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Vibrational spectroscopic and quantum chemical calculations of *(E)-N*-Carbamimidoyl-4-((naphthalen-1-yl-methylene)amino)benzene sulfonamide

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1. Introduction

ABSTRACT

FT-IR and FT-Raman spectra of (*E*)-*N*-Carbamimidoyl-4-((naphthalen-1-yl-methylene)amino)benzene sulfonamide were recorded and analyzed. The vibrational wavenumbers were computing at various levels of theory. The data obtained from theoretical calculations are used to assign vibrational bands obtained experimentally. The results indicate that B3LYP method is able to provide satisfactory results for predicting vibrational frequencies and structural parameters. The calculated first hyperpolarizability is comparable with reported values of similar derivatives and is an attractive object for future studies of non-linear optics. The geometrical parameters of the title compound are in agreement with that of similar derivatives.

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The naphthalene and its derivatives are of great interest in biological activity and widely used as a parent compound to make drugs. Srivastava has investigated the infrared and Raman spectrum of the condensed and liquid phase naphthalene and its cation [1]. Extensive recent studies of vibrational spectra of substituted naphthalene compounds have assigned [1–4] complete vibrational mode and frequency analyses. Naphthalene is classified as a benzenoid polycyclic aromatic hydrocarbon which is crystalline white solid with the structure of two fused benzene rings and do not contain heteroatoms or carry substituents. Like benzene, naphthalene can undergo electrophilic aromatic substitution. It constitute a group of widespread pollutants of great environmental interest [5,6]. It is widely recognized that polycyclic aromatic hydrocarbons and their metabolities are among the most toxic, carcinogenic and mutagenic atmospheric contaminants [7–10]. Sulfonamides form a significant class of compounds in medicinal and pharmaceutical chemistry with several biological applications [11–14]. Many chemotherapeutically important sulfa drugs, like sulphadiazine, sulphathiazole, sulphamerazine and sulfonamides, posses SO_2NH moiety which is an important toxophoric function [15]. The chemistry of sulfonamides has been known as synthons in the preparation of various valuable biologically active compounds [16,17] used as antibacterial [18], protease inhibitor [19], diuretic [20], anti-tumor [21], and hypoglycaemic [22]. To our knowledge, no theoretical HF or density functional theory (DFT) calculations or detailed vibrational spectroscopic analyses have been performed on the title compound.

2. Experimental

All the chemicals were procured from Sigma–Aldrich, USA. 0.5 mg of sulphaguanidine and 0.3 ml of 1-napththaldehyde in 20 ml ethanol is refluxed 2 h and cooled. The light yellow precipitate was filtered off, washed with ethanol and dried. Elemental analysis: found/calculated (%): C 61.2/61.3; H 4.42/4.53; N 15.80/15.50; S 9.01/9.59; O 9.02/9.01. The FT-IR spectrum (Fig. 1) was recorded on a DR/Jasco FT-IR 6300 spectrometer in KBr pellets, number of scans 16, resolution 2 cm⁻¹. The FT-Raman spectrum (Fig. 2) was obtained

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Fig. 1. FT-IR spectrum of *(E)-N*-Carbamimidoyl-4-((naphthalen-1-yl-methylene)amino)benzene sulfonamide.



Fig. 2. FT-Raman spectrum of *(E)-N*-Carbamimidoyl-4-((naphthalen-1-yl-methylene)amino)benzene sulfonamide.

on a BRUKER RFS 100/S, Germany. For excitation of the spectrum the emission of a Nd:YAG laser was used, excitation wavelength 1064 nm, maximal power 150 mW, measurement of solid sample. One thousand scans were accumulated with a total registration time of about 30 min. The spectral resolution after apodization was 2 cm^{-1} .

3. Computational details

Calculations of the title compound were carried out with Gaussin03 program [23] using the HF/6-31G*, B3PW91/6-31G* and B3LYP/6-31G* basis sets to predict the molecular structure and vibrational wavenumbers. The wavenumber values computed contain known systematic errors [24] and we therefore, have used the scaling factor values of 0.8929 and 0.9613 for HF and DFT basis sets. Parameters corresponding to optimized geometry (B3LYP) of the title compound (Fig. 3) are given in Table 1. The



Fig. 3. Optimized geometry (B3LYP) of (*E*)-*N*-Carbamimidoyl-4-((naphthalen-1-yl-methylene)amino)benzene sulfonamide.



Fig. 4. Profile of potential energy surface scan for the torsion angle C_{21} - N_{20} - C_{18} - C_{11} .

absence of imaginary values of wavenumbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. Potential energy distribution is done using GAR2PED program [25]. The assignment of the calculated wavenumbers is aided by the animation option of MOLEKEL program, which gives a visual presentation of the vibrational modes [26,27]. Potential energy surface scan studies have been carried out to understand the stability of planar and non planar structures of the molecule. The profiles of potential energy surface for torsion angles C_{21} – N_{20} – C_{18} – C_{11} , N_{34} – S_{31} – C_{28} – C_{24} , N_{37} – C_{36} – N_{34} – S_{31} and N_{38} – C_{36} – N_{34} – S_{31} are given Figs. 4–7. The energy is minimum for –175.5 (–1463.11766 Hartree), 80.0 (–1463.11278 Hartree), 36.9 (–1463.11599 Hartree) and –146.1 (–1463.11659 Hartree) for the above torsion angles.

4. Results and discussion

The observed IR, Raman bands and calculated (scaled) wavenumbers and assignments are given in Table 2.



Fig. 5. Profile of potential energy surface scan for the torsion angle N_{34} - S_{31} - C_{28} - C_{24} .

Table	1

Optimized geometrical (B3LYP) parameters, atom labeling according to Fig. 3.

Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)	
C ₁ -C ₂	1.3784	A(2,1,6)	119.7	D(6,1,2,3)	0.1
$C_1 - C_6$	1.4171	A(2,1,8)	120.5	D(6,1,2,9)	-179.8
$C_1 - H_8$	1.0848	A(6,1,8)	119.8	D(8,1,2,3)	180.0
$C_2 - C_3$	1.4245	A(1,2,3) A(1,2,0)	121.0	D(8,1,2,9) D(2,1,6,5)	0.0
$C_2 = C_4$	1 4414	A(3,2,9) A(3,2,9)	118.4	D(2,1,0,3) D(2,1,6,13)	_0.2 179.7
$C_3 - C_{10}$	1.4217	A(2,3,4)	119.5	D(8,1,6,5)	180.0
C_4-C_5	1.4255	A(2,3,10)	120.8	D(8,1,6,13)	-0.1
C ₄ -C ₁₁	1.4436	A(4,3,10)	119.6	D(1,2,3,4)	0.2
C_5-C_6	1.3816	A(3,4,5)	117.7	D(1,2,3,10)	-179.7
C_5-H_{12}	1.0833	A(3,4,11)	118.2	D(9,2,3,4)	-1/9.9
C ₁₀ -H ₇	1.0852	A(456)	124.1	D(2345)	-0.4
$C_{10} - C_{15}$	1.3820	A(4,5,12)	120.3	D(2,3,4,11)	179.8
C ₁₁ -C ₁₄	1.3941	A(6,5,12)	118.4	D(10,3,4,5)	179.5
C ₁₁ -C ₁₈	1.4634	A(1,6,5)	120.7	D(10,3,4,11)	-0.3
C ₁₄ -C ₁₅	1.4081	A(1,6,13)	119.6	D(2,3,10,7)	-0.1
$C_{14} - H_{16}$	1.0839	A(5,6,13)	119./	D(2,3,10,15) D(4,2,10,7)	1/9.8
$C_{15} - \Pi_{17}$	1.0847	A(3,10,7) A(3,10,15)	120.9	D(4,3,10,7) D(4,3,10,15)	-180.0 -0.1
$C_{18} - N_{20}$	1.2955	A(7.10.15)	120.5	D(3.4.5.6)	0.3
$C_{21} - N_{20}$	1.4056	A(4,11,14)	119.7	D(3,4,5,12)	-179.4
C ₂₁ -C ₂₂	1.4135	A(4,11,18)	121.5	D(11,4,5,6)	-179.9
C ₂₁ -C ₂₃	1.4105	A(14,11,18)	118.8	D(11,4,5,12)	0.5
$C_{22} - C_{24}$	1.3956	A(11,14,15)	121.5	D(3,4,11,14)	0.5
C ₂₂ -H ₂₅	1.0844	A(11,14,16) A(15,14,16)	117.9	D(5,4,11,18) D(5,4,11,14)	-179.1 -179.3
C ₂₃ -C ₂₆ C ₂₂ -H ₂₇	1.0834	A(10.15.14)	120.0	D(5.4,11,14) D(5.4,11,18)	1.1
C ₂₄ -C ₂₈	1.3922	A(10,15,17)	120.4	D(4,5,6,1)	-0.0
C ₂₄ -H ₂₉	1.0840	A(14,15,17)	119.7	D(4,5,6,13)	-179.9
C ₂₆ -C ₂₈	1.3935	A(11,18,19)	117.7	D(12,5,6,1)	179.6
C ₂₆ -H ₃₀	1.0841	A(11,18,20)	122.3	D(12,5,6,13)	-0.34
$C_{28} - S_{31}$	1.8634	A(19,18,20) A(18,20,21)	120.1	D(3,10,15,14) D(3,10,15,17)	0.3 170.0
S ₂₁ -O ₂₂ S ₂₁ -O ₂₂	1.6380	A(20,21,22)	122.1	D(7 10 15 14)	-179.8
S ₃₁ -N ₃₄	1.8057	A(20,21,23)	117.7	D(7,10,15,17)	0.0
N ₃₄ -H ₃₅	1.0148	A(22,21,23)	119.6	D(4,11,14,15)	-0.3
C ₃₆ -N ₃₄	1.4283	A(21,22,24)	120.4	D(4,11,14,16)	179.8
C ₃₆ -N ₃₇	1.2817	A(21,22,25)	119.9	D(18,11,14,15)	179.3
C ₃₆ -IN ₃₈ NH	1.3882	A(24,22,25) A(21,23,26)	119.8	D(18,11,14,16) D(4,11,18,19)	-0.7
N ₂₈ -H ₂₀	1.0089	A(21,23,20)	118.5	D(4,11,18,19) D(4,11,18,20)	-177.5
N ₃₈ -H ₄₀	1.0085	A(26,23,27)	121.0	D(14,11,18,19)	-177.5
		A(22,24,28)	118.1	D(14,11,18,20)	2.9
		A(22,24,29)	121.2	D(11,14,15,10)	-0.1
		A(28,24,29)	120.7	D(11,14,15,17)	-180.0
		A(23,26,28) A(23,26,30)	118.1	D(16, 14, 15, 10) D(16, 14, 15, 17)	1/9.9
		A(28,26,30)	119.9	D(11,18,20,21)	-175.5
		A(24,28,26)	123.4	D(19,18,20,21)	5.0
		A(24,28,31)	118.6	D(18,20,21,22)	41.4
		A(26,28,31)	118.0	D(18,20,21,23)	-141.1
		A(28,31,32)	107.7	D(20,21,22,24)	178.4
		A(28 31 34)	98.8	D(20,21,22,23) D(23,21,22,24)	0.1
		A(32,31,33)	119.4	D(23,21,22,25)	-177.4
		A(32,31,34)	111.8	D(20,21,23,26)	-179.2
		A(33,31,34)	106.3	D(20,21,23,27)	1.5
		A(31,34,35)	113.5	D(22,21,23,26)	-1.5
		A(31,34,36)	122.3	D(22,21,23,27)	179.1
		A(35,34,36) A(34,36,37)	120.5	D(21,22,24,28) D(21,22,24,28)	-0.4 170.6
		A(34,36,38)	111.2	D(25,22,24,28)	177.9
		A(37,36,38)	121.6	D(25,22,24,29)	-2.1
		A(36,37,41)	114.7	D(21,23,26,28)	1.7
		A(36,38,39)	114.9	D(21,23,26,30)	-178.2
		A(36,38,40)	120.4	D(27,23,26,28)	-179.0
		A(39,38,40)	117.1	D(27,23,20,30) D(27,24,28,26)	1.1
				D(22,24,28,20) D(22,24,28,31)	178 9
				D(29,24,28,26)	-179.4
				D(29,24,28,31)	-1.0
				D(23,26,28,24)	-1.2
				D(23,26,28,31)	-179.6
				D(30,26,28,24) D(30,26,28,21)	1/8.7
				D(JU,2U,20,JI)	0.3

Table 1	(Continue	d)
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Bond lengths (Å)	Bond angles (°)	Dihedral angles (°)	
		D(24,28,31,32)	-172.6
		D(24,28,31,33)	-40.2
		D(24,28,31,34)	71.1
		D(26,28,31,32)	5.9
		D(26,28,31,33)	138.3
		D(26,28,31,34)	-110.4
		D(28,31,34,35)	37.3
		D(28,31,34,36)	-164.3
		D(32,31,34,35)	-75.8
		D(32,31,34,36)	82.6
		D(33,31,34,35)	152.2
		D(33,31,34,36)	-49.4
		D(31,34,36,37)	36.9
		D(31,34,36,38)	-146.1
		D(35,34,36,37)	-166.2
		D(35,34,36,38)	10.8
		D(34,36,37,41)	3.8
		D(38,36,37,41)	-173.0
		D(34,36,38,39)	-171.1
		D(34,36,38,40)	40.0
		D(37,36,38,39)	6.1
		D(37 36 38 40)	-142.7

-1462.3

-1462.4

4.1. IR and Raman spectra

The C=N stretching skeletal bands [28-30] are observed in the range of 1627–1566 cm⁻¹. B3LYP calculations give these modes at 1684 and 1611 cm⁻¹. The C–N stretching vibration [31] is moderately to strongly active in the region 1275 ± 55 cm⁻¹. Primary aromatic amines with nitrogen directly on the ring absorb at 1330–1200 cm⁻¹ because of the stretching of the phenyl C-N bond [32]. For the title compound, the C_{21} - N_{20} stretching mode is observed at 1264 cm⁻¹ in Raman and at 1259 cm⁻¹ theoretically. Panicker et al. [33] reported CN stretching mode at 1219, 1237 (IR), 1222 (Raman) and at 1292, 1234, 1200 cm⁻¹ theoretically. The CN stretching modes C₃₆-N₃₈ and C₃₆-N₃₄ are assigned at 1071 and 918 cm⁻¹ theoretically, which is expected in the range of 850-1115 cm⁻¹ [31]. The band at 2980 cm⁻¹ in Raman and at 2970 cm^{-1} (B3LYP) is assigned as the C₁₈-H₁₉ stretching mode and the bands at 1408 and 977 cm^{-1} (B3LYP) are assigned as the in-plane and out-of-plane CH deformation bands.

