

Molecular structure and vibrational spectra of 1,3-bis(4-piperidyl)propane by quantum chemical calculations

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Received 31 December 2007; received in revised form 9 February 2008; accepted 16 February 2008

Available online 26 February 2008

Abstract

The infrared and Raman spectra of 1,3-bis(4-piperidyl)propane molecule have been recorded between 4000–400 cm⁻¹ region and 3500–150 cm⁻¹ region, respectively. The vibrational frequencies of the molecule are investigated. The molecular geometry and vibrational frequencies of 1,3-bis(4-piperidyl)propane (also named 4,4'-trimethylenedipiperidine (TMDP)) in the ground state have been calculated by using density functional methods (B3LYP and BLYP) with 6-311 G(d,p) and 6-31 G(d) as basis sets. The comparison of the observed fundamental vibrational frequencies of 1,3-bis(4-piperidyl)propane and calculated results by density functional B3LYP and BLYP methods indicates that B3LYP is superior to the scaled BLYP approach for molecular vibrational problems.

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Keywords: Infrared spectra; Raman spectra; Density functional theory; 1,3-bis(4-piperidyl)propane

1. Introduction

1,3-Bis(4-piperidyl)propane molecule is used for making the hyperbranched copolymers. Hyperbranched copolymers possess similar properties to those of dendrimers, such as high solubility, low viscosity, and lack of chain entanglements in the solid state [1–5]. Hyperbranched copoly (sulfone-amine) were prepared by direct polyaddition of 4,4'-trimethylenedipiperidine and 1-(2-aminoethyl)piperazine to divinyl sulfone [6]. TMDP is also used for preparation of polythioamides [7]. In that study they report the results of the novel preparation of polythioamides by the Willgerodt–Kindler reaction and the structure and the properties of the polymers.

Goforth et al. synthesized and structurally characterized five new inorganic–organic salts [8]. The single crystals of five new salts have been grown solvothermally

from BiI₃ and trimethylenedipiperidine hydrate (TMDP·H₂O).

The chemistry of main group metal halides has been widely explored for several decades owing to the interesting physical properties that have often been observed in such systems including luminescence, semiconductivity, and second-order non-linear optical activity [9–13].

Till now a detailed analysis of vibrational modes of TMDP using quantum chemical methods and any experimental methods has not been published.

Numerous works have been found in the literature dealing with the vibrational analysis of piperidine [14–17].

In our previous work [18], we reported the molecular structure and vibrational spectra of piperidine and 4-methylpiperidine by density functional theory and ab initio Hartree–Fock calculations.

In this work, we report DFT/B3LYP, BLYP calculation results on 1,3-bis(4-piperidyl)propane. The aim of this study is to give optimal molecular geometry, vibrational wavenumbers and modes of free TMDP. We have also reported the IR and Raman spectra of this molecule for the first time.

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2. Computational details

The molecular structures of 1,3-bis(4-piperidyl)propane (in vacuum) in the ground state are optimized by B3LYP and BLYP with the 6-311 G(d,p) and 6-31 G(d) basis sets. Density functionals for all studies reported in this paper have the following form

$$E_{XC} = (1 - a_0)E_X^{LSDA} + a_0E_X^{HF} + a_X\Delta E_X^{B88} + a_cE_C^{LYP} + (1 - a_c)E_C^{VWN}$$

where the energy terms are the Slater exchange, the Hartree–Fock exchange, Becke's exchange functional correction, and the gradient corrected correlation functional of Lee, Yang and Parr and the local correlation functional of Vosko et al. [19]. RB3LYP, RBLYP with 6-311 G(d,p) and 6-31 G(d) levels of theory with the optimized geometries have been used to calculate all parameters of 1,3-bis(4-piperidyl)propane molecule.

Two sets of vibrational frequencies for these species are calculated with these methods and then scaled by corresponding scaling factors [20]. Molecular geometry is not restricted and all the calculations are performed by using Gauss-view molecular visualization program and Gaussian 03 program package on the personal computer [21,22].

3. Experimental

The sample of 1,3-bis(4-piperidyl)propane is in solid form at room temperature. The infrared spectrum of the sample was recorded between 4000 and 400 cm^{-1} on a

Mattson 1000 FTIR spectrometer which was calibrated using polystyrene bands. The samples were prepared as a KBr disc. The FT-Raman spectrum of the sample was recorded between 3500 and 150 cm^{-1} region on a Bruker FRA 106/S FT-Raman instrument using 1064 nm excitation from an Nd:YAG laser. The detector is a liquid nitrogen cooled Ge detector.

4. Results and discussion

4.1. Geometrical structures

In the literature, we have found neither experimental data nor calculation for molecular geometric structure of 1,3-bis(4-piperidyl)propane. It is known that the six-membered cyclic molecule piperidine and 4-methylpiperidine ring exist in chair forms to can in principle as conformers with N–H being equatorial (E) and axial (A) [14–17,23–25]. Other conformations that differ from the chair (boat, envelope or twist boat) were not considered because of their high energy [14–17,23–25]. It is also known that 1,3-bis(4-pyridyl)propane is an interesting flexible bidentate ligand that can adopt four discrete conformations. These conformations are *anti-anti* (TT), *gauche-gauche* (GG), *anti-gauche* (TG) and *gauche-gauche'* (GG') depending on the different N-to-N distances or dihedral angles [26,27].

