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Short communication

Molecular structures, spectral and computational studies on nicotinohydrazides

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ABSTRACT

The FT-IR and the high resolution ¹H and ¹³C NMR spectra have been recorded for *N*-(2-methyl-3-phenylallylidene)nicotinohydrazide (**1**) and *N*-(2-methyl-3-phenylallylidene)isonicotinohydrazide (**2**) and analyzed. ¹H-¹H COSY spectra were also recorded for the hydrazides. The spectral studies reveal that both the hydrazides exist in the keto form. Theoretical calculations were performed for some possible conformations of the hydrazide and the minimum energy conformers are predicted to be the one in which the azomethine protons are *syn* to N–NH bond. From the optimized structures, HOMO–LUMO energy gap and geometrical parameters were derived and these parameters were compared with the XRD measurements of hydrazide **1**. The vibrational frequencies in the ground state have been calculated using DFT and HF methods and compared with the observed frequencies. Non-linear optical (NLO) behaviour of the hydrazides was investigated by the determination of the electric dipole moment μ , the polarizability α and the hyperpolarizability β using B₃LYP method.

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1. Introduction

Hydrazones are a versatile class of ligands having great physiological and biological activities and have been used as insecticides, anticoagulants, antitumour agents, antioxidants and plant growth regulators [1,2]. Their metal complexes have found applications in various chemical processes like non-linear optics, sensors, medicine, etc. [3]. Recently, second order NLO effects of organic molecules have been extensively investigated for their advantages over inorganic crystals. The organic NLO materials play an important role in second harmonic generation, frequency mixing and electro-optic modulation [4]. The single crystal structure of a few hydrazones derived from o-aminobenzoylhydrazide and 2-acetylthiophene-o-aminobenzoylhydrazide have been reported [5-8]. Theoretical study of molecular structure and vibrational spectra of 2-acetylthiophene-o-aminobenzoylhydrazone was made by Pekparlak and Atalay recently [9]. Aroylhydrazones such as N-2-hydroxy-4-methoxyacetophenone-N'-4nitrobenzoylhydrazone and 2-hydroxyacetophenone nicotinic acid hydrazone were characterized using spectral and single crystal measurements [10,11]. Conformational analysis of hydrazones from spectral studies were also reported in literature [10,12–14].

Organic molecules with conjugated π -electron system are known to exhibit extremely large optical non-linear responses in terms of their molecular hyperpolarizabilities. Both theoretical and experimental studies have shown that large hyperpolarizabilities generally arise from a combination of strong electron donor and acceptor positioned at opposite ends of a suitable conjugation path and the hyperpolarizability values depend not only on the strength of donor and acceptor groups but also on the path length between them [15,16]. Therefore, it is of considerable interest to synthesize hydrazones derived from cinnamaldehyde since these compounds are expected to exhibit wide range of biological activities and NLO behaviour. To the best of our knowledge experimental data on geometric structure and theoretical calculations on hydrazones derived from nicotinohydrazide are not available in the literature. Recently we report single crystal structure of hydrazone derived from nicotinohyrdazide and *trans*- α -methylcinnamaldehyde [17]. In this study we report, the synthesis, the spectral and computational study of hydrazones derived from nicotinohydrazide and isonicotinohydrazide. The non-linear optical properties are also addressed theoretically.

2. Experimental

2.1. Synthesis of hydrazides 1 and 2

Sodium hydroxide (0.4 g, 0.01 mol) in a stoppered conical flask was kept in an ice-cold environment. Ethanol (40 mL), (95%) was added to dissolve it and the mixture was stirred continuously using a magnetic stirrer. An equimolar quantity of nicotinohydrazide/isonicotinohydrazide (1.371 g, 0.01 mol) and *trans-* α -methylcinnamaldehyde (1.461 g, 0.01 mol) was added to this mixture. The stirring was continued for 5 h in ice-cold con-

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Fig. 1. Structures of hydrazides 1 and 2.

ditions. The mixture was kept overnight in a refrigerator. The mixture was then allowed to stand for 4 days under normal conditions. A yellow solid was obtained. This was filtered, washed and recrystallized from ethanol. Yield 2.2 g, 46% (1), 2.3 g, 46% (2). The compounds 1 and 2 melted at 130° and 135°, respectively.

