydrogen bonds generate S(6) ring

Table 5 : Hydrogen-bonding in SCDS

D-H···A	D-H	H···A	D-A	DH···A
O1A—H1O1···N2A	0.87	1.79	2.608 (4)	157
O1B—H2O1···N2B	0.87	1.91	2.654 (5)	142
N3A—H1N3···O2A	0.95	1.90	2.832 (4)	168
N3B—H2N3....O2B	0.99	1.87	2.837 (4)	168
N4A—H1N4···O1B	0.79	2.40	3.077 (5)	144
N4A—H2N4···O2B	0.90	2.01	2.901 (5)	172
N4B—H3N4···O2A	0.78	2.14	2.911 (5)	167
N4B—H4N4···O1A	0.89	2.20	2.962 (5)	144
C9A—H9AB···Cg1	0.97	2.83	3.733 (19)	156
C10X—H10F···Cg1	0.96	2.71	3.46 (3)	136

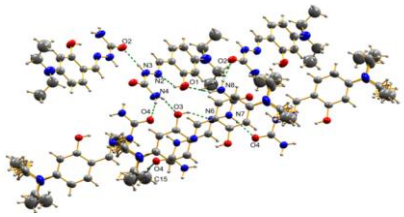

Fig. 11 : Intra and inter molecular hydrogen bonding in SCDS

The intramolecular hydrogen bonds and minor component of disorder are shown as dashed line and open bonds, respectively in the Fig.12.

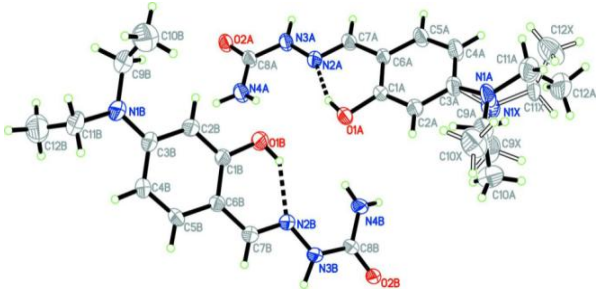

Fig. 12. Intramolecular hydrogen bonding in SCDS

In the crystal, N—H··· O hydrogen bonds link the molecules into sheets lying parallel to the ac plane and C—H interactions are also observed. The crystal packing of the title compound, showing a two-dimensional network parallel to the ac plane and the intermolecular hydrogen bonds are shown as dashed lines (Fig.13).

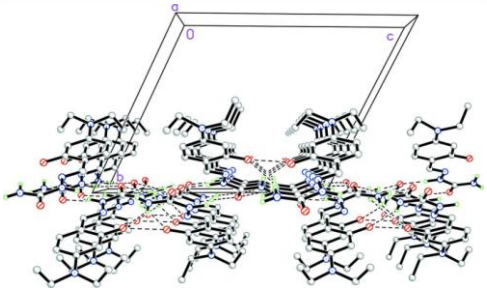

Fig. 13. Intermolecular hydrogen bonding along with crystal packing showing 2D network parallel to ac plane

C - H··· Π INTERACTIONS IN SCDS

The crystal structure is further consolidated by C—H···π interactions, involving the centroid of the benzene ring (Fig. 14).

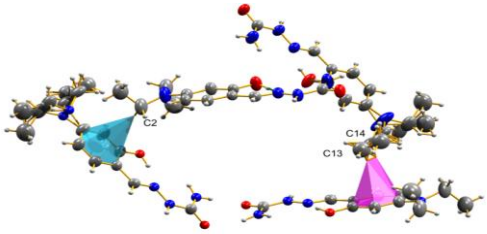

Fig. 14. C—H···π interactions in SCDS

IV. COMPUTATIONAL STUDIES

The Density Functional Theory (DFT) with the three-parameter hybrid functional (B3) [24] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [25] has been used for the computational studies of optimized geometry, molecular structure, vibrational frequencies etc [26]. The computational values contains some systematic errors and thus used a scaling factor of 0.9673 [27]. By combining the results of the GAUSSVIEW'S program [28] with symmetry considerations, vibrational frequency assignments were made with a high extent of accuracy. The optimized geometry of the title compound is given in Fig. 15. The calculated values were compared with Single crystal X-ray diffraction results. For this comparison the platon figure from SXRD was used and the corresponding SXRD platon geometry is as below (Fig.16).