The N-H stretching vibrations generally give rise to bands at $3500-3300 \text{ cm}^{-1}$ [34,35]. In the present case, the bands observed at 3443,3359 (B3LYP) and $3410,3336 \text{ cm}^{-1}$ (IR) are the assigned as NH

stretching vibrations. In the present study, the N₃₄-H₃₅ stretching bands has split into a doublet, 3336, 3215 cm⁻¹ in the IR spectrum owing to the Davydov coupling between neighboring units. The splitting of about 121 cm⁻¹ in the IR spectrum is due to the strong intermolecular hydrogen bonding. Furthermore the NH stretching wavenumber is red shifted by 144 cm⁻¹ in the IR spectrum with a strong intensity from the computed wavenumber which indicate the weakening of the NH bond [36]. In N-monosubstituted amides, the in-plane bending frequency and the resonance stiffened C-N band stretching frequency fall close together and therefore interact. The NH deformation band of guanidine structural motif is expected in the region $1395 \pm 25 \text{ cm}^{-1}$ [31,32]. The B3LYP calculations give this modes at 1356 and 1408 cm⁻¹. The out-of-plane NH deformation is expected in the region $650 \pm 50 \text{ cm}^{-1}$ [31] and bands at 675(IR), 669(Raman) and 668, 575 cm⁻¹ (B3LYP) are assigned as this mode. Wang and Ma [37] reported NH stretching bands in the region, 3365–3374 cm⁻¹ and guanidine C=N stretching bands in the region 1598–1638 cm⁻¹. According to Henry et al. [38] IR spectrum exhibits typical features for Schiff base possessing several bands of vNH and vCH vibration with maxima in the range of $3380-3270 \text{ cm}^{-1}$ and $2950-2890 \text{ cm}^{-1}$, as well as strong and broad bands due to vC=N at 1635 cm⁻¹.





Fig. 7. Profile of potential energy surface scan for the torsion angle $N_{38}-C_{36}-N_{34}-S_{31}$.

 Table 2

 Calculated vibrational wavenumbers (scaled), measured IR and Raman bands and assignments.

HF/6-31G*			B3PW91/6-310	G*		B3LYP/6-31G*			IR	Raman	Assignments ^a
υ (cm ⁻¹)	I _{IR}	R _A	υ (cm ⁻¹)	$I_{\rm IR}$	R _A	υ (cm ⁻¹)	I _{IR}	R _A	$v(\mathrm{cm}^{-1})$	$v(\mathrm{cm}^{-1})$	
3548	52.59	74.91	3615	32.36	115.89	3587	26.82	127.83	-	-	$v_{as}NH_2(99)$
3450	72.11	56.60	3485	54.88	278.72	3460	40.16	234.31	3484	-	$\upsilon_{\rm s} \rm NH_2(98)$
3428	53.22	113.98	3480	17.92	42.99	3443	18.52	98.01	3410	-	UNH(98)
3380	52.87	34.27	3373	22.97	42.27	3359	19.43	41.49	3336, 3215	-	vNH(100)
3051	4.09	117.12	3129	4.84	128.26	3120	5.73	132.76	_	3143	vCHII(98)
3043	2.54	119.35	3121	1.58	61.79	3113	1.21	58.62	_	3125	vCHII(98)
3042	11.75	144.96	3119	7.57	215.75	3112	7.05	123.04	_	_	vCHI(100)
3041	16.46	27.26	3118	24 10	176 56	3108	20.89	197.09	_	_	ν CHI(97)
3037	2.88	39.82	3114	4 59	45 42	3106	3 73	42.69 -	_	_	uCHI(99)
3025	40.96	207 79	3108	36 37	123 30	3007	42.02	168.05			2)CHI(95)
3023	9.61	207.75	3104	17 70	151 20	3094	5 55	31 18			2)CHI(95)
2024	28.01	156.91	2102	274	25.65	2002	24 79	19/02			2/CHI(00)
2007	28.01	130.01	3103	3.74	23.03	2080	24.70	104.95	-	-	0011(99)
3007	8.72	135.40	3091	4.78	130.24	3080	6.70	139.81	-	-	UCHI(93)
3000	1.84	66.95	3083	3.84	95.27	3072	3.83	93.17	-	3067	UCHI(93)
2996	0.34	19.77	3081	1.09	21.28	3069	0.85	18.21	-	3031	vCHI(95)
2948	16.51	23.84	2977	23.98	37.75	2970	24.07	39.19	-	2980	vCH(98)
1713	322.11	15.52	1699	214.05	11.34	1684	200.59	11.53	-	-	υ CN(76), δ NH(15)
1669	490.02	2149.81	1632	89.86	948.59	1620	77.17	855.44	1624	1621	vPhI(40),
											υ CN(15)
1639	38.52	107.68	1623	164.94	1473.63	1611	102.72	1255.17	-	-	vPhI(19),
											vCN(62)
1626	100.84	5.80	1610	95.33	6.35	1609	130.15	81.10	-	-	$\delta NH_2(83)$
1605	4.87	13.95	1593	7.09	26.20	1582	0.92	1.73	-	1591	vPhI(68)
1599	141.70	304.64	1587	47.36	257.97	1574	47.69	267.56	-	-	vPhII(65),
											vPhI(14)
1588	191.68	2153.80 1573	32.33	478.68	1559	28.07	414.62	_	-	-	vPhII(67)
1574	10.65	40.78	1569	344.85	6053.08	1554	352.22	6577.19	1540	-	vPhII(27).
											vPhI(60)
1515	12.81	17 70	1523	12.61	117 90	1515	9.95	65 32	_	1510	$v_{\rm PbI}(70) \delta_{\rm CHI}(20)$
1495	101.89	74.43	1482	52.57	100.10	1478	53.99	118 24	_	-	$\nu PbII(77) \delta CHII(20)$
1467	6.45	33 70	1/65	26.80	270.51	1/63	26.58	277.26	_	1/66	SCHI(68)
1407	774	39.40	1405	20.00 8 13	53.60	1405	9.00	51.82		1/38	21Pbl(49) &CHI(43)
1/10	51/ 91	12.76	1440	12 56	205 12	1445	22.00	270.76		1450	8NH(72)
1410	141.05	12.20	1405	10.00	203.12	1206	1 49	275.70	-	-	SCH(GE)
1414	141.05	11.40	1400	2.95	327.70	1390	1.40	172.24	-	1205	
1599	45.54	11.49	1597	42.07	400.29	1291	45.17	4/5.54	-	1565	0PIII(05),
1204	14.25	226 50	1270	1 1 2	250.20	1201	2.00	240.27			$\partial CHI(27)$
1394	14.35	236.59	1379	1.12	250.30	1361	2.08	348.27	-	-	UPHI(81)
1342	6.33	484.65	1372	692.74	/8./5	1356	633.44	/0.51	-	-	$v_{as}SO_2(53),$
											vCN(44)
1322	63.61	366.51	1351	36.36	223.13	1340	61.84	483.88	-	1346	vPhI(77)
1315	4.80	51.46	1335	11.47	12.54	1316	6.74	7.69	-	-	vPhII(83)
1305	135.68	1.09	1297	4.90	9.05	1300	3.71	8.02	1302	1305	vPhII(16),
											$\delta CHII(72)$
1267	0.82	4.70	1276	12.90	112.97	1274	7.46	79.29	-	-	vPhI(14),
											δCHI(49)
1246	16.66	114.28	1263	10.89	20.29	1259	19.81	18.49	-	1264	vCN(82)
1219	13.14	63.40	1254	20.14	103.79	1250	27.28	193.38	-	-	δCHI(35)
1206	77.60	158.19	1230	8.10	49.19	1223	7.97	55.93	1229	1226	vPhI(65).
-						-				-	$\delta CHI(19)$
1191	10 79	40 44	1202	109 70	766 10	1196	72 37	556 21	_	_	vPhI(44)
	10.75	10, 1 1	1202	105.70	, 00.10	1155	, 2, 37	550.21			$\delta CHI(31) \psi CN(14)$
1180	36.76	97 72	1184	3 1 9	18 38	1182	2 21	14 58	_	1186	δCHI(18)
1100	50.70	51.12	110-1	5.10	10.00	1102	2.21	14.30		1100	0011(10),