2.2. Spectral measurements

2.2.1. IR spectra

The FT-IR spectra were recorded in the range 400–4000 cm⁻¹ with a resolution of ± 4 cm⁻¹ and an accuracy of ± 0.01 cm⁻¹ on a NICOLET AVATAR 360 FT-IR spectrometer. The sample was mixed with KBr and the pellet technique was adopted.

2.2.2. ¹H and ¹³C NMR spectra

¹H and ¹³C NMR spectra were recorded in DMSO- d_6 at room temperature on AMX 500 NMR spectrometer operating at 500 and 125 MHz for ¹H and ¹³C NMR spectra, respectively. Samples were prepared by dissolving about 10 mg of the sample in 0.5 mL of DMSO- d_6 containing 1% TMS for ¹H NMR spectra. Proton spectra have the following experimental parameters: number of scans 32; spectral width 5682 Hz; acquisition time 2.88 s. Solutions for the measurement of ¹³C NMR spectra were prepared by dissolving 0.5 g of the sample in 2.5 mL of DMSO- d_6 containing a few drops of TMS as internal reference. The solvent DMSO- d_6 also provided the internal field frequency lock signal. The experimental parameters are: spectral width 29,412 Hz; number of scans 1125; acquisition time 0.56 s. The ¹H–¹H COSY and ¹H–¹³C COSY spectra were performed on a DRX-500 NMR spectrometer using standard pulse sequences.

2.3. Computational study

Computational calculations are carried out initially at semiempirical level (PM₃) to predict the favoured conformation (minimum energy conformer). Further geometry optimizations and vibrational frequencies of the favoured conformers were carried out at basic DFT level using B₃LYP-6-31G(d,p) basis set and at HF level using 6-31G(d,p) basis set available in Gaussian-03 package [18]. The total static dipole moments, the polarizability α and first order hyperpolarizability β were calculated by finite field approach using B₃LYP-6-31G^{*} basis set.



Fig. 2. FT-IR spectra of (a) hydrazide 1 and (b) hydrazide 2.

3. Results and discussion

The FT-IR spectra and the high resolution ¹H and ¹³C NMR spectra of N'-(2-methyl-3-phenylallylidene)nicotinohydrazide (**1**) and N'-(2-methyl-3-phenylallylidene)isonicotinohydrazide (**2**) (Fig. 1) have been recorded and analyzed.

The prominent peaks around 3300, 1640 and 1600 cm⁻¹ in the FT-IR spectra (Fig. 2) are attributed to ν_{N-H} , $\nu_{C=0}$ and $\nu_{C=N}$ modes, respectively. The observation of lower $\nu_{C=0}$ around 1640 cm⁻¹ is due to extended conjugation of C=O group with the nearby pyridine ring. The C=C stretching vibration of the aromatic ring appeared around 1500 cm⁻¹. The peaks around 1000 and 750 cm⁻¹ are due to ν_{N-N} and aromatic C–H out of plane bending vibrations, respectively. The in plane bending vibration and rocking vibrations of methyl group are characterized by bands in the range of 1400, 1150 and 1050 cm⁻¹, respectively. The signals in the ¹H NMR spectra were assigned based on their positions, integrals and multiplici-



Fig. 3. Syn and anti-conformers of hydrazides.