We propose that 1,3-bis(4-piperidyl)propane may have similar conformations as above, which we present in Fig. 1 and Table 1. As it can be seen from Table 1, the TT conformation of 1,3-bis(4-piperidyl)propane is the most stable,

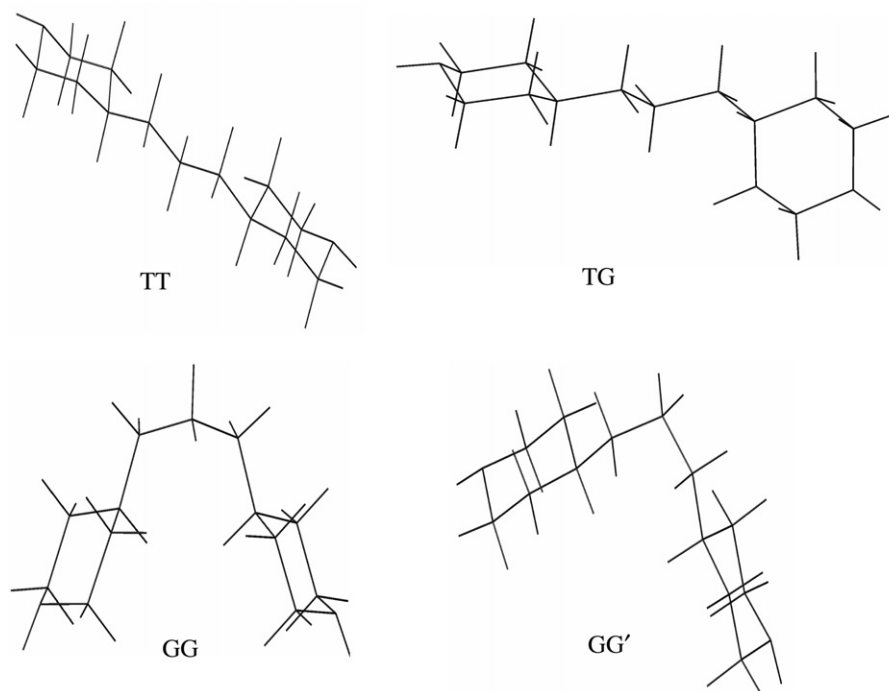


Fig. 1. Conformations of 1,3-bis(4-piperidyl)propane ligand.

Table 1

The selected molecular properties of conformations of the 1,3-bis(4-piperidyl) propane (with the B3LYP/6-311 g(d,p))

	TT	TG	GG	GG'
Symmetry	C_s	C_1	C_s	C_2
Optimized energy (a.u)	-620.714430419	-620.713095441	-620.708747685	-620.711928532
Energy diff. (kcal/mol)	0	0.83	1.43	1.56
E_{HOMO} (eV)	-6.019	-6.020	-6.024	-6.027
E_{LUMO} (eV)	1.074	1.018	0.798	0.899
$\Delta E_{HOMO-LUMO}$ (eV)	7.093	7.038	6.822	6.926
μ_{TOTAL} (Debye)	1.672	1.1008	1.4819	1.277
Dihedral angles ($^\circ$)				
$C_3-C_6-C_7-C_8$	-176.2358	63.3607	-80.0914	57.2938
$C_6-C_7-C_8-C_9$	176.2358	175.9766	80.0914	57.2938
N-N distances (Å)	10.539	10.154	7.87	9.13

among others. This is because of the lowest optimized energy.

The numbering of atoms in 1,3-bis(4-piperidyl)propane is given in Fig. 2. The calculated structural parameters are presented in Table 2. Since the crystal data of 1,3-bis(4-piperidyl) propane is not available, the optimized geometric parameters of the ligand are compared with those of piperidine [27,28] and X-ray data of the complexes $[(H_2TMDP)_2(Bi_2I_9)]$ [8].

Generally, the C-N-C bond angles are slightly larger than the C-C-C or N-C-C bond angles [28]. Gundersen and Rankin reported the C-N-C (110.7°), C-C-C (109.6°) and N-C-C (110.5°) bond angles by using electron diffraction technique [27]. We calculate C-N-C (111.84°), C-C-C (111.55° , 111.75°) and N-C-C (109.56° , 109.77°)

bond angles, by B3LYP calculation, in Table 2. The C-N bond lengths are predicted to be slightly shorter than the C-C bond lengths. Gundersen and Rankin reported N-C (1.469 Å) and C-C (1.530 Å) by using electron diffraction technique. We calculate N-C (1.462 and 1.463 Å) and C-C (1.530 and 1.540 Å) bond lengths by B3LYP/6-311 G(d,p) calculation. We have noticed that the DFT calculations are consistent with the results of X-ray and electron diffraction data.