HF/6-31G*			B3PW91/6-310	-* L		B3LYP/6-31G*			IR	Raman	Assignments ^a
υ (cm ⁻¹)	I _{IR}	R _A	υ (cm ⁻¹)	I _{IR}	R _A	υ (cm ⁻¹)	I _{IR}	R _A	v (cm ⁻¹)	v (cm ⁻¹)	
1178	12.34	5.47	1177	0.43	5.72	1177	0.54	3.11	1177	-	δ CHI(80)
1160	33.00	79.90	1170	87.88	518.96	1168	125.64	802.97	-	-	$\upsilon_{s}SO_{2}(53),\delta CHII(35)$
1144	75.08	7.49	1156	7.60	70.56	1154	8.40	85.46	-	-	vPhI(33), δ CHI(45)
1126	15.57	29.49	1122	84.24	5.16	1123	84.34	3.96	1137	1136	$\delta NH_2(78),$
1108	0.64	2.96	1108	3.36	0.18	1109	3.46	0.61	-	-	vPhI(26),
1084	97.45	3.11	1091	2.07	83.38	1088	2.91	102.92	1086	1092	vPhII(56),
1072	1.55	25.18	1080	63.19	5.59	1071	67.71	6.62	-	-	$\delta CHI(24)$ $\delta NH(40),$
1000	10.50	22.45	1050	64 50	100 54	10.17	40.45	105.05		1050	vCN(50)
1063	16.52	33.15	1058	61.73	123.74	1047	49.15	105.87	-	1050	vCHII(68)
1061	23.24	48.92	1037	18.13	44.51	1033	22.41	71.16	-	-	vPhI(62)
1055	3.56	8.17	1018	8.99	106.49	1014	7.34	96.20	-	-	UPhI(68)
1049	0.75	3.74	1003	13.57	21.14	1000	10.50	7.53	-	-	δPhII(30), γCH(16),γCHI(43)
1033	3.11	22.61	999	0.32	64.67	996	3.87	125.18	-	-	γCHI(56), δPHII(17)
1033	1.16	1.56	995	3.98	67.42	990	5.23	71.10	-	-	γ CHI(71)
1023	26.34	89.63	988	1.20	0.90	984	0.52	2.25	-	-	γ CHII(79)
1016	4.89	4.82	981	14.79	208.84	977	14.50	207.18	-	-	γCH(69), γCHI(27)
1007	0.50	40.22	960	0.18	10.47	955	0.26	15.19	-	_	ν CHII(80)
992	0.55	36.05	957	1.29	1.39	952	1.19	1.49	-	_	ν CHI(89)
989	1.95	12.32	940	119.28	5.47	934	0.67	9.07	_	-	ν CHI(87)
956	195.54	5.97	937	5.44	11.77	918	151.47	11.23	_	-	vCN(64)
912	11.33	3.34	926	169.13	8.66	906	129.20	8.17	_	_	v CN(67)
901	32.44	3.24	877	26.90	88.53	876	27.82	97.31	_	_	$\delta PhI(78)$
889	200.77	6.78	870	3.78	1.65	868	3.71	1.71	-	-	γCHI(63), τPhI(25)
880	3 79	26.98	862	166.02	14 53	856	129 34	14 37	_	_	vSN(69)
863	24 29	21.47	852	33.13	625	850	44 16	6 60	_	_	ν CHII(68)
843	32 39	32.78	843	21 70	23.90	840	18.08	24 70	_	_	γ CHII(77)
836	53.90	2 22	823	12.94	21.82	819	17.73	28.21	821	818	γ CHII(72)
829	49.11	20.71	816	67.07	14 75	806	41 33	1 18	-	-	γ CHI(75)
025	15.11	20.71	010	07.07	1 1.75	000	11.55	1.10			$\tau PhI(11)$
811	90.28	7 36	806	41 89	1 39	797	54 24	12 38	_	_	$\delta SO_2(32)$
011	50.20	7.50	000	11.05	1.55	151	5 1.2 1	12.50			$v SN(11) \delta NH_{2}(41)$
795	10.21	6.50	790	0.62	10.69	789	2.70	10.83	_	_	δPhI(64),
786	1.34	2.85	780	63.81	11.13	779	58.22	11.68	-	_	vPhI(11) τ PhI(46),
											γCHI(34)
760	5.02	3.15	756	4.64	15.16	752	3.51	13.07	-	-	δPhII(36), υPhI(20)
759	4.97	6.31	739	25.88	34.08	735	4.88	7.08	-	740	γ CHI(67), τ PhI(22)
740	13.19	4.85	735	6.10	6.03	727	25.68	34.07	-	-	$\delta CN(42),$
707	137.38	3.39	717	10.16	5.64	713	8.29	8.19	-	713	τ PhII(61),
679	14.35	4.48	674	104.68	13.57	668	86.22	5.95	675	669	γCN(14) γCN(21),
											$\gamma NH(42)$
650	3.86	3.57	665	7.51	23.16	663	39.60	31.86	-	-	δ PhI(44), δ PhII(22)

