Conformational analysis and vibrational spectroscopic investigation of 3-phenylpropylamine
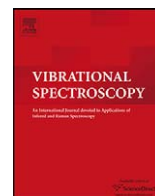
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Conformational analysis and vibrational spectroscopic investigation of 3-phenylpropylamine

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ABSTRACT

The possible stable forms of 3-phenylpropylamine (3-PPA) molecule were experimentally and theoretically studied by infrared and Raman spectroscopy. FT-IR and Raman spectra of 3-PPA were recorded in the regions of 4000–400 cm^{-1} and 3700–60 cm^{-1}, respectively. The potential energy surface corresponding to the internal rotations of the molecule was investigated by semi-empirical quantum mechanical methods, and appropriate conformers defined with B3LYP hybrid density functional theory method along with the basis sets of different size and type. Results from experimental and theoretical data showed the *trans–trans–gauche* (TTG) to be the most stable form of a 3-PPA molecule.

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1. Introduction

3-Phenylpropylamine (3-PPA) molecule is a monodentate ligand with the aromatic sp^2 ring carbon bonding to the primary carbon of propylamine moiety. The molecule is used to synthesize compounds such as vanadium oxide nanotubes [1–3], Ru[II] half-sandwich [4], protein–ligand [5] and n-(3-phenylpropyl)guanidinium bromide complexes [6] where the 3-PPA molecule is in different forms. To the best of our knowledge, conformational and vibrational spectroscopic analyses have not yet been reported for 3-PPA molecule. However conformational or spectroscopic studies for *n*-propylamine [7–14] and toluene molecules [15–24] are available resulting in the motivation of this work. The *n*-propylamine has two stable conformers, the *trans–trans* (TT) and *trans–gauche* (TG). The TT conformer is the most stable according to the ab initio calculations [12,13]. The conformers of toluene are either planar or orthogonal with the orthogonal being the most stable one [20–24].

In the current study, the stable conformers of 3-PPA molecule were considered within the density functional theory at any basis sets. The infrared and Raman vibrational assignments were also provided experimentally. The most stable conformer of 3-PPA was found to be of the *trans–trans–gauche* (TTG) form.

2. Experimental part

The 3-PPA was obtained from Aldrich Europe and used without any further purification that is in liquid phase and colourless at room temperature. The FT-IR spectrum of 3-PPA between KBr windows was recorded by using a Bruker Optics IFS66v/s FTIR spectrometer with the resolution of 2 cm^{-1} in the spectral region of 4000 cm^{-1} and 400 cm^{-1} in vacuum. The Raman spectrum was recorded by using a Bruker Senterra Dispersive Raman microscope spectrometer with 532 nm excitation from a 3B diode laser having 3 cm^{-1} resolution in the spectral region of 3700 cm^{-1} and 60 cm^{-1}. The FT-IR and Raman spectra of the molecule are given in Figs. 1 and 2.

3. Theoretical part

First, potential energy surfaces (PES) were determined via MOPAC2002 geometry optimization using either PM3 or PM5 semi-empirical Hamiltonian within Fujitsu CAChe WS Pro v.7.5.0 Windows software package [25] on a personal workstation for the possible stable structures of 3-PPA where the torsion angles $\tau_1(C_4C_5C_7C_8)$, $\tau_2(C_5C_7C_8C_9)$, $\tau_3(C_7C_8C_9N_{10})$ and $\tau_4(C_8C_9N_{10}H_{22})$ were changed by 3° steps. The appropriate structures were then selected by considering the minimum positive heat of formation energy (ΔH).