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¹ H Chemical s	shifts (ppm) and cou	pling constants (Hz	:) of hydrazides 1 and	d 2 .						
Hydrazide	H(10)	H(12)	H(22)/H(26)	H(23)/H(25)	H(24)	H(2)	H(3)	H(4)	H(5)	H(6)	CH ₃
1	8.22	6.86	7.48 (d, 7.53)	7.42 (t, 15.17) ^a	7.32 (t, 14.46) ^a	9.05	I	8.23 (d, 8.05)	7.54 (dd, 7.71, 4.87)	8.74 (d, 3.69)	2.49
2	8.26	6.87	7.48 (d, 7.44)	7.42 (t, 15.36) ^a	7.32 (t, 14.59) ^a	8.76 (dd, 4.55, 1.39)	7.82 (dd, 4.33, 1.47)	I	7.82 (dd, 4.33, 1.47)	8.76 (dd, 4.55, 1.39)	2.49
Values within	parenthes	es are obs	erved coupling con	istants in Hz.							
^a Total widt	th in Hz.										

ties and these assignments were further confirmed from the results derived from ¹H–¹H COSY and ¹H–¹³C COSY spectra. Tables 1 and 2 report ¹H and ¹³C chemical shifts of the hydrazides **1** and **2**, respectively.

3.1. Conformation of hydrazides

Since the hydrazides are derived from *trans-\alpha-* methylcinnamaldehyde, they are having the structural moiety as shown below.



There are two possible ways of attaching the hydrazide moiety as shown in Fig. 3. In the conformation **A** the azomethine proton is *syn* to N–NH bond whereas in **B** they are *anti*. The hydrazides may exist in the enol form also. The possible conformations are shown in Fig. 4.

3.1.1. Spectral studies

The possibility of existing in the enol form in solution as well as in solid state is ruled out based on the observation of amide carbonyl peaks around 160 ppm in 13 C NMR spectra and peaks around 1630 cm $^{-1}$ in the IR spectra.

Generally in azines and hydrazides protons which are syn to N-N bond are expected to resonate at upfield compared to anti protons [19,20]. Comparison of the chemical shifts of azomethine protons in N-2-hydroxy-4-methoxybenzaldehyde-N'-4-nitrobenzovlhydrazone (8.57 ppm) [21] with that of aldehydic proton of 4-methoxysalicylaldehyde (10.24 ppm) reveals that conversion of aldehyde to hydrazides shields the CH proton by 1.67 ppm. The conformation of N-2-hydroxy-4methoxybenzaldehyde-N'-4-nitrobenzoylhydrazone is predicted to be the one in which the azomethine proton is syn to N-NH bond. Similar comparison of the chemical shifts of azomethine protons in the hydrazides 1 and 2 [8.22 and 8.26 ppm] with that of aldehydic proton of *trans*- α -methylcinnamaldehyde (9.56 ppm) reveals that conversion of aldehyde to hydrazides also shields the C-H proton and the shielding magnitude is \approx 1.3 ppm. From this it is concluded that the favoured conformations of hydrazides 1 and 2 in solution are predicted to be the one in which the azomethine protons are syn to N-NH bond [conformation A].

3.1.2. Theoretical studies

Computational calculations were carried out initially at semiempirical level [PM₃] for the possible conformations shown in Fig. 4. The conformer in which heat of formation is minimum is predicted to be the stable conformer and the heat of formation for this conformer can be taken as zero and the values of the other conformers are reported as relative values with respect to this favoured conformer. The relative heat of formations thus determined in this manner for the hydrazides were displayed in Table 3 and the values reveal that the minimum energy conformers are **1A** and **2A** same as those determined in solution. For **1A** and **2A** geometry optimizations were also carried out according to DFT [B₃LYP functional] and HF methods available in Gaussian-03 package using 6-31G(d,p) basis set.

The optimized structures of the stable conformers by DFT and HF methods for the hydrazides **1** and **2** are shown in Fig. 5. For the hydrazide **1** single crystal measurements were made recently (Figs. 6 and 7) and XRD indicates that the

Table 2	
¹³ C Chemical shifts (ppm) of hydrazides 1 and 2 .	