4.2. Assignment of fundamentals

In TT conformation of 1,3-bis(4-piperidyl)propane shows C_s symmetry. 1,3-Bis(4-piperidyl)propane molecule has 41 atoms. The 117 normal vibrations are distributed

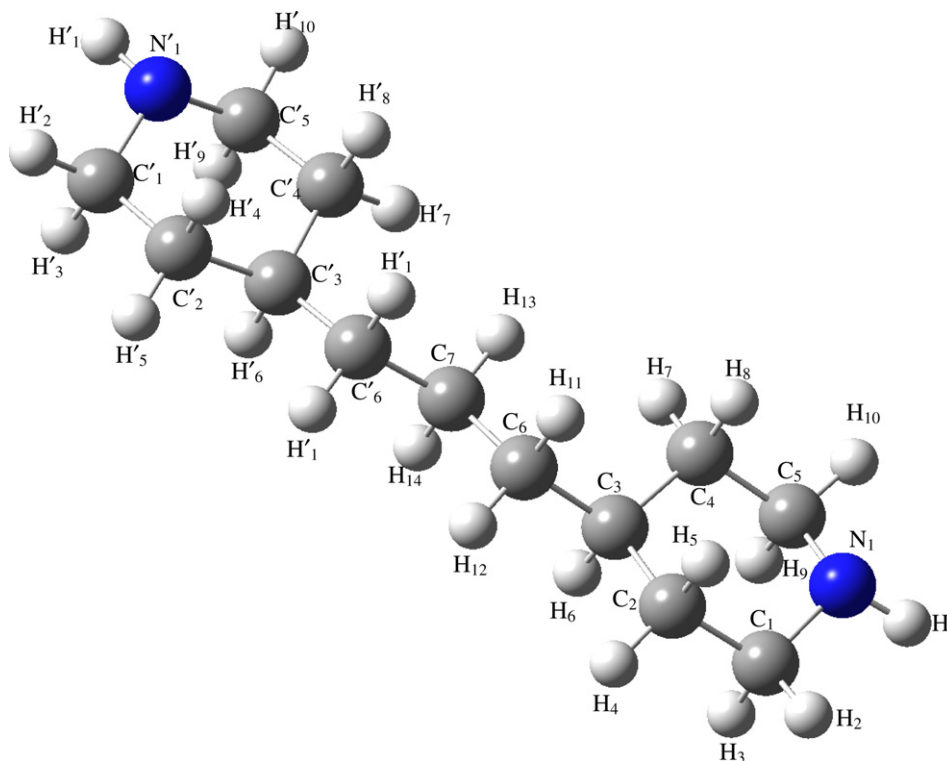


Fig. 2. 1,3-Bis(4-piperidyl)propane structure and atoms numbering (TT conformation).

Table 2
Bond lengths and bond angles for 1,3-bis(4-piperidyl)propane (in TT conformation)

Parameters	E.D. [28]	X-ray [8]	B3LYP 6-311 G(d,p)	B3LYP 6-31 G(d)	BLYP 6-311 G(d,p)	B3LYP 6-31 G(d)
<i>Bond lengths (Å)</i>						
C ₁ –C ₂	1.530	1.526	1.530	1.532	1.542	1.543
C ₁ –N ₁	1.469	1.482	1.463	1.463	1.477	1.478
C ₁ –H ₂	1.098	–	1.093	1.096	1.100	1.104
C ₁ –H ₃	1.098	–	1.107	1.109	1.114	1.118
C ₂ –C ₃	1.530	1.526	1.540	1.541	1.552	1.553
C ₂ –H ₄	1.098	–	1.095	1.098	1.102	1.105
C ₂ –H ₅	1.098	–	1.096	1.098	1.102	1.105
C ₃ –C ₆	–	1.525	1.537	1.539	1.550	1.551
C ₃ –C ₄	1.530	1.509	1.540	1.541	1.553	1.554
C ₃ –H ₆	–	–	1.100	1.103	1.107	1.110
N ₁ –C ₅	1.469	1.502	1.462	1.463	1.477	1.478
N ₁ –H ₁	1.015	–	1.013	1.017	1.022	1.027
C ₆ –C ₇	–	1.534	1.534	1.535	1.546	1.547
C ₄ –H ₇	1.098	–	1.094	1.096	1.100	1.104
C ₄ –H ₈	1.098	–	1.096	1.098	1.103	1.106
C ₄ –C ₅	1.530	1.495	1.531	1.532	1.542	1.544
C ₅ –H ₉	1.098	–	1.107	1.109	1.114	1.118
C ₅ –H ₁₀	1.098	–	1.093	1.096	1.100	1.104
<i>Bond angles (°)</i>						
C ₂ –C ₁ –N ₁	110.5	109.4	109.5	109.5	109.4	109.4
H ₂ –C ₁ –H ₃	110.0	–	107.2	107.1	107.3	107.1
C ₁ –C ₂ –C ₃	109.6	111.5	111.7	111.6	111.7	111.6
H ₄ –C ₂ –H ₅	110.0	–	107.3	107.3	107.3	107.3
C ₂ –C ₃ –C ₆	–	110.4	111.2	111.2	111.3	111.3
C ₂ –C ₃ –C ₄	111.1	108.9	109.4	109.3	109.5	109.3
C ₆ –C ₃ –C ₄	–	114.8	113.2	113.2	113.2	113.3
C ₁ –N ₁ –C ₅	–	111.9	111.8	111.6	111.5	111.3
C ₁ –N ₁ –H ₁	108.4	–	110.1	109.7	109.6	109.2
C ₅ –N ₁ –H ₁	108.4	–	110.1	109.7	109.7	109.2
C ₃ –C ₆ –C ₇	–	117.5	115.2	115.1	115.3	115.2
C ₆ –C ₇ –C ₆	–	111.9	112.8	112.7	112.9	112.9
C ₃ –C ₄ –C ₅	109.6	110.6	111.5	111.4	111.5	111.4
H ₇ –C ₄ –H ₈	110.0	–	107.4	107.3	107.4	107.3
N ₁ –C ₅ –C ₄	110.5	110.2	109.7	109.7	109.6	109.6
H ₉ –C ₅ –H ₁₀	110.0	–	107.2	107.1	107.2	107.1