For the selected structures, local minima or transition states on the PES were then examined through geometric optimizations and vibrational frequency analyses using Becke-3-Lee–Yang–Parr
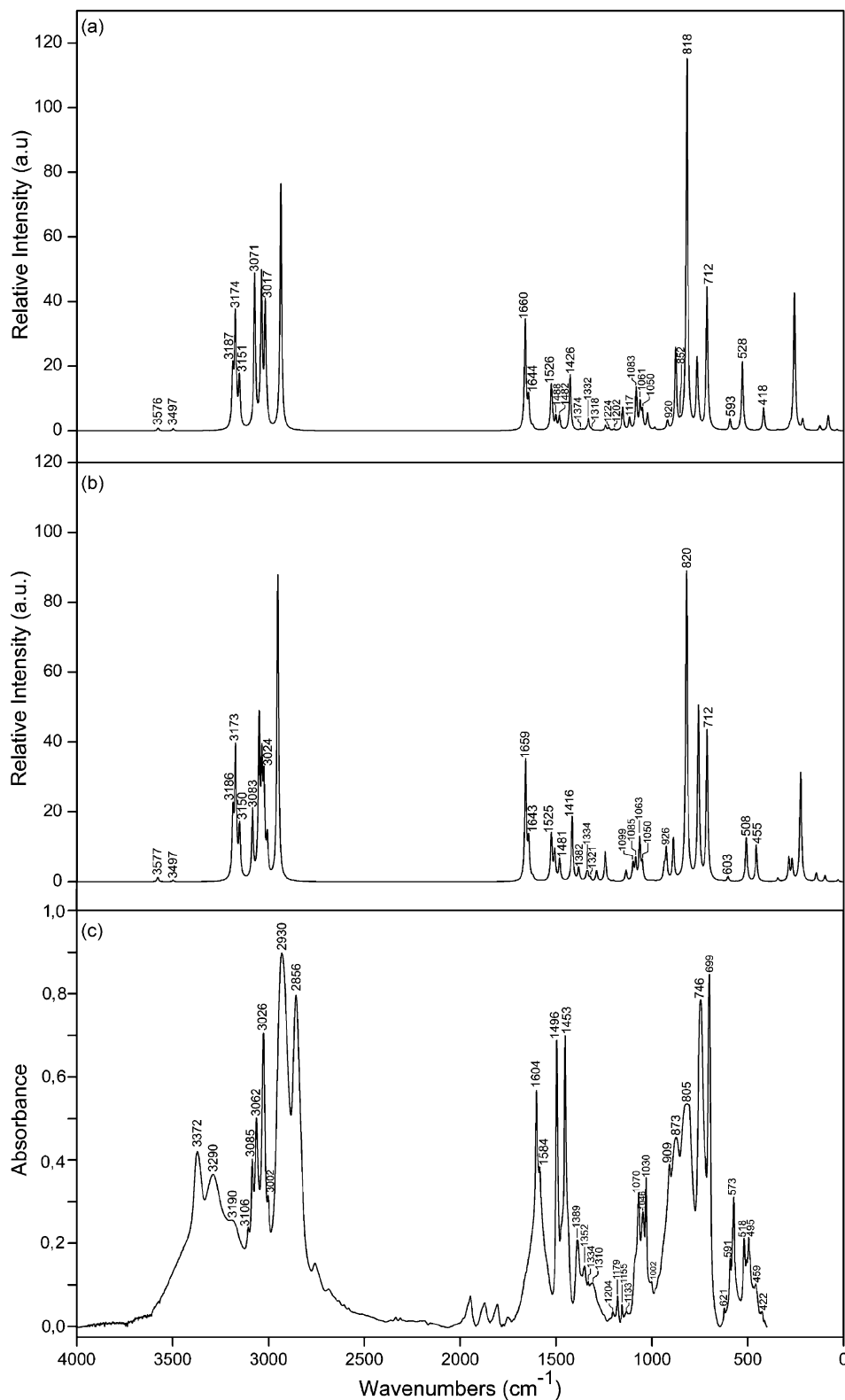
Fig. 1. The IR spectra of 3-phenylpropylamine molecule: (a) TTG isomer, calculated; (b) TGG isomer, calculated; (c) experimental FT-IR spectrum.

(B3LYP) hybrid Density Functional Theory (DFT) method with 6-31G(d) basis set [26,27] within the Gaussian03W program package as well as the GaussView molecular visualization program [28,29]. The calculations were also repeated with the B3LYP/6-31++G(d,p) double and B3LYP/6-311++G(d,p) triple zeta contracted Gaussian basis sets (see Tables S1 and S2 given as supplementary tables). In conjugated π systems, electrons are highly delocalized including

additional diffuse and polarization functionals to the basis set used in the electronic structure calculations, in many cases, lead to more accurate results. From our calculations, eight conformers were obtained which were reduced to four using the mirror reflection symmetry operation (σ). The conformers were identified by three letters (ABC) through orientation of the torsions τ_2, τ_3 and τ_4, respectively. The 3-PPA molecule possesses four possible rota-
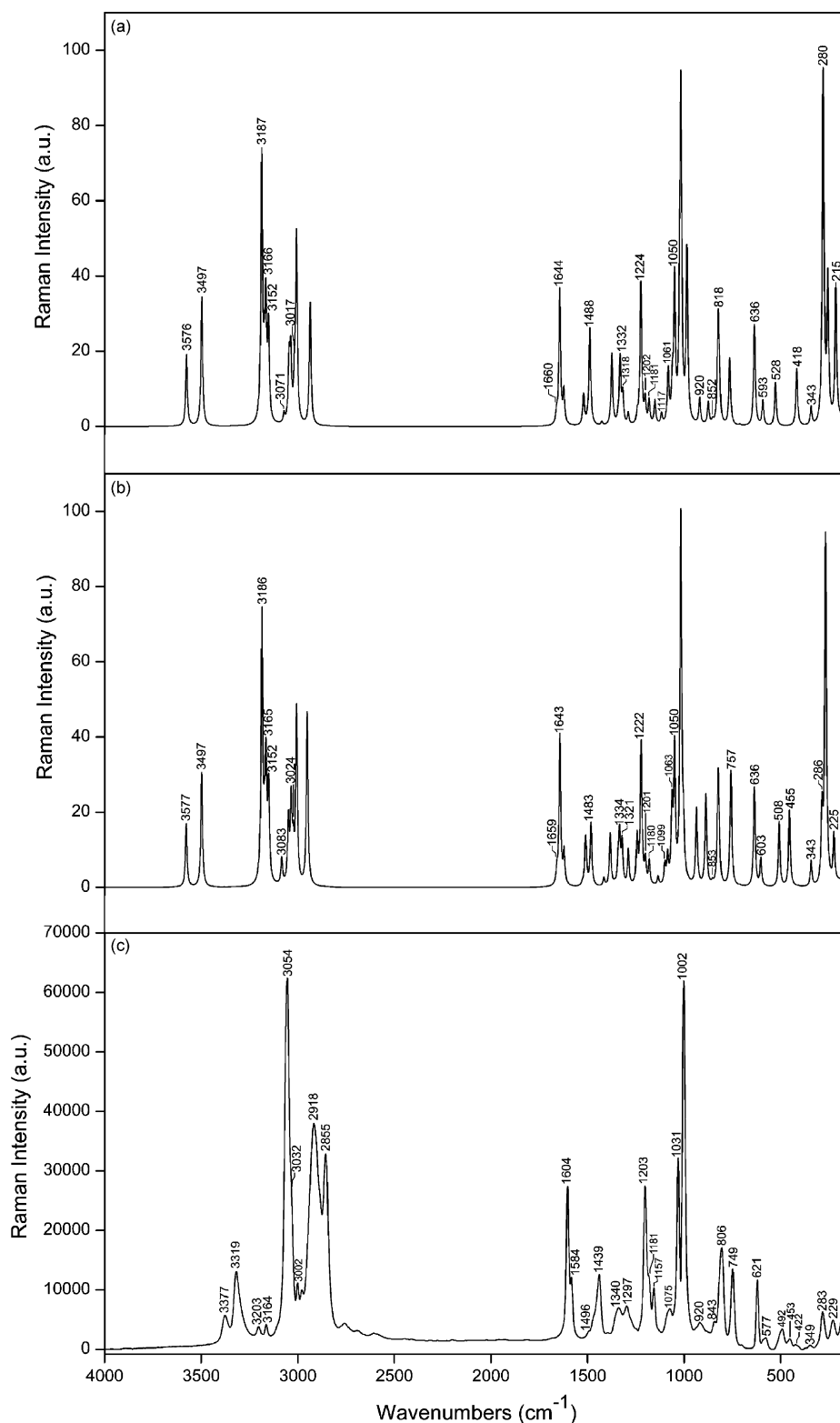
Fig. 2. The Raman spectra of 3-phenylpropylamine molecule: (a) TTG isomer, calculated; (b) TGG isomer, calculated; (c) experimental Raman spectrum.