Hydrazide	C(10)	C(11)	C(12)	C=0	C(21)	C(22)/C(26)	C(23)/C(25)	C(24)	C(2)	C(3)	C(4)	C(5)	C(6)	CH_3
1	153.71	136.27	137.20	161.80	134.45	129.36	128.44	127.75	148.65	129.52	135.44	123.54	152.09	12.86
2	154.78	136.67	137.91	162.13	134.86	129.82	128.90	128.25	150.68	122.07	141.24	122.07	150.68	13.27



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ÇH₃

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2A

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Fig. 4. Possible conformations of hydrazides 1 and 2.

Table 3
Relative heat of formation values (kcal/mol) of various conformers for hydrazides 1 and 2.

Hydrazide	Conformers			
	A	В	С	D
1	0	1.82	4.60	5.09
2	0	1.76	5.75	5.92

Table 4

Selected geometric parameters (bond length, bond angle and torsional angle) in hydrazides 1 and 2.

Geometric parameters	1			2			
	XRD	DFT	HF	DFT	HF		
Bond length (Å)							
C21-C12	1.46	1.48	1.48	1.46	1.48		
C12-C11	1.35	1.35	1.33	1.36	1.33		
C11-C13	1.50	1.51	1.51	1.51	1.51		
C11-C10	1 45	1 49	1 47	1 46	1 47		
N9-C10	1 29	1 30	1.26	1 29	1.26		
N9_N8	1 39	1 38	1 36	1.25	1.20		
N8_C7	1.35	1.36	1.50	1.50	1.50		
67 07	1.55	1.50	1.57	1.56	1.50		
67 62	1.23	1.52	1.15	1.22	1.19		
NO 110	1.50	1.45	1.00	-	- 1.00		
IN8-H8	0.88	1.05	1.00	1.02	1.00		
07-04	-	-	-	1.51	1.51		
Bond angle (°)							
C22-C21-C12	124.3	121.6	122.6	124.2	122.6		
C26-C21-C12	118.3	119.2	119.0	118.0	119.0		
C21-C12-C11	129.5	124.8	128.7	130.4	128.7		
C12-C11-C13	125.2	122.2	126.4	126.2	126.4		
C13-C11-C10	118.2	119.1	116.7	117.2	116.7		
C11-C10-N9	121.4	120.6	121.5	121.8	121.5		
C10-N9-N8	114.1	122.6	117.5	116.7	117.4		
N9–N8–C7	118.6	119.8	120.0	120.8	120.2		
N8_C7_07	123.5	119.0	123.9	123.8	120.2		
N8 C7 C3	115.2	121.7	11/ 3	125.0	124.4		
$(7 \ (2 \ (2)$	117.6	121.7	117.0				
$C_1 = C_2 = C_2$	124.2	1217	117.5	—	_		
$C_{4} = C_{3} = C_{7}$	124.5	121.7	116.0	-	116.0		
	110.0	118.7	121.0	116.6	116.9		
07 - 07 - 03	121.3	118.9	121.8	-	-		
$C_{-C_{4}-C_{3}}$	-	-	-	117.6	118.1		
07-04-05	-	-	-	124.6	123.7		
N8-C7-C4	—	-	-	114.1	114.1		
07-C7-C4	-	-	-	121.5	122.1		
Torsional angle (°)							
C22-C21-C12-C11	-22.6	50.4	45.4	27.2	45.3		
C26-C21-C12-C11	156.9	-132.8	137.3	-154.7	137.4		
C21-C12-C11-C13	-1.4	3.1	2.9	2.3	2.7		
C21-C12-C11-C10	178.6	-177.0	-178.3	-178.8	178.4		
C10-N9-N8-C7	179.3	178.2	170.5	175.0	172.5		
N9-N8-C7-07	-2.1	-3.8	-0.3	-1.6	-0.1		
N9-N8-C7-C3	179.3	176.9	180.0	_	_		
N8_N9_C10_C11	179.1	179.0	179 5	179 7	179.7		
C_{2} C_{3} C_{7} O_{7}	23.0	26.7	27.8	175.7	175,7		
$C_2 = C_3 = C_7 = 07$	154.9	152.6	-27.8	_	_		
C2-C3-C7-N8	154.0	152.0	151.9	—	_		
(4 - (3 - (7 - 0)))	156.4	151.2	150.1	—	_		
$U_4 - U_3 - U_7 - N_8$	-24.9	-29.4	-30.2	-	-		
H8-N8-C/-07	_	1/5.3	162.6	169.3	166.4		
C12-C11-C10-C9	-177.0	176.9	179.3	-179.5	179.32		
N9-N8-C7-C4	-	-	-	179.1	179.6		
C3-C4-C7-07	-	-	-	-24.2	-30.4		
C5-C4-C7-07	-	-	-	153.9	148.3		
C3-C4-C7-N8	-	-	-	155.1	149.3		
C5-C3-C7-N8	-	_	_	-26.8	-32.2		