as 60A' (in-plane) + 57A'' (out-of-plane). All the vibrations are active in both IR and Raman. The calculated infrared and Raman frequencies together with experimental data of the ligand are presented in Table 3. The IR and Raman spectra of TMDP are given in Figs. 3 and 4. The total energy distribution (TED) was calculated by using the Parallel Quantum Solutions program [29] and fundamental vibrational modes were characterized by their TED. The assignment of the calculated wavenumbers is aided by the animation option of GaussView graphical interface for Gaussian programs, which gives a visual presentation of the shape of the vibrational modes.

To make comparison with experimental frequencies, we present rms deviation based on the calculation at the bottom of Table 3 [30]. Among our result, the best reliable vibrational frequencies RMS values are 28.98 and 27.10 for 6-311 G(d,p) basis set and 24.02 and 23.43 for 6-31

G(d) basis set (respectively, B3LYP and BLYP methods). The calculated 6-31G(d) values are more reliable than 6-311G(d,p) basis set. In the 1,3-bis(4-piperidyl) propane, the B3LYP methods lead to vibrational frequencies which are much closer to experimental data for both 6-311 G(d,p) and 6-31G(d) basis set.

The raw methylene sensitive modes characterized at B3LYP/6-311 G(d,p) level in TMDP molecule are plotted in Fig. 5. The vibrational motions are represented the vector corresponding to the atomic displacement for each atom and computed wavenumber. Displacements are indicated by dark arrow. The raw methylene sensitive modes appear characterized by direction of the displacement vector.

Heterocyclic compounds containing a N–H group exhibit N–H stretching absorption in the region from 3500 to 3200 cm⁻¹. The stretching vibration of the N–H group observed at 3242 cm⁻¹. These vibrations calculated at 3406 cm⁻¹ for B3LYP/6-311 G(d,p) method and 3366 cm⁻¹ for B3LYP/6-31 G(d) method.

The infrared bands observed at 2980–2900 cm⁻¹ region are assigned CH stretching for piperidine [18,31]. In the 1,3-bis(4-piperidyl)propane, the stretching of CH modes experimentally observed at 2799–2930 cm⁻¹ region. These modes theoretically calculated at 2790–2968 cm⁻¹ region for B3LYP/6-311 G(d,p) calculation. The stretching of CN modes are observed at 1180–1100 cm⁻¹ region for piperidine [18,31]. In the 1,3-bis(4-piperidyl)propane, these modes calculated in the same region for B3LYP/6-311 G(d,p) calculation. Piperidine ring CC stretching modes shown at 1350–760 cm⁻¹ region [18,31]. In the 1,3-bis(4-piperidyl)propane, the stretching vibrations of the CC calculated at 1067–1088 cm⁻¹ region for B3LYP/6-311 G(d,p).

The C–H stretching absorption of methylene group centered around 2925 cm⁻¹. The infrared band observed at 2886 cm⁻¹ is assigned to symmetric CH₂ for methylene group. This band is calculated at 2891 and 2904 cm⁻¹ for 6-311 G(d,p) (respectively, B3LYP and BLYP). The asymmetric stretching mode of methylene group is observed at 2919 cm⁻¹. This band calculated at 2923 and 2934 cm⁻¹ for 6-311 G(d,p) (respectively, B3LYP and BLYP calculations). Fig. 4 shows the normal coordinate displacements for selected modes.

Several calculated thermodynamic parameters are presented in Table 4. Total energies are found to decrease with the increase of the basis set dimension. The changes in total entropy of 1,3-bis(4-piperidyl)propane at room temperature at different basis set are only marginal.

5. Conclusion

Comparison of the observed fundamental vibrational frequencies 1,3-bis(4-piperidyl) propane and the results calculated by density functional B3LYP and BLYP indicate that B3LYP is superior to the scaled BLYP approach for molecular vibrational problems.