040	38.17	21.83	641	2.78	5.86	640	2.47	5.41	-	635	τPhI(25),
											vCS(65)
634	0.85	8.32	627	1.83	8.47	629	1.57	8.85	-	622	δPhII(73)
609	86.11	6.25	603	129.07	11.15	600	116.18	8.78	608	-	δPhI(52),
											δPhII(21)
580	33.24	13.15	579	95.01	31.85	575	97.11	39.34	-	-	δCN(27),
											γCN(12),γNH(41)
569	28.01	8.46	552	146.37	9.36	551	2.50	18.99	-	-	τPhI(55)
566	175.58	3.34	551	40.03	27.08	546	182.31	11.43	547	547	γNH ₂ (38),
											$\delta CN(23), \gamma CN(15)$
555	37.42	3.56	541	19.25	34.21	541	10.57	43.71	-	-	τ PhII(31),
520	10.41	10.00	521	21 52	10.44	521	22.01	20.00		510	$\delta PhI(24), \delta CN(20)$
526	10.41	18.98	521	21.53	19.44	521	22.01	20.89	-	518	δPhI(69)
503	6.80	6.08	501	13.30	7.13	501	11.95	6.67	-	-	$\partial P\Pi(38),$
405	1 4 4	0.71	477	0.02	0.70	470	4.20	775			τ Phil(26), γ CN(20)
485	1.44	2./1	4//	8.03 45.10	9.70	4/8	4.20	1./0	-	-	$\tau PIII(51)$
4/4	33.20 49.22	12.17	4/1	45.12	7.60	4/1	21.45	15.40	-	-	(PIII(71) (SO (40)
407	40.33	4.10	404	07.15	7.09	402	109.04	10.52	-	400	$\delta O_2(40), \delta O_2(40), \tau D D D D D D D D D D D D D D D D D D $
433	29 59	2.45	430	45 57	4 76	426	40.94	3 7 3	_	_	$\tau PhI(22), \tau I III(10)$
455	23,33	2.45	450	43.37	4.70	420	40.54	5.25			$\delta SO_2(52)$
429	9.23	5 29	421	22 52	2 34	422	17 82	3.03	_	_	$\tau PhI(35)$
125	5.25	5.25	121	22.52	2.5 1	122	17.02	5.05			$\delta SO_2(40)$
418	67.91	7.72	416	0.39	26.25	418	0.74	24.81	_	417	τ PhII(78)
406	29.40	3.80	401	31.61	8.36	402	35.94	9.06	406	_	$\delta CN(34)$.
											τ PhI(32)
381	46.00	4.97	374	34.10	15.74	370	26.58	2.45	-	373	$\tau NH(66)$
363	35.80	3.20	361	24.64	5.23	364	66.31	25.17	-	-	$\tau NH_2(73)$
344	58.90	3.26	353	22.37	6.11	351	9.43	11.10	-	342	δSO ₂ (58),
											τNH2(15)
333	38.66	2.68	319	81.47	15.81	319	52.86	17.98	-	-	τNH(45),
											$\delta SO_2(24), \tau PhII(23)$
292	36.75	4.30	297	10.35	8.49	288	9.96	18.84	-	291	$\delta SO_2(40)$,
											δCN(29)
276	16.90	7.68	280	13.39	7.30	277	18.76	6.13	-	-	$\delta SO_2(44),$
											δCN(32)
272	5.18	8.65	263	3.11	18.53	264	2.57	21.11	-	-	$\tau PhI(64)$
267	2.17	6.59	251	3.22	4.94	247	1.89	4.72	-	-	$\delta SO_2(56),$
227	10.21	5.10	222	0.00	11.00	222	7.01	10.20		214	δCS(10)
227	10.21	5.10	223	9.98	11.92	222	7.81	10.20	-	214	$0SU_2(32),$
200	0.00	2.25	102	2.05	6.52	104	2.01	0.41			τ PnII(40)
206	9.98	3.30	193	3.95	0.52	194	2.81	9.41	-	-	$05U_2(40),$
170	E 47	1.02	190	6 27	6.26	101	6 17	E / E			$\sigma DbI(64)$
170	J.47 4.56	8.50	156	10.05	0.50	101	10.64	30.54	_	_	$\delta SO_{-}(22)$
155	4.50	0.50	150	10.05		157	10.04	55.54	-	_	$\tau CN(36)$
150	7 5 2	0.74	149	0.79	2 41	149	1 33	1 35	_	_	δNH(33)
150	1.52	0.74	145	0.75	2,41	145	1,55	1.55			$\tau PhI(47)$
142	5.21	14 30	146	0.16	21.46	146	0.17	25.82	_	_	$\tau PhI(64)$
126	0.63	3 63	122	0.80	2 54	121	0.96	2.66	_	117	$\tau SO_2(39)$
	2.000	2.00		2.00			2.00	2.00			δCC(18).
											τ PhII(19)
91	1.13	7.74	94	0.53	15.46	95	0.62	16.03	-	-	τPhI(63),
											τCN(13)

HF/6-31G*			B3PW91/6-31G*			B3LYP/6-31G*			IR	Raman	Assignments ^a
$v(\mathrm{cm}^{-1})$	I _{IR}	RA	$v(\mathrm{cm}^{-1})$	I _{IR}	$R_{\rm A}$	$v(\mathrm{cm}^{-1})$	IIR	$-R_{A}$	$v(\mathrm{cm}^{-1})$	$v(\mathrm{cm}^{-1})$	
83	2.45	1.36	71	1.03	1.65	68	1.30	1.67	I	I	γNH(28),
											$\tau CN(13), \delta SO_2(10), \delta SO_2$
i	0	0	c L	000		9	1				ycs(10)
54	0.66	3.66	50	0.96	5.07	49	1.79	4.77	I	1	tNH(68)
48	7.68	5.91	47	7.66	8.05	44	5.78	8.13	I	I	γNH(30),
											τNH(36),τCN(12)
39	0.57	6.32	35	0.62	5.44	35	1.08	6.02	I	I	$\tau SO_{2}(44)$,
											τCN(31)
25	3.56	4.24	26	2.06	7.24	27	1.82	6.99	I	I	τNH(20),
											$\tau SO_2(16), \tau CN(32)$
22	0.43	3.46	23	1.26	5.42	23	1.16	6.39	I	I	τCN(33),
											τ PhII(20), γ CS(21)
10	0.68	5.01	12	0.72	6.45	13	0.97	6.26	I	I	$\tau SO_{2}(47),$
											τCN(21)
υ, stretching; δ, in-բ	slane deformat	ion; γ , out-of-plane	s deformation; τ , twise	ting; Phl, napht	halene ring; Phl	ll, para substituted p	bhenyl ring.				

^a Percentage PED analysis is given in the brackets and PED contribution less than 10% is neglected: I_R, Infrared intensity; R_A, Raman activity.