hydrazide exists in the keto form in the solid state. Table 4 reports selected bond lengths, bond angles and torsional angles in the optimized structures for the hydrazides along with the values derived from single crystal measurement of **1** [17].

The bond lengths derived from theoretical calculations are closer to the values observed in XRD except in C7–O7 and N8–H8. Low scattering factors of hydrogen atoms in the X-ray diffraction experiment is responsible for the deviation observed in N8–H8. In most of the cases the bond angles are slightly lower than the single crystal measurements. The maximum deviation is 8.5°. The torsional angles especially C22–C21–C12–C11 and C26–C21–C12–C11 deviate to a greater extent compared to XRD measurements. These values indicate that phenyl ring is distorted from the plane of the side chain moiety and this distortion is predicted to have large magnitude by theoretical calculations. The torsional angles

N8–C7–C3–C2, N8–C7–C3–C4, C2–C3–C7–O7 and C4–C3–C7–O7 in hydrazide **1** and the torsional angles N8–C7–C4–C3, N8–C7–C4–C5, C3–C4–C7–O7 and C5–C4–C7–O7 in hydrazide **2** also indicate the twisting of the pyridine ring from the plane of the side chain moiety.

The HOMO–LUMO energies were also calculated and the values and figures are listed in Table 5 and Fig. 8, respectively. The energy gap (ΔE) between HOMO and LUMO energies is higher for the hydrazide **1** relative to **2**. The HOMO energy of hydrazide **1** is less than that of hydrazide **2**. The plot of HOMO–LUMO energies reveals that the HOMO orbitals are mainly derived from $2p_z$ orbitals of carbon atoms present in the cinnamaldehyde moiety and nitrogen and oxygen atoms present in the hydrazide moiety. LUMO orbitals are localized on the orbitals of the pyridine ring and p_z orbitals of nitrogen, carbon and oxygen present in the side chain.

Table 5

Calculated HOMO-LUMO energies (eV) of hydrazides **1** and **2**.

Hydrazide	DFT			HF		
	LUMO	НОМО	Energy gap (ΔE)	LUMO	НОМО	Energy gap (ΔE)
1	1.864	-8.181	10.045	2.254	-8.227	10.481
2	-1.945	-5.830	3.885	2.110	-8.269	10.379

Table 6

Theoretical and experimental IR spectral data (cm⁻¹) of hydrazides **1** and **2**.