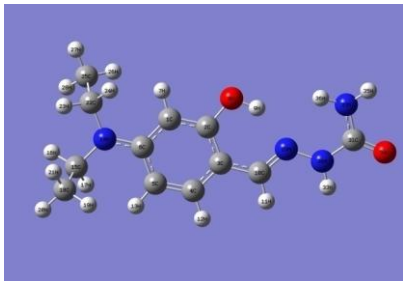

Fig. 15. Optimized geometry of SCDS

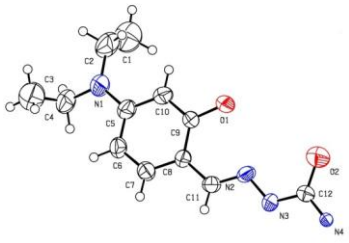

Fig. 16. Platon diagram of SCDS

Theoretical calculations were carried out by considering the compound as in gaseous phase. The comparative study of bond lengths, bond angles and torsional angles in experimental and theoretical results are listed in Tables 6, 7 and 8. The theoretical and experimental values of bond lengths and bond angles shows almost good agreements but torsional angles shows some deviations in some values may be due to sterric factors.

Table 6: Comparison of bond lengths of SCDS Bond length(A^0)

Atoms connected	Cal	Exptl

C_1-C_2	1.3821	1.394
C_1-C_6	1.4003	1.396
C_2-C_3	1.4022	1.402
C_3-C_4	1.3948	1.393
C_4-C_5	1.3706	1.370
C_5-C_6	1.4136	1.406
C_6-N_{14}	1.369	1.370
N_{14}-C_{15}	1.4543	1.467
C_{15}-C_{18}	1.5285	1.443
N_{14}-C_{22}	1.4546	1.486
C_{22}-C_{25}	1.5285	1.472
C_2-O_8	1.2311	1.230
C_3-C_{10}	1.4581	1.444
C_{10}-N_{29}	1.2601	1.285
N_{29}-N_{30}	1.3667	1.376
N_{30}-N_{31}	1.3719	1.349
C_{31}-O_{34}	1.1976	1.240
C_{31}-N_{32}	1.3569	1.323
C_1-H_7	1.0699	0.9300
C_{10}-H_{11}	1.0854	0.9300
C_4-H_{12}	1.0772	0.9300
C_5-H_{13}	1.0699	0.9300
C_{15}-H_{16}	1.0846	0.9700
C_{15}-H_{17}	1.0826	0.9700
C_{18}-H_{19}	1.0844	0.9600
C_{18}-H_{20}	1.087	0.9600
C_{18}-H_{21}	1.0859	0.9600
C_{22}-H_{23}	1.0847	0.9700
C_{22}-H_{24}	1.0825	0.9700
C_{25}-H_{26}	1.0842	0.9600
C_{25}-H_{27}	1.0869	0.9600
C_{25}-H_{28}	1.086	0.9600
N_{30}-H_{33}	0.9972	0.878
N_{32}-H_{35}	0.993	0.851
N_{32}-H_{36}	0.9915	0.849

Table 7 : Comparison of bond angles of SCDS

Bond angle(°)		
Atoms connected	Cal	Exptl
C_2-C_1-C_6	121.6869	121.3
C_1-C_2-C_3	121.1448	121.3
C_2-C_3-C_4	116.6311	116.1