The NH₂ stretching modes of guanidine are expected in the region 3260-3390 cm⁻¹ [31] and in the present case bands at 3587, 3460 cm⁻¹ (B3LYP) and 3484 (IR) are assigned as NH₂ stretching modes. Topacli and Topacli [39] reported the calculated wavenumbers in the range of $3670-3920 \text{ cm}^{-1}$ for NH₂ stretching modes. The bands corresponding to the δNH_2 vibrations are expected in the region $1610 \pm 30 \text{ cm}^{-1}$ [31]. In the IR and Raman spectrum δNH_2 is not observed. The calculated value is 1609 cm⁻¹. The rocking/twisting mode of NH₂ is expected in the region 1195 ± 90 cm⁻¹ and the B3LYP calculations give this mode at 1123 cm⁻¹. Experimentally bands are observed at 1137 in the IR spectrum and at 1136 cm^{-1} in the Raman spectrum. The wagging mode of NH₂ is expected in the range $840 \pm 55 \text{ cm}^{-1}$ [31]. The B3LYP calculations give this mode at 797 cm^{-1} . The torsion NH₂ mode is expected in the range 355 ± 65 cm⁻¹ [31] and the band at 364 (B3LYP) cm⁻¹ is assigned as this mode. For sulfonamide derivatives, the NH₂ modes are reported at 3390, 3395, 3399 cm⁻¹ and NH modes at 3253, 3230, 3255 cm^{-1} [40].

The antisymmetric and symmetric stretching modes of SO₂ group appear in the region 1360-1310 and 1165-1135 cm⁻¹, respectively [31]. The B3LYP calculations give the antisymmetric and symmetric stretching modes at 1356 and 1168 cm⁻¹. The SO₂ stretching mode is not pure, but contains contributions from other modes also. Although the region of the SO₂ scissors ($560 \pm 40 \text{ cm}^{-1}$) and that of SO₂ wagging vibration $(500 \pm 55 \text{ cm}^{-1})$ partly overlap, the two vibrations appear separately [31]. The B3LYP calculations give these modes at 462 and 426 cm⁻¹. Hangen et al. [41] reported the SO₂ stretching vibrations at 1314, 1308, 1274, 1157, 1147, 1133 cm⁻¹ and SN stretching modes at 917, 920, 932, 948 cm⁻¹ for sulfonamide derivatives. Chohan et al. [40] reported SO₂ stretching modes at 1345, 1110 cm⁻¹ and SN and CS stretching modes at 833 cm⁻¹ for sulfonamide derivatives. The twisting SO₂ mode is expected in the region $440 \pm 50 \text{ cm}^{-1}$ and the rocking mode at around 350 cm⁻¹ [31]. The B3LYP calculations give these modes at 422 and 351 cm⁻¹. The SN stretching vibration [31] is expected in the region $905 \pm 30 \text{ cm}^{-1}$. The band calculated at 856 cm^{-1} is assigned as SN stretching mode. The C-S stretching mode is observed at 635 (Raman) cm^{-1} and the band at 640 cm^{-1} (B3LYP) is assigned as this mode [31].

In the following discussion, naphthalene ring and para substituted phenyl ring are designated as PhI and PhII, respectively. The naphthalene ring modes are influenced more C-C bands. The ring stretching vibrations are expected within the region 1620–1390 cm⁻¹ [42]. Most of the ring modes are altered and missing by the substitutions to aromatic ring of naphthalene. Generally the C-C stretching vibrations in aromatic compounds form the strong bands. Govindarajan et al. [43] reported the C-C stretching vibrations at 1564, 1490, 1417, 1340, 1261, 1212 and 1114 cm⁻¹ experimentally and at 1570, 1496, 1424, 1354, 1269, 1213, 1120 cm⁻¹ theoretically for the naphthalene ring. Naphthalene CH stretching vibrations are reported in the IR spectrum at 3259, 3171, 3067, 3057 and 3046 cm⁻¹ as weak bands and the corresponding Raman band is observed at 3058 cm⁻¹ as strong band as expected [44,45]. Krishnakumar et al. [46] reported 1055, 1037, 778, 742, 690, 675, 538, 488, 458, 355, 298, 257 cm⁻¹ as inplane and out-of-plane ring deformation bands of naphthalene ring. Ravikumar et al. [47] reported Raman bands at 1440, 1420 and 1141 cm⁻¹ and the IR bands at 1440, 1424, 1238, 1187, 1147 and 1140 cm⁻¹ correspond to the naphthalene C-H in-plane bending modes, which are mixed with other vibrational modes. In 1substituted naphthalene derivatives, the CH out-of-plane bending vibrations occur at 810-785 cm⁻¹ due to three adjacent hydrogen atoms on the ring, and at 780–760 cm^{-1} for four adjacent hydrogen atoms [44]. In 1-substitued naphthalenes, the ring C-C stretching vibrations normally appear in the region 1580-1300 cm⁻¹ [44,45,48]. Arivazhagan et al. [42] reported the naphthalene ring stretching modes at 1684, 1605, 1590, 1532, 1519, 1490, 1420, 1297, 1286, 1256, 1231 and 1208 cm⁻¹. Sellers et al. [49] reported 354. 505. 512. 626, 757, 792, 940, 1003, 1023, 1137, 1156, 1158, 1170. 1204, 1255, 1272, 1341, 1385, 1391, 1458, 1515, 1590, 1595, 1644 cm⁻¹ as the in-plane modes and 172, 188, 387, 471, 480, 622, 705, 773, 777, 825, 879, 952, 969, 981, 987 cm⁻¹ as out-ofplane modes of the naphthalene ring. For the title compound, the naphthalene ring stretching modes are assigned at 1624, 1540. 1229 cm⁻¹ in the IR spectrum, 1621, 1591, 1510, 1346, 1226 cm⁻¹ in the Raman spectrum and at 1620, 1582, 1554, 1515, 1361, 1340, 1223, 1196, 1033, 1014 cm⁻¹ theoretically (B3LYP). The CH in-plane deformations of the naphthalene ring are observed at 1177 cm⁻¹ in the IR spectrum and at 1438, 1466 cm⁻¹ in the Raman spectrum, whereas the B3LYP calculations give these modes at 1154, 1177, 1250, 1274, 1396, 1443 and 1463 cm⁻¹. The out-of-plane CH deformations of the naphthalene ring are assigned in the range of 735–1000 cm⁻¹ theoretically (B3LYP). The ring stretching modes of the naphthalene ring for the title compound are in good agreement with the literature [44,50].