vvavenumber	(cm ⁻¹)								
Hydrazide 1				Hydrazide 2					
Observed values	DFT	HF	Approximate assignments	Observed values	DFT	HF	Approximate assignments		
3444	_	3424	$\nu_{\rm N-H}$	3452	_	3426	$\nu_{\rm N-H}$		
3079	3085	3020	v_{C-H} (aromatic)	3026	3056	3038	ν_{C-H} (aromatic)		
2860	2843	2878	ν_{C-H} (CH ₃)	2969	2996	2955	v_{C-H} (CH ₃ symmetric		
							and asymmetric)		
				2926	2907	2948			
1637	1609	1615	ν _{C=0}	1671	_	1664	ν _{C=0}		
1594	1565	1592	$\nu_{C=N}$	1647	1611	1621	$\nu_{C=N}$		
				1600	1583	1580			
1548	1555	1539	V _{C=C}	1557	1500	1542	$\nu_{C=C}$ (aromatic)		
				1446	1472	1433			
1402	1379	1412	Methyl in plane	1358	1336	1363	Methyl in plane		
			bending vibration				bending vibration		
1300	1298	1343	N–H bending mode	1296	1295	1249	N–H bending mode		
1222	1249	1248	ν_{C-N}	1193	1220	1196	ν_{C-N}		
1147	1133	1147	CH ₃ rocking vibration	1152	1131	1141	CH ₃ rocking vibration		
1066	1082	1057		1073	1074	1056			
1018	997	1054	ν_{N-N}	1022	1049	1039	ν_{N-N}		
970	989	973	The C–H out of plane	958	935	974	The C–H out of plane		
			bending vibration of				bending vibration of		
			benzene ring				benzene ring		
924	907	900		920	908	905			
848	867	828		860	820	851			
753	754	738		752	742	749			
				703	688	703			
689	707	697	Phenyl ring puckering	625	663	668	Phenyl ring puckering		
520		510	mode	510	515	511	mode		
520	-	513		519	515	511			
-	-	-	-	4/1	_	451	-		

Vibrational frequencies for the minimum energy conformer were also calculated by HF and DFT methods. These values were corrected using scale factor 0.9613 [DFT] and 0.8929 [HF] [22] and the corrected frequencies and proposed assignments were summarized in Table 6 along with the observed values. These values indicate that there is a close agreement between the calculated values and observed values. The values calculated according to HF method are slightly



Fig. 5. Minimum energy conformers of hydrazides 1 and 2.

The electric dipole moment μ (*D*) the average polarizability α_{tot} (×10⁻²⁴ esu) and the first hyperpolarizability β_{tot} (×10⁻³¹ esu) of hydrazides 1 and 2. Hydrazide 1 Hydrazide 2 Hydrazide 1 Hydrazide 2 3.249 3 4 4 8 -2062.453 -2909 720 μ_{x} β_{XXX} 5.833 3.696 β_{xxy} -63.585 -147.442 μ_{v} -1.058 -0.624 -63.519 12.261 μ_z β_{xyy} 6 7 6 0 119 225 5 0 9 3 β_{yyy} 154 381 μ_{tot} 411.715 427.814 83.694 17.409 α_{xx} β_{xxz} 4.739 22.586 50.730 21.495 α_{xy} Bxvz 181.954 189.598 -41.297 -22.840 β_{yyz} α_{vv} 4 5 0 9 3 4 3 4 1 1 3 5 4.669 α_{xz} β_{XZZ} -11.879 α_{yz} 6923 10.694 $\beta_{\nu zz}$ 8 5 6 5 86.323 78.680 -0.570 -0.264 α_{77} BIZZ 226.664 232.031 2127.500 2893.073 β_{tot} <α> 33.592×10^{-34} 34.387×10^{-34} 18.380×10^{-30} 24.994×10^{-30} $\alpha_{\rm tot} \, ({\rm esu})$ β_{tot} (esu)

higher than the DFT values and the observed values in some cases.

4. Hyperpolarizability calculations

Table 7

The polarizability α and the hyperpolarizability β and the electric dipole moment μ of the hydrazides are calculated by finite field



Fig. 6. XRD structure of hydrazide 1.



Fig. 7. Close packing of hydrazide 1.

method using $B_3LYP/6-31G^*$ basis set available in DFT package. To calculate all the electric dipole moments and the first hyperpolarizabilities for the isolated molecules, the origin of the Cartesian coordinate system (*x*, *y*, *z*)=(0, 0, 0) was chosen at own centre of mass of each compound.

In Table 7 the results of the electric dipole moment $\mu_{(i=x,y,z)}$ polarizability α_{ij} and the first hyperpolarizability β_{ijk} for the hydrazides **1** and **2** are listed. It is seen that the electric dipole moment of the hydrazide **1** has slightly greater value than the hydrazide **2**. The β_{tot} value of hydrazide **2** obtained by numerical second derivative of electric dipole moments according to the FF approach is rather greater than that of hydrazide **1**.