tional isomers as shown in Newman projection (see Fig. 3). The first letter, T (*trans*) or G (*gauche*), refers to the skeletal atom conformation indicating the position of the phenyl and methylamine groups relative to the C_7C_8 bond. The second letter refers to the skeletal atomic conformation representing the position of the benzyl and amino groups relative to the C_8C_9 bond. The third letter refers to the amino group and represents the position of the lone

electron pair on the nitrogen and phenylethyl relative to the central C_9N_{10} bond.

Further analyses of the conformers were made via statistical thermodynamic factors that include conformational relative energies having significant contributions from the harmonic modes of vibration. The statistical weighting factors for the population analysis were calculated on the basis of Gibbs free
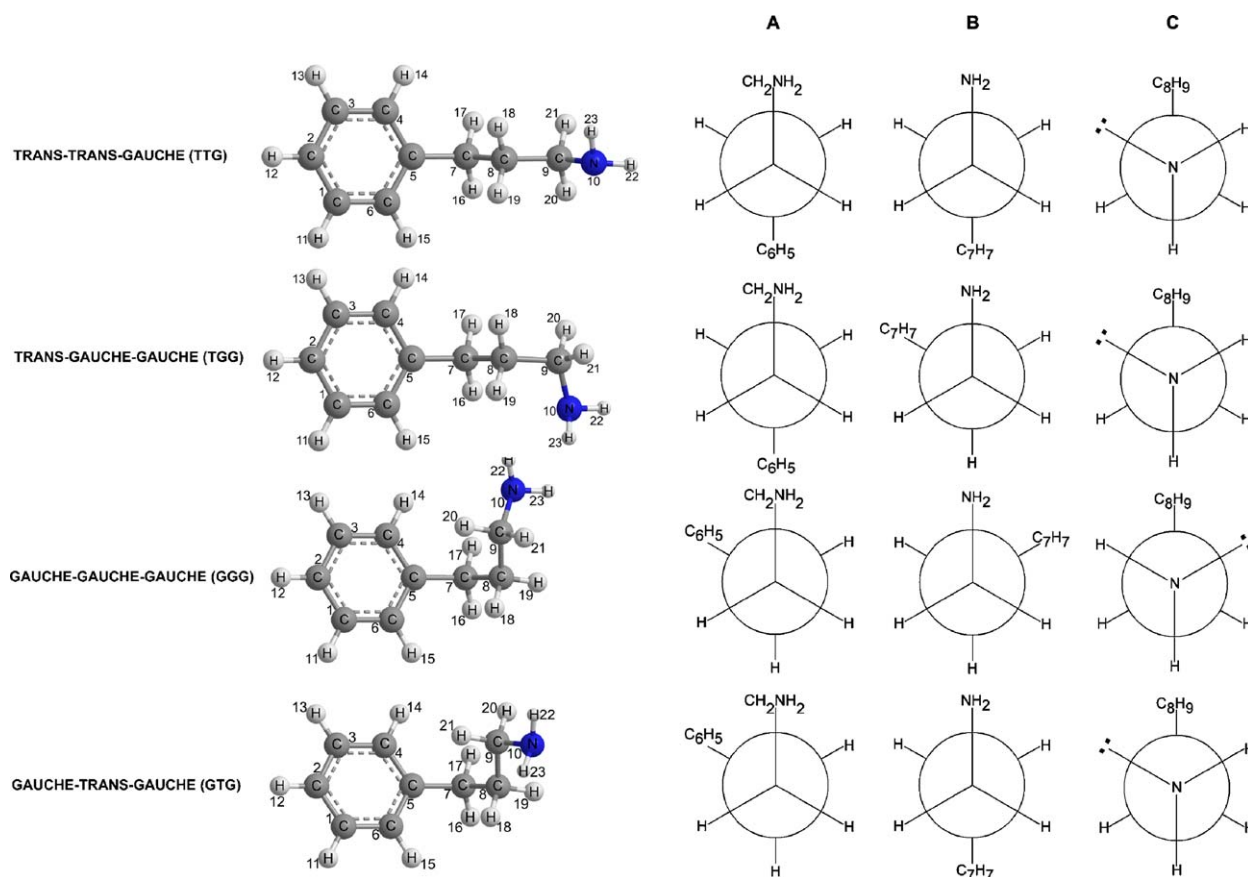
Fig. 3. TThe illustrations for the four conformers of 3-phenylpropylamine: (A) Newman projections along to the C_7–C_8 bond; (B) Newman projections along to the C_8–C_9 bond; (C) Newman projections along to the C_9–N_{10} bond.