The benzene ring possesses six ring stretching vibrations of which the four with the highest wavenumbers occurring near 1600, 1580, 1490 and 1440 cm^{-1} are good group vibrations [31]. With heavy substituents, the bands tend to shift to some what lower wavenumbers, and the greater the number of substituents on the ring, the broader the absorption regions [31]. In the case of C=O substitution, the band near 1490 cm⁻¹ can be very weak [31]. The fifth ring stretching vibration is active near $1315 \pm 65 \text{ cm}^{-1}$, a region that overlaps strongly with that of the CH in-plane deformatin [31]. The sixth ring stretching vibration, the ring breathing mode, appears as a weak band near $1000 \,\mathrm{cm}^{-1}$ in mono, 1,3-di and 1,3,5trisubstituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from the other modes. The ring stretching modes of the phenyl ring are assigned at 1316, 1391, 1478, 1559, 1574 cm⁻¹ theoretically (B3LYP). According to literature [33] for para substituted benzenes, the ring breathing mode is expected in the interval $1050-1100 \text{ cm}^{-1}$, and in the present case the band at 1086 in the IR, 1092 in Raman and 1088 cm⁻¹ (B3LYP) is assigned as the ring breathing mode of the para substituted phenyl ring PhII. Panicker et al. [33] reported 1062 (IR) and 1061 cm⁻¹ (DFT) as ring breathing mode of para substituted phenyl rings. The in-plane and out-ofplane CH deformations are assigned theoretically (B3LYP) at 1300, 1182, 1109, 1047 cm⁻¹ and 984, 955, 840, 819 cm⁻¹, respectively. For the title compound, these bands are observed at 1302, 821 in the IR and 1305, 1186, 1050, 818 cm⁻¹ in the Raman spectrum. The CH stretching modes of the phenyl ring are observed at 3143 and $3125\,\mathrm{cm}^{-1}$ in the Raman spectrum and the theoretical values are 3120, 3113, 3106 and 3094 cm⁻¹ (B3LYP).

4.2. Geometrical parameters and first hyperpolarizability

No X-ray crystallographic data of the title compound have yet been reported to best of our knowledge. However, the theoretical results (B3LYP) obtained are almost comparable with the reported structural parameters of similar derivatives. Govindarajan et al. [43] reported $C_1-C_2 = 1.3792$, $C_1-C_6 = 1.4123$, $C_2-C_3 = 1.4238$, $C_3-C_4 = 1.4388$, $C_3-C_{10} = 1.4467$, $C_4-C_5 = 1.4207$, $C_4-C_{11} = 1.4190$, $C_5-C_6 = 1.3746$, $C_{10}-C_{15} = 1.3897$, $C_{11}-C_{14} = 1.3739$, $C_{14}-C_{15} = 1.4090$ Å for naphthalene derivatives. Unlike benzene, the C-C bonds in the naphthalene are not of the same length. For the title compound, the bonds C_1-C_2 , $C_{11}-C_{14}$, C_5-C_6 , $C_{10}-C_{15}$, and $C_{14}-C_{15}$ are 1.3784, 1.3941, 1.3816, 1.3820, 1.4081 Å in length, whereas the other C-C bonds lie in the range of 1.4171–1.4436 Å. This difference, which was established by X-ray diffraction, in consistent with the valence bond modes of bonding in naphthalene that involves three resonance structures where as

the bonds C_1-C_2 , $C_{11}-C_{14}$, C_5-C_6 , $C_{14}-C_{15}$ and $C_{10}-C_{15}$ are double in two of the structures, the other are double in only one [51]. Jas et al. [52] showed that the $C_{14}-C_{11}$, C_4-C_3 , $C_{11}-C_4$ and C_2-C_3 bond lengths were 1.409, 1.358, 1.421, 1.417 Å, respectively and also the geometrical parameters reported in the literature [1,53,54] are very close to our calculated data.

The calculated dihedral angles $C_{15}-C_{10}-C_3-C_2$ (179.8°), $C_1-C_2-C_3-C_{10}$ (-179.7°), $C_{14}-C_{11}-C_4-C_5$ (-179.3°) and $C_6-C_5-C_4-C_{11}$ (-179.9°) show that the naphthalene ring is coplanar. For the naphthalene ring, the bond angles $C_5 - C_6 - C_1 = 120.7$, $C_6 - C_1 - C_2 = 119.7$, $C_1 - C_2 - C_3 = 121.0$, are $C_3 - C_{10} - C_{15} = 120.9$, $C_{10} - C_{15} - C_{14} = 120.0$, $C_2 - C_3 - C_{10} = 120.8$, $C_{14}-C_{11}-C_4 = 119.7$, $C_{11}-C_4-C_3 = 118.2$, $C_{15} - C_{14} - C_{11} = 121.5$, $C_3-C_4-C_5 = 117.7$, $C_5-C_4-C_{11} = 124.1^\circ$ where as the corresponding reported values are 120.4, 120.4, 120.3, 121.6, 120.4, 120.3, 120.3, 121.3, 119.3, 119.0, 121.6 [46]. Loughrey et al. [55] reported the bond lengths, $S_{31}-O_{32} = 1.4337$, $S_{31}-O_{33} = 1.4256$, $S_{31}-N_{34} = 1.6051$, $S_{31}-C_{28} = 1.7737$, $C_{21}-N_{20} = 1.4212$, $C_{18}-N_{20} = 1.2712$ Å, whereas the corresponding values for the title compound are, 1.6355, 1.6380, 1.8057, 1.8634, 1.4056 and 1.2955 Å.

Petrov et al. [56] reported the molecular structure and conformations of benzenesulfonamide by gas electron diffraction and quantum chemical calculations and according to their results, the bond lengths, CS, SN, SO vary in the range of 1.7756–1.7930, 1.6630–1.6925, 1.4284–1.4450 Å and the bond angles, CSN, CSO, NSO, HNS, HNH vary in the range, 103.9–107.1, 107.6–107.8, 105.5–107.7, 111.0–113.7, 112.6–113.6°. These values are in agreement with the corresponding values for the title compound. Lasibal et al. [57] reported the bond lengths SO=1.4269–1.4291, SN=1.6202, SC=1.7582, N₃₈–C₃₆=1.4103, N₃₇–C₃₆=1.2723, N₃₄–C₃₆=1.3483 Å, whereas the corresponding values in the present case are 1.6355–1.6380, 1.8057, 1.8634, 1.3882, 1.2817, 1.4283 Å.

At C₁₁ position, the bond angles C₄–C₁₁–C₁₄, C₄–C₁₁–C₁₈ and C₁₄–C₁₁–C₁₈ are 119.7, 121.5 and 118.8°, respectively. This asymmetry in angles reveals the interaction between azomethane and the phenyl groups. At C₂₁ position, the exocyclic angles C₂₂–C₂₁–N₂₀ is increased by 2.7° and C₂₃–C₂₁–N₂₀ is reduced by 2.3° from 120° which reveals the interaction between N₂₀ and H₂₅ atoms. At C₂₈ position C₂₆–C₂₈–S₃₁ = 118.0 and C₂₄–C₂₈–C₂₆ = 123.4°, which shows the interaction between SO₂ group with H₃₀ atom. At N₃₄ position, S₃₁–N₃₄–H₃₅ is reduced by 6.5° and S₃₁–N₃₄–C₃₆ is increased by 2.3° from 120° which shows the interaction between H₃₅ and O₃₂.