Table 3

Comparison of the observed and calculated vibrational spectra of free 1,3-bis(4-piperidyl)propane (in TT conformation)

		B3LYP/6-311 G(d,p)			B3LYP/6-31 G(d)			BLYP/6-311	BLYP/6-31	Exp.	Exp.	TED ^c (%)	Approx. mode descriptions
		Freq. ^a	IR	Ra	Freq. ^b	IR	Ra	G(d,p) Freq. ^c	G(d) Freq. ^d	IR	RA		
ν_1	A''	13	0.010	0.050	14	0.014	0.044	16	16			$\Gamma_{\text{CCCH}}(31) + \Gamma_{\text{CCCC}}(30)$	Ring def.
ν_2	A'	30	0.007	0.040	31	0.009	0.032	29	31			$\Gamma_{\text{CCCC}}(53) + \Gamma_{\text{CCCH}}(42)$	Ring def.
ν_3	A'	47	0.030	0.055	48	0.028	0.033	47	48			$\delta_{\text{CCC}}(50)$ (Me)	CCC bend (Me)
ν_4	A''	84	0.619	0.052	84	0.639	0.086	84	85			$\Gamma_{\text{CCCC}}(34)$	Ring def.
ν_5	A'	100	0.014	0.087	101	0.013	0.061	99	102			$\Gamma_{\text{CCCC}}(28) + \Gamma_{\text{CCCH}}(22)$	Ring def.
ν_6	A''	130	0.400	0.063	132	0.358	0.049	127	131			$\Gamma_{\text{CCCC}}(31) + \Gamma_{\text{CCCH}}(26) + \delta_{\text{CCC}}(19)$	Ring def.
ν_7	A'	156	0.321	0.267	157	0.342	0.297	157	158			$\Gamma_{\text{CCCC}}(18) + \Gamma_{\text{CCCH}}(13)$	Ring def.
ν_8	A'	184	0.046	3.473	184	0.047	3.110	183	184			$\nu_{\text{CC}}(38) + \delta_{\text{CCC}}(15)$ (M)	CC str. (Me)
ν_9	A''	208	0.479	0.004	207	0.424	0.000	210	211		199 vw	$\delta_{\text{CCC}}(21)$ (M) + $\Gamma_{\text{CCCC}}(11)$	CCC bend (Me)
ν_{10}	A'	238	0.458	0.088	240	0.578	0.105	239	242			$\Gamma_{\text{CCCN}}(18)$	Ring def.
ν_{11}	A''	239	0.220	0.152	240	0.231	0.113	239	242		263 vw	$\Gamma_{\text{CCCN}}(19)$	Ring def.
ν_{12}	A'	302	0.080	0.407	301	0.091	0.433	302	302			$\delta_{\text{CCC}}(40)$	CCC bend
ν_{13}	A''	333	4.878	0.121	333	4.905	0.220	335	337			$\Gamma_{\text{CNCH}}(21) + \Gamma_{\text{CCNC}}(17)$	Ring def.
ν_{14}	A'	341	1.055	0.229	342	0.921	0.225	344	346			$\Gamma_{\text{CHCC}}(18) + \Gamma_{\text{CHCH}}(11)$	Ring def.
ν_{15}	A''	372	3.159	0.449	372	3.258	0.418	373	374			$\delta_{\text{CCC}}(12)$	CCC bend
ν_{16}	A'	420	2.840	3.302	420	2.743	2.302	422	423			Combination	Combination
ν_{17}	A''	428	4.269	0.227	428	4.221	0.243	429	431	428 vw		$\Gamma_{\text{CCCH}}(25)$	Ring def.
ν_{18}	A''	447	0.557	0.849	445	0.521	0.881	449	449	443 vw	444 m	$\delta_{\text{CCN}}(17) + \delta_{\text{CCC}}(13)$	CCC, CCN bend
ν_{19}	A'	450	1.520	2.252	448	1.650	2.181	451	451			$\delta_{\text{CCN}}(19) + \delta_{\text{CCC}}(13)$	CCC, CCN bend