energy. Boltzmann weighting factors (N_i) were determined for each conformer using the relation,

$$N_i = \frac{\exp(-G_i/RT)}{\sum_i \exp(-G_i/RT)} \tag{1}$$

where $R = 1.987 \times 10^{-3}$ kcal/mol, G_i is the Gibbs free energy of conformer i and $T = 300$ K were used. The results given in Table 1

indicate that the TTG and TGG forms have dominant features among the isomers.

Although accurate vibrational frequencies are more difficult to compute, it is well known that DFT calculations give excellent agreement between molecular structure parameters and experimental vibrational frequencies of organic compounds provided the calculated frequencies are scaled to compensate the approximate treatment of electron correlation, basis set deficiencies and

Table 1

The possible stable conformers of 3-phenylpropylamine molecule and their molecular properties within DFT B3LYP method with 6-31G(d), 6-31++G(d,p), 6-311++G(d,p) basis sets.

	B3LYP/6-31G(d)				B3LYP/6-31++G(d,p)				B3LYP/6-311++G(d,p)			
	TTG	TGG	GGG	GTG	TTG	TGG	GGG	GTG	TTG	TGG	GGG	GTG
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1	C_1	C_1	C_1	C_1	C_1
ΔZPE (kcal/mol)	–	0.02	0.16	0.31	–	0.02	0.11	0.15	–	0.02	0.12	0.16
ΔSCF (kcal/mol)	–	0.47	1.03	1.17	–	0.96	1.50	1.64	–	0.71	1.19	1.33
ΔG (kcal/mol)	–	0.40	0.71	1.21	–	0.22	0.56	1.97	–	0.25	0.57	0.91
μ_{TOTAL} (Debye)	1.61	1.77	1.76	1.16	1.75	1.69	1.51	1.05	1.72	1.65	1.46	1.01
E_{HUMO} (eV)	−6.24	−6.15	−6.21	−6.13	−6.52	−6.45	−6.44	−6.51	−6.60	−6.51	−6.50	−6.57
E_{LUMO} (eV)	0.15	0.24	0.26	0.05	−0.41	−0.35	−0.46	−0.38	−0.43	−0.35	−0.51	−0.41
$\Delta E_{HUMO-LUMO}$ (eV)	6.39	6.39	6.48	6.18	6.12	6.11	5.98	6.13	6.12	6.15	5.99	6.17
N_i (%)	52	26	15	7	44	30	17	9	44	30	17	9
Torsion angles (°)												
$\tau_1(C_4C_5C_7C_8)$	95	90	100	107	95	90	100	107	95	90	100	107
$\tau_2(C_5C_7C_8C_9)$	−179	177	−65	−66	−179	177	−65	−66	−179	177	−65	−66
$\tau_3(C_7C_8C_9N_{10})$	−178	−65	−62	−178	−178	−65	−62	−178	−178	−65	−62	−178
$\tau_4(C_8C_9N_{10}H_{22})$	56	51	52	55	56	51	52	55	56	51	52	55

The relative energies of the conformers were given in respect to the calculated self-consistent field (SCF), zero point energy (ZPE) and Gibbs free energy (ΔG) of the *trans–trans–gauche* (TTG) conformer. For the TTG conformer, the ZPE, SCF, ΔG calculated using DFT B3LYP method with 6-31G(d), 6-31++G(d,p), 6-311++G(d,p) basis sets that are (127.85, −254476.60, −254559.79), (127.22, −254502.71, −254397.90), (126.84, −254550.98, −254446.84) kcal/mol, respectively. N_i is the Boltzmann weighting factors for population analysis.

Table 2
The experimental geometric structures of toluene and *gauche*-ethylamine molecule together with the calculated data for the rotational isomers of the 3-phenylpropylamine molecule at B3LYP/6-311++G(d,p) theory level.

Geometrical coordinate	Toluene[a]	g-Ethylamine[b]	Isomers of 3-PPA			
			TTG	TGG	GGG	GTG
r(C–C)$_{av}$/Å aromatic	1.399	–	1.3957	1.3960	1.3962	1.3959
r(C–H)$_{av}$/Å aromatic	1.098	–	1.0850	1.0851	1.0850	1.0850
r(C–C)$_{av}$/Å	1.511	1.524	1.5343	1.5360	1.5376	1.5355
r(C–H)$_{av}$/Å	1.12	1.107	1.0969	1.0964	1.0960	1.0964
r(C–N)/Å	–	1.475	1.4680	1.4698	1.4702	1.4702
r(N–H)/Å	–	1.052	1.0150	1.0149	1.0150	1.0152
C–C–N/(deg)	–	109.7	110.7	111.2	111.3	110.8
<C–C–H$_{av}$/(deg)	–	113.2	109.2	108.9	108.7	109.1
<C–N–H$_{av}$/(deg)	–	112.4	111.0	110.9	110.9	110.7

[a] Taken from Ref. [19].
[b] Taken from Ref. [43].