The C₁₈–N₂₀ moiety is slightly tilted from the naphthalene ring as is evident from the torsion angles, $C_3-C_4-C_{11}-C_{18} = -179.1$, $C_4 - C_{11} - C_{18} - N_{20} = -177.5$, $C_{15} - C_{14} - C_{11} - C_{18} = 179.3,$ $C_{14}-C_{11}-C_{18}-N_{20}=2.9^{\circ}$ and is more tilted from the para substituted phenyl ring PhII as is evident from the torsion angles, $C_{24}-C_{22}-C_{21}-N_{20} = 178.4$, $C_{22}-C_{21}-N_{20}-C_{18} = 41.4$, $C_{26} - C_{23} - C_{21} - N_{20} = -179.2$ and $C_{23}-C_{21}-N_{20}-C_{18}=-141.1^{\circ}$. The torsion angles $S_{31}-N_{34}-C_{36}-N_{38} = -146.1$ and $S_{31}-N_{34}-C_{36}-N_{37} = 36.9^{\circ}$, which shows that the N_{38} and N_{37} atoms are in different planes.

For the title compound, the DFT calculations give the bond angles, $C_{28}-S_{31}-O_{33}=110.9$, $C_{28}-S_{31}-O_{32}=107.7$, $S_{31}-N_{34}-H_{35}=113.5$, $O_{33}-S_{31}-O_{32}=119.4$, $O_{33}-S_{31}-N_{34}=106.3$, $O_{32}-S_{31}-N_{34}=111.8$, $N_{34}-S_{31}-C_{28}=98.8$, $C_{21}-N_{20}-C_{18}=122.1$, $S_{31}-C_{28}-C_{26}=118.0$, $S_{31}-C_{28}-C_{24}=118.6$, $C_{28}-C_{26}-C_{23}=118.1$, $C_{26}-C_{23}-C_{21}=120.5$, $C_{23}-C_{21}-C_{22}=119.6$, $N_{20}-C_{21}-C_{22}=122.7$, $N_{20}-C_{21}-C_{23}=117.7$, $C_{21}-C_{22}-C_{24}=120.4$, $N_{20}-C_{18}-C_{11}=122.3^{\circ}$, whereas the corresponding reported values are, 106.5, 107.4, 110.0, 119.5, 106.1, 107.7, 109.3, 118.8, 120.5, 119.1, 120.4, 119.9, 120.3, 119.3, 122.4, 118.2, 120.4, 124.4^{\circ}[55]. The values of the bond angles $O_{33}-S_{31}-O_{32}=118.6$, $O_{32}-S_{31}-N_{34}=108.9$, $O_{33}-S_{31}-N_{34}=104.9$, $O_{33,32}-S_{31}-C_{28}=107.9-108.3$, $N_{34}-S_{31}-C_{28}=107.9$, $C_{36}-N_{34}-S_{31}$

= 123.0° reported by Lasibal et al. [57] are in agreement with our values. Loughrey et al. [55] reported the torsion angles, $O_{33}-S_{31}-C_{28}-C_{26} = -142.0$, $O_{33}-S_{31}-C_{28}-C_{24} = 38.5$, $O_{32}-S_{31}-C_{28}-C_{26} = -12.8$, $O_{32}-S_{31}-C_{28}-C_{24} = 167.7$, $N_{34}-S_{31}-C_{28}-C_{26} = 103.8$, $N_{34}-S_{31}-C_{28}-C_{24} = -75.7$, $C_{18}-N_{20}-C_{21}-C_{23} = 143.9$, $C_{18}-N_{20}-C_{21}-C_{22} = -39.2$, $C_{21}-N_{20}-C_{18}-C_{11} = 117.6$, $S_{31}-C_{28}-C_{26}-C_{23} = -179.9$, $C_{24}-C_{28}-C_{26}-C_{23} = -0.4$, $S_{31}-C_{28}-C_{24}-C_{22} = 179.2$, $C_{26}-C_{23}-C_{21}-N_{20} = 178.1$, $N_{20}-C_{21}-C_{22}-C_{24} = -178.6$, $N_{20}-C_{18}-C_{11}-C_{14} = 8.1$, $N_{20}-C_{18}-C_{11}-C_{4} = -172.6^\circ$. For the title compound, the corresponding torsion angles are 138.3, -40.2, 5.9, -172.6, -110.4, 71.1, -141.1, 41.4, -175.5, -179.6, -1.2, 178.9, -179.2, 178.4, 2.9, -177.5° .

There has been growing interest in using organic materials for nonlinear optical (NLO) devices, functioning as second harmonic generators, frequency converters, electro-optical modulators, etc. because of the large second order electric susceptibilities of organic materials. Since the second order electric susceptibility is related to first hyperpolarizability, the search for organic chromophores with large first hyperpolarizability is fully justified. The organic compound showing high hyperpolarizability are those containing an electron-donating group and an electron withdrawing group interacting through a system of conjugated double bonds. In the case of sulfonamides, the electron withdrawing group is the sulfonyl group [58,59]. Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase, or other physical properties [60]. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing, and dynamic image processing [61,62]. In this context, the dynamic first hyperpolarizability of the title compound is also calculated in the present study. The first hyperpolarizability (β_0) of this novel molecular system is calculated using B3LYP/6-31G(d) method, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [63]. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electric field is weak and homogeneous, this expansion becomes,

$$\begin{split} E &= E_0 - \sum_i \mu_i F^i - \frac{1}{2} \sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F^i F^j F^k - \\ & \frac{1}{24} \sum_{ijkl} \gamma_{ijkl} F^i F^j F^k F^l + \cdots \end{split}$$

where E_0 is the energy of the unperturbed molecule, F^i is the field at the origin, μ_i , α_{ii} , β_{iik} and γ_{iikl} are the components of dipole moment, polarizability, the first hyperpolarizabilities, and second hyperpolarizibilites, respectively. The calculated first hyperpolarizability of the title compound is 31.1×10^{-30} esu, which comparable with the reported values of similar derivatives, but experimental evaluation of this data is not readily available. Kucharski et al. [64] reported the first hyperpolarizability of certain sulfonamide amphiphiles by calculation and hyper-Rayleigh scattering in the range $0.2156\text{--}0.189\times10^{-30}\,\text{esu}.$ The $C_{36}\text{--}N_{34}$ and $C_{36}\text{--}N_{38}$ bond lengths in the calculated molecular structures vary from 1.4283 to 1.3882 Å which are intermediate between those of a C-N single bond (1.48) and a C=N double bond (1.28). Therefore, the calculated data suggest an extended π -electron delocalization over the sulfaguanidine moiety which is responsible for the nonlinearity of the molecule [65,66]. We conclude that the title compound is an attractive object for future studies of nonlinear optical properties.

5. Conclusion

The FT-IR and FT-Raman spectrum of the title compound were recorded and analyzed. The molecular geometry and vibrational wavenumbers were calculated using HF and DFT methods and the optimized geometrical parameters (B3LYP) are in agreement with that of reported similar derivatives. Potential energy surface scan studies have been carried out to understand the stability of planar and non planar structures of the molecule. The calculated first hyperpolarizability is comparable with the reported value of similar derivative and may be an attractive object for further studies of non linear optics. The predicted infrared intensities and Raman activities are reported.

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