The highest value of dipole moment is observed for the component μ_y in both the hydrazides. The calculated polarizability α_{ij} is dominated by the diagonal components (α_{xx} , α_{yy} , α_{zz}) and the hyperpolarizability β is dominated by the longitudinal components of β_{xxx} , β_{xxy} , β_{xyy} , β_{yyy} , β_{xxz} , β_{xyz} and β_{yyz} . From this it is inferred that a substantial delocalization of charges is noticed in these directions.

In the present study the crystal structure of 1 has been recognised as the space group $P2_1/c$, with one molecule in the asymmetric unit (centrosymmetric). The hydrazide 2 differs from the hydrazide 1 in the position of nitrogen atom only and hence it is also expected to have centrosymmetric structure. Lacroix et al. have investigated crystal structure and molecular hyperpolarizabilities of a Schiff base derived from 4-(diethylamino)salicylaldehyde and 4-nitroaniline and its metal complexes [23]. The X-ray structure analysis of the Schiff base reveals the space group $P2_1/c$ with one molecule in the asymmetric unit which is also centrosymmetric. The polarizability associated with this Schiff base is explained based on significant conjugation of the whole π -system and large intramolecular charge transfer. The hydrazides 1 and 2 are also polar molecules having non-zero dipole moment components and such compounds may have large microscopic hyperpolarizability and hence may have rather well microscopic NLO behaviour. The higher dipole moment values are associated in general with even larger projection of β_{tot} quantities.

The NLO responses can be qualitatively understood by examining the energetics of frontier molecular orbitals [HOMO–LUMO] of hydrazides **1** and **2**. The HOMO–LUMO energy gap of hydrazide **1** is relatively higher than that of hydrazide **2** and shows lower β value than that of the hydrazide **2**. It is evident that there should be inverse relationship between HOMO–LUMO gap and the first order hyperpolarizability [24].

5. Thermodynamic properties

Thermodynamic properties were calculated and the calculated parameters are presented in Table 8. The hydrazides 1 and 2 have same molecular formula but differ in the position of nitrogen atom only. The hydrazide 2 is stabilized by an amount of -0.025187 a.u.



Fig. 8. HOMO-LUMO plots of hydrazides 1 and 2 (DFT).

Table 8

Theoretically computed energies (a.u.), zero-point vibrational energies (kcal mol⁻¹), rotational constants (GHz), entropies (cal mol⁻¹ K^{-1}) and dipole moment (D) for hydrazides **1** and **2**.

Parameters	Hydrazide 1		Hydrazide 2	
	DFT	HF	DFT	HF
Total energy	-857.89523	-852.52564	-857.920417	-852.5249
Zero-point energy	174.00835	188.37797	175.61750	188.37796
	1.63038	1.46215	1.37309	1.43492
Rotational constants	0.08820	0.09159	0.09087	0.09163
	0.08478	0.08760	0.08594	0.08758
Entropy total	133.728	137.223	141.773	137.273
Translational	42.624	42.624	42.624	42.624
Rotational	34.532	34.571	34.660	34.589
Vibrational	56.571	60.628	64.489	60.060

(DFT) and of -0.00074 a.u. (HF) over the hydrazide **1**. The total entropy of hydrazide **2** is slightly higher than that of hydrazide **1** by both DFT and HF methods.

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6. Conclusion

Hydrazides **1** and **2** were synthesized and characterized by spectral studies. From the spectral measurements conformations were derived and they were found to be same as those derived from theoretical investigations. The dipole moments, polarizability and first order polarizability were also computed and calculated. The first order hyperpolarizabilities reveal that both hydrazides behave as interesting NLO materials. Geometrical parameters derived from theoretical investigations are compared with the single crystal measurements for hydrazide **1**. Vibrational frequencies were also computed and the calculated vibrational frequencies are in good agreement with the experimental ones.

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