anharmonicity [30–38]. In this respect, two different scaling approaches, namely scaling harmonic wavenumbers by dual scale factors and scaling harmonic wavenumbers in the scaled quantum mechanics force field (SQM FF) methodology [39,33,34], were implemented. In the first one, two different scale factors (0.954 for B3LYP/6-31++G(d,p) and 0.960 for B3LYP/6-311++G(d,p) basis sets) were used for fitting the harmonic wavenumbers lower or equal to 1700 cm^{-1} while one scale factor (0.980) for both basis sets was used for those higher than 1700 cm^{-1}. In the latter, the scaled wavenumbers were calculated using the scaled harmonic force constants obtained from the harmonic force constants at B3LYP/6-31++G(d,p) and B3LYP/6-311++G(d,p) theory level where the scaling factors proposed by Baker et al. [40] for the B3LYP method were employed without any modification of the scaling of the force constants.

The scaling factors were not applied to the IR and Raman intensities. The Raman intensity (I^R), which simulates the measured Raman spectrum was calculated using the following relation:

$$I_i^R = C(\nu_0 - \nu_i) \cdot \nu_i^{-1} \cdot B_i^{-1} \cdot S_i \qquad (2)$$

where S_i is the Raman scattering activity of the normal mode Q_i obtained by DFT methods, C is a constant and I_i^R is in arbitrary units [41,42]. Here, the excitation frequency ($\nu_0 = 18797$ cm^{-1}), that is the wavelength of 532 nm of a 3B diode laser and $C = 10^{-14}$ were used. For the B_i factor, the values at $T = 300$ K were determined with the equation given below.

$$B_i = 1 - \exp\left(\frac{h\nu_i c}{kT}\right) \qquad (3)$$

4. Results and discussion

Possible stable conformers for the 3-PPA molecule and their molecular properties are given in Table 1. The table points out that the TTG is a more stable conformer at room temperature among the others taking into account the energies along with the population factors values. It is also worth noticing that the various basis sizes effect on ΔZPE, ΔSCF and ΔG energies are not great and that the stability order for the conformers remains the same with the basis sets. The conformers are also in agreement with the X-ray crystal structural data reported by Melchart et al. for the Ru^{II} half-sandwich complexes [4], by Leiros et al. for the trypsin-3phenylpropylamine (1.tnk) protein–ligand complex [5] and by Standford et al. for the n-(3-phenylpropyl)guanidinium bromide [6] where the 3-PPA has the GGG, GTG or TTG forms.

In Table 2, the calculated geometrical parameters for the rotational isomers of the 3-PPA are given with the experimental data of the toluene and *gauche*-ethylamine molecule. The comparison implies that the bond lengths and also the angles of the TTG isomer are much closer to the experimental data. The experimental lengths of 3-PPA molecule were reported as *ca.* 0.9–1.0 nm in the vanadium oxide nanotubes [1–3]. The experimental length agrees with the obtained length of the TTG–TGG isomers. The lengths of the TTG–TGG and GGG–GTG isomers were determined as *ca.* 0.9 nm and 0.8 nm.

Before offering an explanation for the vibrational assignments of isomers, the IR and Raman frequencies of 3-PPA molecule together with the vibrational assignments of toluene and n-propylamine molecule are presented in Table 3. The N–H$_2$ asymmetric and symmetric stretching fundamental bands appearing at 3372 cm^{-1}, 3290 cm^{-1} (IR) and 3377 cm^{-1}, 3319 cm^{-1} (Ra) are attributed to the n-propylamine molecule. The bands between 3085–3026 cm^{-1} (IR) and 3054–3032 cm^{-1} (Ra) are from the C–H stretching of toluene group while the bands at 2930 cm^{-1}, 2856 cm^{-1} (IR) and 2918 cm^{-1}, 2855 cm^{-1} (Ra) are due to the CH$_2$ asymmetric and symmetric stretching bands of n-propylamine. The other bands that appeared at 1604 cm^{-1}, 1584–1496 cm^{-1} and 1002 cm^{-1} (IR, Ra) represent the NH$_2$ deformation of n-propylamine, C–C stretching vibrations and ring breathing of toluene. The CH$_2$ vibrations are deformation, twisting, wagging, and rocking that appear in the expected frequency regions of 1453–746 cm^{-1}. Hence the 3-PPA molecule shares the vibration modes of the n-propylamine and toluene.

In the spectral analysis, the TTG and TGG isomers were considered due to the weighting of population factor that is *ca.* %74 of the total. The scaled vibrational frequencies of the isomers at B3LYP/6311++G(d,p) theory level were compared to the experimental infrared and Raman vibrational frequencies of the 3-phenylpropylamine in Table 4 for the spectral region of 4000 cm^{-1} and 400 cm^{-1} (see also Tables S3 and S4). As seen from the table, the fundamental bands of TTG and TGG forms of the 3-PPA have nearly same frequencies. On the other hand, the modes with the number 11 and 10 corresponding to the CCCN deformation vibrations are close to the TGG form. However, the modes with the number 56, 53, 44, 42, 12 are close to the TTG form. Within the vibrational bands, the bands corresponding to the vibrational frequencies of TTG form are strong bands and relative intensities of the vibrational frequencies are also higher. In the light of these results, the TTG form of the molecule possesses the dominant feature compared to the TGG form. It might be worth mentioning that the correlation between experimental and theoretical wavenumbers were found to be 0.9995, 0.9996 and 0.9994, 0.9994 for scaling harmonic wavenumbers by dual scale factors

Table 3
The measured IR and Raman frequencies (cm^{-1}) of 3-phenylpropylamine molecule together with the vibrational assignments of toluene and *n*-propylamine molecules.