C_3-C_4-C_5	123.1703	123.5
C_4-C_5-C_6	120.0898	120.1
C_1-C_6-C_5	117.2735	117.5
C_1-C_6-N_{14}	121.3384	120.8
C_5-C_6-N_{14}	121.3881	121.7
C_2-C_3-C_{10}	124.036	122.8
C_4-C_3-C_{10}	119.3311	121.1
C_1-C_2-O_8	116.6728	117.2
C_3-C_2-O_8	122.1792	121.5
C_3-C_{10}-N_{29}	124.197	122.6
C_6-N_{14}-C_{15}	122.0564	121.5
C_6-N_{14}-C_{22}	121.9604	121.8
C_{15}-N_{14}-C_{22}	115.9816	115.8
N_{14}-C_{15}-C_{18}	114.0665	112.1
N_{14}-C_{22}-C_{25}	114.0937	112.6
C_{10}-N_{29}-N_{30}	117.404	116.2
N_{29}-N_{30}-C_{31}	121.748	121.4
N_{30}-C_{31}-N_{32}	116.0584	118.4
N_{30}-C_{31}-O_{34}	120.2943	122.3
N_{32}-C_{31}-O_{34}	123.6466	122.3

Table 8 : Comparison of torsional angles of SCDS
Torsional angles

Atoms connected	Cal	Exptl
C_6-C_1-C_2-C_3	0.2023	-0.8
C_6-C_1-C_2-O_8	179.54	178.9
C_2-C_1-C_6-C_5	-0.4302	3.3
C_2-C_1-C_6-N_{14}	179.6095	-176.8
C_1-C_2-C_3-C_4	0.3313	-2.1
C_1-C_2-C_3-C_{10}	179.8278	179
O_8-C_2-C_3-C_4	-178.9783	178.3
O_8-C_2-C_3-C_{10}	0.5183	-0.6
C_2-C_3-C_4-C_5	-0.6547	2.5
C_{10}-C_3-C_4-C_5	179.8239	-178.6
C_2-C_3-C_{10}-N_{29}	4.8028	-3.9
C_4-C_3-C_{10}-N_{29}	-175.7135	177.3
C_3-C_4-C_5-C_6	0.4348	0
C_4-C_5-C_6-C_1	0.1202	-2.9
C_4-C_5-C_6-N_{14}	-179.9195	177.2
C_1-C_6-N_{14}-C_{15}	173.0572	163.5
C_1-C_6-N_{14}-C_{22}	-6.4497	-5

C_5-C_6-N_{14}-C_{15}	-6.9014	-16.6
C_5-C_6-N_{14}-C_{22}	173.5916	175
C_3-C_{10}-N_{29}-N_{30}	-179.3656	-178.2
C_6-N_{14}-C_{15}-C_{18}	89.0058	105
C_6-N_{14}-C_{22}-C_{25}	88.4537	86.2
C_{15}-N_{14}-C_{22}-C_{25}	-91.0814	-82.8
C_{10}-N_{29}-N_{30}-C_{31}	176.6171	-171.5
N_{29}-N_{30}-C_{31}-N_{32}	14.0267	-1.6
N_{29}-N_{30}-C_{31}-O_{34}	-166.2901	178.5

The comparison of experimental and theoretical values in both ^{13}C and ^{1}H NMR studies are given in tables 9 and 10 respectively and the values show good agreements with each other.

Table 9 : Experimental and Theoretical ^{13}C NMR Chemical Shifts

Atoms	Experimental	Theoretical
C_1	94.83	103
C_2	159.79	156.48
C_3	105.09	128.9
C_4	131.59	140.5
C_5	101.68	107.79
C_6	149.83	149
C_{10}	97.52	94.83
C_{15}	43.72	41.84
C_{18}	12.52	8.93
C_{22}	43.72	43.02
C_{25}	12.52	8.32
C_{31}	157.7	151.45

Table 10 : Experimental and Theoretical ^{1}H NMR Chemical Shifts

Atoms	Experimental	Theoretical
H_7	6.185	5.79
H_9	9.83	9.05
H_{11}	7.326	7.15
H_{12}	6.206	6.62
H_{13}	6.201	5.88
H_{16}	3.285	2.83
H_{17}	3.320	3.05
H_{19}	1.071	1
H_{20}	1.089	0.64
H_{21}	1.106	0.89
H_{23}	3.303	2.84
H_{24}	3.338	3.07
H_{26}	1.071	1.04
H_{27}	1.089	0.64