ν_{20}	A''	477	1.760	1.287	476	1.473	1.223	476	477	479 w	463 m	$\delta_{\text{CCC}}(27) + \nu_{\text{CC}}(11)$	CCC bend
ν_{21}	A'	480	13.78	0.370	480	13.16	0.554	482	484	500 w	492 w	$\Gamma_{\text{CCCH}}(19)$	Ring def.
ν_{22}	A''	545	29.32	0.755	546	27.08	1.184	548	550	563 vw		$\Gamma_{\text{CCNH}}(7) + \Gamma_{\text{CCNH}}(8) + \delta_{\text{CCN}}(6) + \delta_{\text{CCC}}(6)$	Ring def.
ν_{23}	A'	583	19.45	1.828	582	18.17	1.426	585	586	590 m		$\delta_{\text{CCC}}(8)$	CCC bend
ν_{24}	A'	712	5.564	0.867	714	4.557	0.878	714	720	725 w		$\Gamma_{\text{HCCH}}(57)$	Ring torsion
ν_{25}	A''	750	12.53	1.180	753	3.162	1.054	742	751			$\nu_{\text{CC}}(40)$	CC str.
ν_{26}	A'	757	89.20	6.608	766	77.06	11.57	748	760			$\nu_{\text{CC}}(36) + \nu_{\text{CN}}(17)$	Ring str.
ν_{27}	A''	761	47.25	2.983	771	58.44	4.574	757	769			$\Gamma_{\text{HCNH}}(13) + \nu_{\text{CN}}(12)$	Ring def.
ν_{28}	A'	789	6.826	2.933	793	8.657	1.369	787	795		784 vs	Combination	Combination
ν_{29}	A''	793	0.218	0.194	797	0.366	0.437	792	800	798 vw		Combination	Combination
ν_{30}	A'	799	18.57	13.73	805	34.09	11.13	796	805	815 s	805 m	$\Gamma_{\text{HNCH}}(21)$	Ring breathing
ν_{31}	A''	836	3.856	0.172	841	7.504	0.473	836	845	826 vw	824 vw	$\nu_{\text{CC}}(16)$	CC str.
ν_{32}	A'	863	0.045	7.936	867	0.717	8.086	857	866	852 m	851 w	$\nu_{\text{CN}}(39) + \nu_{\text{CC}}(27)$	Ring str.
ν_{33}	A''	864	0.890	0.776	868	0.079	1.170	858	867			$\nu_{\text{CN}}(35) + \nu_{\text{CC}}(17)$	Ring str.
ν_{34}	A'	880	0.688	2.547	882	0.307	3.289	872	879	871 m	872 w	$\nu_{\text{CC}}(46) + \nu_{\text{CN}}(12)$	Ring str.
ν_{35}	A''	890	0.260	0.018	891	0.286	0.022	885	890	904 w	917 w	$\nu_{\text{CC}}(39)$	CC str.
ν_{36}	A''	946	3.040	0.067	950	2.348	0.042	939	947			$\nu_{\text{CC}}(40)$	CC str.
ν_{37}	A'	958	2.063	0.703	963	2.189	0.902	958	966	961 m		Combination	Combination
ν_{38}	A''	962	0.332	0.495	967	0.488	1.116	962	971			$\nu_{\text{CC}}(8)$	CC str.
ν_{39}	A'	968	4.327	1.105	971	3.647	1.424	963	972			$\nu_{\text{CC}}(38)$	CC str.
ν_{40}	A'	973	0.192	1.622	976	0.211	2.145	974	981	972 vw		$\nu_{\text{CC}}(10) + \delta_{\text{CCH}}(7)$ (Me)	CC str., CH ₂ rock (Me)
ν_{41}	A'	999	2.088	2.478	1002	2.031	2.481	989	996	998 w	994 w	$\nu_{\text{CC}}(42)$ (Me)	CC str. (Me.)
ν_{42}	A''	1016	1.689	0.017	1018	1.276	0.034	1005	1013	1004 vw		$\nu_{\text{CC}}(52)$ (Me)	CC str. (Me.)