Assignment[a,b]	Toluene[a,b]			Assignment[c]	Propylamine[c]		3-Phenylpropylamine[d]	
	IR-Raman[a]	IR[b]	Raman[b]		IR	Raman	IR	Raman
–	–	–	–	ν(NH$_2$) as.	3314 (8b)	3314 (8)	3372 m	3377 vw
					3308 (7b)	–		
2xν(CC)	–	3203 vw br sh	3205 p	2xNH$_2$ def.	3245 (3bb)	–	3190 vw br	3203 vw
–	–	–	–	ν(NH$_2$) s.	3182 (4bb)	3185 (3b)	3290 w	3319 w
2xν(CC)	–	3167.5 vw	3168 p	–	–	–	–	3164 vw
2xν(CC)	–	3104.1 w	–	–	–	–	3106 vw	–
ν(CH)	3085	3086.4 m	–	–	–	–	3085 m	–
ν(CH)	3070	3062.1 m br	3065 p	–	–	–	3062 m	–
ν(CH)	3058	3055 m br sh	3055 p	–	–	–	–	3054 vs
ν(CH)	3037	–	3038 dp	–	–	–	–	3032 m br sh
ν(CH)	3028	3027.0 m	–	–	–	–	3026 s	–
3xRing	–	–	–	–	–	–	3002 w	3002 w
ν(CH$_3$) as.	2979	–	–	ν(CH$_3$) as., ν(CH$_3$) s.	2955 (1)	2959 (10)	–	–
ν(CH$_3$) as.	2950	2950 m sh	–		2953 (12)			
ν(CH$_3$) s.	2920	2919.9 m	2920 p	ν(CH$_2$) as.	2928 (1)	2940 (6bb)	2930 vs	2918 m
					2924 (10)	–		
					2897 (3)	2900 (12)		
–	–	–	–	ν(CH$_2$) s., ν(CH$_3$) s.	2870 (5)	2871 (11)	2856 vs	2855 m
					2862 (9)	–		
					2852 (4)	2855 (3b)		
ν(CC)	1604	1604.6 m	1604 dp	NH$_2$ def.	1618 (1)	–	1604 s	1604 m
					1615 (6bb)	–		
					1605 (6bb)	–		
ν(CC)	1584	1586.7 w br	1585 dp	–	–	–	1584 m	1584 w
ν(CC)	1493	1495.7 s	–	–	–	–	1496 vs	1496 vw br sh
δ(CH$_3$) as., ν(CC)	1455	1460.3 m br	–	CH$_3$ def. as., CH$_2$ def.	1459 (4s)	1456 (7s)	1453 vs	1439 w
–	–	–	1442 dp		1446 (2s)	1452 (7s)	–	–
					1442 (4s)	1424 (4s)		
δ(CH$_3$) s.	1378	1378.9 m	1378 p	CH$_3$ def. s.	1375 (2s)	–	–	–
					1372 (2s)	–		
–	–	–	–	CH$_2$ wag.	1366 (2)	–	1389 w	–
					1357 (1)	–	1352 w	–
					1349 (1)	–		
ν(CC)	1331	1332.0 w	1332 p	CH$_2$ tw.	1294 (1)	–	1334 vw	1340 vw
β(CH)	1313	1312.7 w	–		1291 (1)	1291 (3)	1310 vw	1297 vw
					1217 (2s)	–		
ν(C–CH$_3$) X–sens	1208	1210.2 w	1210 p	–	–	–	1204 vw	1203 m
β(CH)	1176	1178.6 m	1179 dp	ν(CCCN)	1124 (3)	1124 (5s)	1179 vw	1181 vw br sh
β(CH)	1153	1155.9 w	1156 dp				1155 vw	1157 w
							1133 vw	–
β(CH)	1080	1081.4 m	–	ρ(CH$_3$)	1074 (2)	1075 (1b)	1070 m	1075 vw
r(CH$_3$)	1040	1041.4 m	–	NH$_2$ tw.	1040 (2b)	–	–	–
β(CH)	1028	1030.1 m	1031 p	ν(CCCN)	1022 (2s)	1023 (2s)	1046 m	–
							1030 m	1031 m
Ring	1002	1002.3 w	1003 p	–	–	–	1002 w sh	1002 vs
γ(CH)	983	980.7 w	–	–	–	–	–	–
γ(CH)	973	966.4 w br	–	–	–	–	–	–
γ(CH)	893	895.4 m	–	–	–	–	909 m	920 vw
–	–	–	–	NH$_2$ wag.	963 (2bb)	–	805 s br	806 m
					939 (4b)	–		
γ(CH)	841	842.7 m	842 dp	ν(CCCN)	877 (1)	–	873 m	843 vw
					866 (1)	–		
					855 (3s)	853 (3)		
α(CCC) X–sens	784	785.6 m	786 p	ρ(CH$_2$)	747 (6s)	–	746 vs	749 w
					745 (6s)–	–		
γ(CH)	734	729.9 vs	–	–	–	–	–	–
φ(CC)	690	694.8 vs	–				699 vs	–
α(CCC)	620	622.0 w	622 dp	–	–	–	621 vw	621 w
							591 w	–
–	–	–	–	ν(skeletal)	556 (4bb)	–	573 m	577 vw
α(CCC) X–sens	524	521.0 m	521 p	–	–	–	518 w	–
φ(CC) X–sens	467	464.4 vs	–	CCN def.	471 (6)	469 (2)	495 w	492 vw
					455 (1)	–	459 w	453 vw
					445 (5)	–		
φ(CC)	406	–	–	–	–	–	422 vw	422 vw br
β(C–CH$_3$) X–sens	347	–	346 dp	–	–	–	–	349 vw br
–	–	–	–	–	–	–	–	283 vw
γ(C–CH$_3$) X–sens	217	–	217 dp	–	–	–	–	229 vw

ν: bond stretching, δ: bending; β and α: in plane angle bending, γ and φ: out of plane angle bending, def.: deformation, ρ and r: rocking, tw.: twisting, wag.: wagging, s.: symmetric, as.: asymmetric, vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder, br: broad, p: polarized, dp: depolarized.