H_{28}	1.106	0.89
H_{33}	7.348	6.23
H_{35}	7.9	3.73
H_{36}	7.9	4.64

Table 11 : Experimental and Theoretical IR frequencies

U (cm-1) Theoretical	IR Intensity	U (cm-1) Experimental	Assignments
23.27720393	0.4842	----	O=C-N & N-CH_2 bend
33.53841906	1.541	----	O=C-N & N-CH_2 bend
50.7629367	2.3813	----	N-CH_2 out f pln bend
51.80539591	0.1903	----	N-CH_2 out f pln bend
58.50452879	0.8042	----	C-CH_3 bend
91.45995614	0.768	----	C-CH_3 bend
94.7402639	0.3714	----	C-CH_3 bend
100.2908248	0.8015	----	Both CH_3 bend
169.8595244	2.7826	----	CH_3 inpln bend
202.6595067	0.4703	----	CH_3 inpln bend
204.5684732	8.5205	----	C-NH_2 bend
211.3715908	3.8342	----	CH_3 inpln bend
222.8712402	0.4055	----	CH_3 inpln bend
233.8722463	0.3232	----	Phen C-C bend
252.3525128	1.0327	----	N-N bend
267.9365864	3.442	----	C-CH_3str &Ph C-C bend
315.2444242	3.6318	----	C-CH_3str
335.566043	161.3928	----	NH_2 inpln bend
355.2475026	3.0566	----	C-CH_3 out f pln bend
388.8219053	61.6351	----	NH bend
390.7907477	24.956	----	NH bend
407.8796499	11.1485	----	NH bend & NH_2 bend
421.8713542	35.3305	----	NH & ph C-C str
446.0346049	11.5832	424	CH & NH str
471.2618856	3.7318	----	Phen C-C str
498.8623402	37.0974	----	NH_2 out f pln bend
509.4273842	38.4546	----	CH_2 out f pln bend
541.5226884	5.2787	524.7	C-N str
552.8070168	4.5599	----	Phen C-C str&NH_2 ben
570.1002127	29.9004	560.72	C=O bend
632.3864009	14.4792	----	Ph C-C Str
635.3646208	1.6785	----	Ph C-C & N-C str
654.9726624	70.7755	646.29	OH bend
693.0985017	9.4201	----	Phen C str
703.2205224	5.3265	----	Phen CH bend
723.5491057	22.1032	703.86	OCN sciss
765.1340098	22.5071	----	CH_2-CH_3 bend
768.0888211	7.7655	775.03	CH_2-CH_3 out f pln bnd
769.7634109	13.3333	----	CH_2-CH_3 out f pln bnd
799.0404865	7.7982	----	Phen str
814.7205163	23.2033	----	Phen CH bend