(continued on next page)

Table 3 (continued)

		B3LYP/6-311 G(d,p)			B3LYP/6-31 G(d)			BLYP/6-311	BLYP/6-31	Exp. IR	Exp. RA	TED ^c (%)	Approx. mode descriptions
		Freq. ^a	IR	Ra	Freq. ^b	IR	Ra	G(d,p) Freq. ^c	G(d) Freq. ^d				
ν_{43}	A'	1024	2.526	12.08	1026	3.268	14.42	1020	1027	1040 w	1048 w	$\nu_{CC}(31) + \nu_{CN}(15)$	CC str.
ν_{44}	A''	1024	0.345	14.82	1027	0.916	19.57	1020	1028	1059 vw	1063 s	$\nu_{CC}(23) + \nu_{CC}(14)$ (Me)	CC str. (Pip., Me)
ν_{45}	A''	1032	0.029	3.014	1033	0.021	3.780	1027	1034			$\nu_{CC}(7)$	CC str.
ν_{46}	A''	1067	1.989	0.687	1070	1.913	0.864	1055	1062			$\nu_{CC}(46)$	CC str.
ν_{47}	A'	1070	12.32	0.795	1074	13.00	0.739	1061	1071			$\nu_{CC}(26)$	CC str. (Pip., Me)
ν_{48}	A''	1070	1.416	2.582	1075	2.767	2.519	1065	1076			$\nu_{CC}(14)$	CC str.
ν_{49}	A'	1088	8.581	3.967	1092	7.993	3.974	1068	1078	1080 w	1081 w	$\nu_{CC}(26)$	CC str.
ν_{50}	A''	1119	6.043	2.677	1125	6.824	2.895	1095	1106	1103 w	1102 w	$\nu_{CN}(52)$	CN str.
ν_{51}	A'	1126	28.99	4.363	1130	28.87	4.122	1109	1118	1117 w		$\nu_{CN}(46)$	CN str.
ν_{52}	A''	1134	6.493	5.826	1138	1.999	1.904	1130	1142	1132 m		$\nu_{CN}(12)$	CN str.
ν_{53}	A'	1135	2.100	1.608	1139	2.071	10.70	1135	1142			Combination	Combination
ν_{54}	A'	1137	0.531	8.304	1141	6.285	4.656	1137	1134	1140 s	1146 w	Combination	Combination
ν_{55}	A''	1155	0.569	1.790	1160	0.991	2.644	1154	1162	1159 m	1156 s	$\delta_{CCH}(8)$	CH ₂ twist
ν_{56}	A''	1180	0.001	0.339	1184	0.693	0.496	1181	1189	1180 vw		$\delta_{CCH}(6) + \delta_{NCH}(6)$	CH ₂ twist
ν_{57}	A'	1192	1.059	6.165	1196	1.000	9.124	1191	1199	1190 vw		$\delta_{CCH}(13)$	CH ₂ twist
ν_{58}	A'	1223	6.433	0.377	1229	7.825	0.262	1225	1236	1213 w	1212 w	$\delta_{CCH}(11)$ (M)	CH ₂ twist (Me)
ν_{59}	A''	1229	0.141	4.576	1234	0.720	7.410	1232	1241	1235 vw		$\delta_{CCH}(21) + \Gamma_{HCCH}(9)$ (Me)	CH ₂ wagg (Me)
ν_{60}	A''	1251	0.662	3.914	1257	0.619	5.018	1252	1263			$\delta_{CCH}(17)$	CH ₂ twist
ν_{61}	A'	1258	1.301	7.690	1264	1.202	12.21	1258	1269			$\delta_{CCH}(15)$	CH ₂ twist
ν_{62}	A''	1263	3.514	25.18	1269	3.322	39.51	1262	1273			$\delta_{NCH}(14)$	NCH bend
ν_{63}	A'	1272	3.399	0.585	1278	2.987	0.543	1273	1285	1272 m	1273 vs	$\delta_{CCH}(15)$ (Me)	CH ₂ twist (Me)
ν_{64}	A'	1279	1.453	11.26	1285	2.056	17.49	1281	1292	1289 w	1287 vw	$\delta_{CCH}(12)$	CH ₂ twist
ν_{65}	A''	1282	1.976	12.02	1288	1.709	21.53	1284	1295			$\delta_{CCH}(26)$	CH ₂ twist
ν_{66}	A''	1296	0.193	3.405	1303	0.368	5.198	1298	1311			$\delta_{CCH}(16)$	CH ₂ twist
ν_{67}	A'	1300	1.962	0.210	1307	0.802	0.951	1300	1313			$\delta_{CCH}(15)$	CH ₂ twist
ν_{68}	A''	1302	1.550	2.604	1312	0.273	3.341	1301	1315			$\delta_{CCH}(14)$ (Me)	CCH bend (Me)
ν_{69}	A'	1306	48.34	3.561	1315	58.98	5.274	1301	1316			$\delta_{CCH}(17)$	CH ₂ wagg
ν_{70}	A''	1308	5.032	0.513	1317	7.718	1.259	1307	1321	1321 s	1314 w	$\delta_{CCH}(17)$	CH ₂ wagg
ν_{71}	A'	1328	0.534	1.357	1339	0.706	1.199	1328	1345			$\delta_{CCH}(15)$ (Me) + $\delta_{CCH}(14)$ + $\Gamma_{HCCH}(6)$	CCH bend (Pip., Me)
ν_{72}	A''	1335	0.008	1.488	1347	0.199	0.799	1331	1349			$\delta_{CCH}(15) + \Gamma_{HCCH}(7) + \nu_{CC}(6)$	CCH bend
ν_{73}	A'	1345	5.025	6.051	1357	5.629	7.567	1340	1359			$\delta_{CCH}(15) + \Gamma_{HCCH}(12) + \nu_{CC}(6)$	CH ₂ wagg
ν_{74}	A''	1348	4.714	2.905	1361	2.108	5.119	1341	1361			$\Gamma_{HCCH}(9)$	CH ₂ wagg
ν_{75}	A'	1350	0.214	4.948	1364	0.085	4.034	1343	1362			$\Gamma_{HCCH}(18)$	CH ₂ wagg
ν_{76}	A''	1356	0.594	0.170	1370	0.552	1.043	1348	1368	1369 m	1356 m	$\Gamma_{HCCH}(17) + \delta_{CCH}(11)$	CH ₂ wagg
ν_{77}	A''	1379	10.42	1.998	1393	24.18	5.575	1376	1397			$\delta_{CCH}(14) + \Gamma_{CNCH}(13)$	CH ₂ wagg
ν_{78}	A'	1379	1.149	1.238	1393	2.250	1.747	1376	1397	1415 s		$\delta_{CCH}(14) + \Gamma_{CNCH}(13)$	CH ₂ wagg
ν_{79}	A'	1423	4.765	3.808	1439	4.861	0.196	1429	1444			$\delta_{HCH}(24)$	CH ₂ scis
ν_{80}	A''	1423	0.966	2.104	1439	0.658	0.081	1429	1444			$\delta_{HCH}(25)$	CH ₂ scis
ν_{81}	A'	1433	1.919	0.150	1446	0.273	14.53	1435	1456			$\delta_{HCH}(19)$ (Me)	CH ₂ scis (Me)
ν_{82}	A''	1435	4.598	0.921	1447	0.000	9.448	1435	1457			$\delta_{HCH}(20) + \Gamma_{HCCH}(19)$ (Me)	CH ₂ scis (Pip., Me)