[a] Taken from Ref. [16].
[b] Taken from Ref. [18].
[c] Taken from Ref. [8]; s: sharp, b: broad, bb: breit broad.
[d] Assigned from the FT-IR and Raman spectra of 3-phenylpropylamine molecule recorded in this study.

Table 4
The experimental vibrational assignments of the 3-phenylpropylamine molecule and comparison with the calculated data of TTG and TGG isomers at B3LYP/6-311++G(d,p) theory level.

Mode	Experiment[a] 3-PPA			B3LYP/6-311++G(d,p) TTG isomer					B3LYP/6-311++G(d,p) TGG isomer					P.E.D.[e] (Potential Energy Distribution) Description (%)	
	IR[a]	Ra[a]	Assignment[a]	R.I.[b] (IR)	R.I.[b] (Ra)	ν^b	ν^c	ν^d	R.I.[b] (IR)	R.I.[b] (Ra)	ν^b	ν^c	ν^d	TTG isomer	TGG isomer
63	3372 m	3377 vw	ν(NH$_2$) as.	1	19	3576	3433	3451	1	17	3577	3434	3451	ν_{as}(NH$_2$) (100)	ν_{as}(NH$_2$) (100)
62	3290 w	3319 w	ν(NH$_2$) s.	1	35	3497	3357	3375	1	31	3497	3357	3374	ν_s(NH$_2$) (100)	ν_s(NH$_2$) (100)
	3190 vw br	3203 vw	2xNH$_2$ def.	–	–	–	–	–	–	–	–	–	–	–	–
	–	3164 vw	2xν_R(CC)	–	–	–	–	–	–	–	–	–	–	–	–
	3106 vw	–	NH$_2$ def.+ν(CC)	–	–	–	–	–	–	–	–	–	–	–	–
61	3085 m	–	ν_R(CH)	22	75	3187	3060	3061	23	76	3186	3059	3060	ν_R(CH) (95)	ν_R(CH) (95)
60	3062 m	–	ν_R(CH)	36	28	3174	3047	3049	40	28	3173	3046	3048	ν_R(CH) (99)	ν_R(CH) (99)
59	–	3054 vs	ν_R(CH)	17	40	3166	3039	3041	18	40	3165	3038	3040	ν_R(CH) (100)	ν_R(CH) (100)
58	–	3032 m br sh	ν_R(CH)	18	30	3152	3026	3028	17	31	3152	3026	3027	ν_R(CH) (98)	ν_R(CH) (97)
57	3026 s	–	ν_R(CH)	17	30	3151	3025	3026	17	29	3150	3024	3025	ν_R(CH) (100)	ν_R(CH) (100)
	3002 w	3002 w	3xR. breath.	–	–	–	–	–	–	–	–	–	–	–	–
56	2930 vs	2918 m	ν(CH$_2$) as.	46	4	3071	2948	2950	21	8	3083	2960	2966	ν_{as}(CH$_2$) (94)	ν_{as}(CH$_2$) (93)
53	2856 vs	2855 m	ν(CH$_2$) s.	41	22	3017	2896	2898	33	18	3024	2903	2907	ν_s(CH$_2$) (83)	ν_s(CH$_2$) (89)
50	1604 s	1604 m	NH$_2$ def.	35	6	1660	1627	1589	35	7	1659	1626	1589	NH$_2$ sci. (87)	NH$_2$ sci. (86)
49	1584 m	1584 w	ν_R(CC)	12	37	1644	1611	1587	14	41	1643	1610	1585	ν_R(CC) (85)	ν_R(CC) (84)
47	1496 vs	1496 vw br sh	ν_R(CC)	15	4	1526	1495	1481	14	2	1525	1495	1481	ν_R(CC) (67), δ_R(CH) (16)	ν_R(CC) (67), δ_R(CH) (16)
44	1453 vs	1439 w	ν_R(CC), CH$_2$ def.	3	27	1488	1458	1449	6	17	1483	1453	1441	CH$_2$ sci. (67)	CH$_2$ sci. (76)
43	1453 vs	1439 w	ν_R(CC), CH$_2$ def.	5	12	1482	1452	1442	7	17	1481	1451	1438	ν_R(CC) (28), δ_R(CH) (50)	ν_R(CC) (25), δ_R(CH) (45)
42	1389 w	–	CH$_2$ wag.	18	1	1426	1397	1389	19	3	1416	1388	1380	CH$_2$ wag. (85)	CH$_2$ wag. (89)
41	1352 w	–	CH$_2$ wag.	4	20	1374	1347	1340	4	15	1382	1354	1350	CH$_2$ wag. (61)	CH$_2$ wag. (60)
38	1334 vw	1340 vw	ν_R(CC), CH$_2$ tw.	4	20	1332	1305	1295	3	17	1334	1307	1295	ν_R(CC). (12), CH$_2$ tw. (54)	ν_R(CC). (12), CH$_2$ tw. (52)
37	1310 vw	1297 vw	β_R(CH), CH$_2$ tw.	1	10	1318	1292	1286	1	14	1321	1295	1287	δ_R(CC) (20), CH$_2$ tw. (45)	δ_R(CC) (41), CH$_2$ tw. (25)
34	1204 vw	1203 m	ν(C$_R$–CH$_2$)	1	39	1224	1200	1188	1	40	1222	1198	1188	ν(C$_R$–CH$_2$) (73)	ν(C$_R$–CH$_2$) (71)
33	1179 vw	1181 vw br sh	β_R(CH)	0	9	1202	1178	1168	0	9	1201	1177	1168	δ_R(CH) (93)	δ_R(CH) (93)