856.3742921	0.0926	825	Phen & CH_2-CH_3 bnd
897.2113766	1.8652	----	CH_3 out f pln bend
903.5207843	0.7963	----	CH-C-CH out f pln bend
928.6382765	11.7838	946.95	CH-C-CH wag
939.3347766	5.7628	----	Phen CH sciss
956.0246676	4.091	----	C-NH_2 str & C-C str
989.8270628	33.9543	----	Phen & CH str
1049.754877	15.4853	1010	CH_3 wag
1058.517261	66.7285	----	CH_3 wag & NH_2 rock
1061.540267	28.1631	----	CH_3 wag & NH_2 rock
1076.70134	15.8903	1075	CH2 rock
1114.894793	366.7837	----	H-C-C-H sciss
1122.932863	1.2479	----	H-C-C-H sciss
1147.388528	18.8278	1125	N-N str
1178.253717	35.97	----	Phen CH sciss
1207.410074	27.2238	----	Phen CH sciss
1224.593094	118.088	----	HC-CH str
1228.209249	211.7072	----	Phen C str
1269.002514	46.2459	1233	OH bend
1285.74551	34.163	1290	CH_2 twist
1315.117188	36.4173	----	CH_2 twist
1326.487799	39.5914	----	Phen C str
1333.870233	7.4792	----	Ch & NH bend
1349.089247	256.7744	----	CH_2 wag
1356.627416	209.3385	----	CH_2 wag
1363.807684	35.484	1347.58	CH_3 wagC-N & O-H str
1365.959056	61.6401	----	CH_3 wag
1369.391036	197.9417	----	CH_2 & CH_3 wag
1401.206598	84.9645	----	CH_2 rock
1438.365911	154.0522	1404	OH & NH bend
1442.386396	19.4846	----	CH_3 rock
1443.790626	2.1736	----	CH_3 rock
1447.772613	68.1352	----	CH_2 sciss
1452.915263	2.3186	----	CH_2 sciss
1458.576967	36.4967	1469	NH bend
1466.474585	37.2836	----	NH bend
1477.893658	5.0591	----	CH_2 sciss
1505.418179	215.2827	----	Phen C---N str
1530.309807	106.7212	----	C-O-H scis
1550.653577	418.6132	1511	NH_2 sciss
1595.761001	87.5629	1583	N=C str
1617.627688	617.754	1625.85	C-O-H scis & phe C str
1711.131162	816.0281	1683	C=O str
2929.287939	25.338	----	CH_3 sym str
2929.731639	24.5069	----	CH_3 sym str
2935.089804	41.2774	----	CH_2 sym str
2944.612969	83.2271	----	CH_2 sym str
2945.292981	20.5561	2920	N=C-H str

2971.105962	2.3408	----	CH_2 asym str
2972.837719	4.7488	----	CH_2 asym str
2991.276489	37.397	----	CH_3 asym str
2991.631585	44.5852	----	CH_3 asym str
3005.681133	4.1201	----	CH_3 asym str
3007.117574	67.613	2970	Phen CH str
3054.123517	11.0651	----	Phen CH str
3114.65009	9.9263	----	Phen CH str
3115.538942	6.4025	----	Phen CH str
3372.112849	247.2708	3177.97	OH str
3429.083143	22.3153	----	NH str
3484.856307	26.9545	3292	NH_2 sym str
3604.692976	84.9895	3435	NH_2 asym str.

Supplementary Data

CCDC 1513345 contains the supplementary crystallographic data for SCDS ($C_{12}H_{18}N_4O_2$) and these data can be obtained via E-mail : deposit@ccdc.cam.ac.uk or from the Cambridge Crystallorgaphic Data Centre.

V. CONCLUSIONS

The compound 4-(N,N Diethylamino) Salicylaldehyde semicarbazone (SCDS) was synthesized. The compound was analysed by various spectral techniques such as FT-IR, NMR, UV-VIS, Thermal studies etc. The stoichiometry of the compound was determined by using CHN analysis. The amido form of the compound was confirmed by FT-IR and NMR spectral studies. The existence of this amido form can be again confirmed by SXRD and theoretical studies. Thermal studies showed that SCDS is stable up to 225^0C and decomposes in three stages. The single crystals of SCDS were grown by slow evaporation technique using methanol as solvent. The single crystal X-ray diffraction revealed that SCDS crystallizes in triclinic space group 'P -1' and exists in amido form. The DFT calculations of the title compound were done and that revealed that the theoretical values are in good agreement with the experimental values except one or two values that may be due to the presence of neighbouring groups in gaseous phase and that may cause hydrogen bonding in theoretical conditions.

VI. ACKNOWLEDGEMENTS

The authors are thankful to the SAIF, STIC, Cochin University of Science and Technology for providing the instrumental facilities. We are greatly thankful to the University of Kerala for the financial assistance in the form of Junior Research Fellowship. We also express our sincere thanks to DR. M.R.Prathapachandra Kurup for his immense help in SXRD study. We also thankful to DR. Sithambaresan M, Department of Chemistry, Faculty of Science, Eastern University, Sri Lanka, Chenkalady, Sri Lanka for helping us in SXRD study. We thankful to the god almighty for his blessings.

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