32	1155 vw	1157 w	β_R(CH)	0	8	1181	1157	1149	0	8	1180	1156	1148	δ_R(CH) (93)	δ_R(CH) (92)
30	1070 m	1075 vw	β_R(CH)	4	4	1117	1095	1087	6	7	1099	1077	1066	δ_R(CH) (52)	δ_R(CH) (40), ν(CN) (27)
29	1046 m	–	ν(CCCN)	14	16	1083	1061	1045	7	10	1085	1063	1052	ν_{as}(CCCN) (43), ν_R(CC) (7)	ν_{as}(CCCN) (72)
28	1030 m	1031 m	ν(CCCN)	9	18	1061	1040	1031	13	26	1063	1042	1034	ν_s(CCCN) (42), ν_R(CC) (7)	ν_{as}(CCCN) (54)
27	1002 w sh	1002 vs	R. breath.	7	43	1050	1029	1022	7	41	1050	1029	1022	R. breath. (89)	R. breath. (99)
21	909 m	920 w	γ_R(CH)	4	8	920	902	899	10	6	926	907	906	γ_R(CH) (83)	γ_R(CH) (66)
19	873 m	843 vw	γ_R(CH)	5	3	852	835	835	3	3	853	836	836	γ_R(CH) (98)	γ_R(CH) (99)
17	805 s br	806 m	NH$_2$ wag.	115	31	818	802	798	90	25	820	804	801	NH$_2$ wag. (64)	NH$_2$ wag. (72)
15	746 vs	749 w	ρ(CH$_2$)	8	5	755	740	737	51	31	757	742	740	ρ(CH$_2$) (74)	γ_R(CCH) (57)
14	699 vs	–	γ_R(CC)	45	1	712	698	692	44	1	712	698	693	γ_R(CCH) (63)	γ_R(CCH) (88)
13	621 vw	621 w	β_R(CCC)	0	27	636	623	631	0	27	636	623	631	δ_R(CC) (84)	δ_R(CC) (84)
12	573 m	577 vw	ν(skeletal)	4	7	593	581	586	2	8	603	591	597	δ_R(CCC) (38) s., δ_s(CCC) (15)	δ_R(CCC) (28) s., δ_{as}(CCC) (13)
11	495 w	492 vw	CCCN def.	22	12	528	517	518	13	18	508	498	497	τ_R(CC) (37), δ_{as}(CCC,CCN) (21)	τ_R(CC) (45), δ_s(CCC) (4)
10	459 w	453 vw	CCCN def.	7	15	418	410	411	11	21	455	446	451	τ_R(CC) (14), δ_s(CCC,CCN) (67)	τ_R(C$_R$C) (7), δ_s(CCC,CCN) (62)
9	422 vw	422 vw br	γ_R(CC)	3	9	413	405	401	0	1	414	406	402	γ_R(CH) (99)	γ_R(CH) (99)
8	–	349 vw br	β(C$_R$–CH$_2$)	0	6	343	336	344	1	7	343	336	343	δ(C$_R$C$_R$C) (77)	δ(C$_R$C$_R$C) (72)
7	–	283 vw	–	3	96	280	274	275	7	26	286	280	282	τ_R(CC) (6), δ_s(CCN) (59)	τ_R(CC) (31), δ_s(CCN) (28)
5	–	229 vw	γ(C$_R$–CH$_2$)	4	38	215	211	210	32	15	225	221	220	τ_R(CC) (23), δ_{as}(CCN) (51)	τ(NH$_2$) (74)

[a] Assigned in this study by the obtained IR and Raman spectra of 3-phenylpropylamine along with the assignments of related molecules; vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder, br: broad; ν: bond stretching, β: in plane angle bending, γ: out of plane angle bending, ρ: rocking, def.: deformation; tw.: twisting, wag.: wagging, breath.: breathing, R: ring, s: symmetric, as: asymmetric.

[b] Calculated values (unscaled).

[c] Wavenumbers scaled with the dual scale factors.

[d] Wavenumbers scaled by SQM FF methodology.

[e] ν: bond stretching, δ: in plane angle bending, γ: out of plane angle bending, τ: torsion, ρ: rocking, sci.: scissoring, tw.: twisting, wag.: wagging, breath.: breathing, R: Ring, s: symmetric, as: asymmetric.

and scaling harmonic wavenumbers in SQM FF methodology at B3LYP/6-31++G(d,p) and B3LYP/6-311++G(d,p) theory level, respectively.

5. Conclusion

The results presented, both theoretically and experimentally, show that the TTG form of the 3-phenylpropylamine molecule is more compatible with the experimental data. Similarity it can be concluded that *trans–trans–gauche* (TTG) is the most stable form of 3-PPA molecule.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.vibspec.2009.01.006.

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