ν_{83}	A''	1437	0.000	7.772	1453	0.718	2.983	1440	1465			$\delta_{\text{HCH}}(19) + \delta_{\text{HCH}}(6)$ (Me)	CH ₂ scis (Pip., Me)
ν_{84}	A'	1437	7.887	6.697	1455	0.730	30.59	1442	1466			$\delta_{\text{HCH}}(17) + \delta_{\text{HCH}}(7)$ (Me)	CH ₂ scis (Pip., Me)
ν_{85}	A'	1439	5.001	41.25	1458	7.474	21.39	1445	1469	1435 s	1439 vs	$\delta_{\text{CNH}}(22) + \delta_{\text{HCH}}(15)$	CH ₂ scis
ν_{86}	A''	1441	3.618	0.270	1460	3.285	0.518	1448	1472			$\delta_{\text{CNH}}(20) + \delta_{\text{HCH}}(7)$	CH ₂ scis
ν_{87}	A'	1449	0.372	9.916	1468	1.802	14.80	1452	1476		1451 vs	$\Gamma_{\text{HCC}}(29) + \delta_{\text{HCH}}(27)$ (Me)	CH ₂ scis (Me)
ν_{88}	A''	1449	0.059	4.775	1468	0.325	7.092	1452	1476			$\Gamma_{\text{HNC}}(21) + \delta_{\text{CNH}}(21) + \delta_{\text{HCH}}(12)$	CH ₂ scis
ν_{89}	A'	1458	9.490	1.273	1476	4.690	0.496	1462	1487			$\Gamma_{\text{HNC}}(21) + \delta_{\text{CNH}}(21) + \delta_{\text{HCH}}(14)$	CH ₂ scis
ν_{90}	A''	1459	2.852	8.763	1478	1.593	11.83	1462	1488	1461 vw	1460 vw	$\delta_{\text{HCH}}(28)$	CH ₂ scis
ν_{91}	A'	1460	0.552	4.832	1479	0.764	10.13	1467	1491			$\delta_{\text{HCH}}(28)$	CH ₂ scis
ν_{92}	A''	2790	8.394	6.390	2794	7.632	4.425	2787	2795			$\nu_{\text{CH}}(99)$	CH str.
ν_{93}	A'	2790	53.36	37.71	2794	48.80	25.91	2787	2795	2743 m	2743 s	$\nu_{\text{CH}}(99)$	CH str.
ν_{94}	A''	2796	4.544	9.572	2801	3.659	6.525	2793	2803			$\nu_{\text{CH}}(98)$	CH str.
ν_{95}	A'	2796	301.5	341.1	2801	272.7	246.6	2794	2803	2814 w	2816 w	$\nu_{\text{CH}}(97)$	CH str.
ν_{96}	A''	2869	0.008	0.525	2868	0.003	0.384	2879	2881	2839 s	2839 vs	$\nu_{\text{CH}}(95)$	CH str.
ν_{97}	A'	2869	37.06	189.6	2868	43.56	144.3	2879	2882			$\nu_{\text{CH}}(93)$	CH str.
ν_{98}	A''	2891	0.044	1.087	2891	0.027	0.896	2904	2908		2886 w	$\nu_{\text{CH}_2}(96)$ (Me)	Symm. CH ₂ str. (Me)
ν_{99}	A'	2893	8.913	143.5	2894	14.05	113.6	2906	2911			$\nu_{\text{CH}_2}(90)$ (Me)	Symm. CH ₂ str. (Me)
ν_{100}	A'	2903	46.19	41.52	2903	47.81	35.58	2915	2920			$\nu_{\text{CH}_2}(88)$ (Me)	Symm. CH ₂ str. (Me)
ν_{101}	A''	2913	3.571	10.12	2916	2.286	9.822	2926	2934			$\nu_{\text{CH}_2}(66) + \nu_{\text{CH}}(22)$	Symm. CH ₂ str.
ν_{102}	A'	2913	39.53	41.25	2916	43.41	50.47	2926	2934			$\nu_{\text{CH}_2}(92)$	Symm. CH ₂ str.
ν_{103}	A''	2917	23.25	1.925	2921	25.26	3.131	2930	2938			$\nu_{\text{CH}_2}(81) + \nu_{\text{CH}}(13)$ (Me)	Symm. CH ₂ str.
ν_{104}	A'	2917	66.01	245.6	2921	51.19	180.2	2931	2939			$\nu_{\text{CH}_2}(87)$	Symm. CH ₂ str.
ν_{105}	A'	2922	34.39	48.49	2924	25.48	51.59	2934	2940			$\nu_{\text{CH}_2}(79)$ (Me)	Symm. CH ₂ str. (Me)
ν_{106}	A''	2923	0.435	2.912	2925	1.299	3.525	2934	2941	2919 vs	2915 m	$\nu_{\text{CH}_2}(92)$ (Me)	Asymm. CH ₂ str. (Me)
ν_{107}	A'	2951	94.27	62.95	2954	116.0	51.65	2962	2970			$\nu_{\text{CH}_2}(75)$ (Me)	Asymm. CH ₂ str. (Me)
ν_{108}	A''	2952	33.71	81.29	2954	36.65	90.36	2962	2970	2934 sh	2938 m	$\nu_{\text{CH}_2}(90)$	Asymm. CH ₂ str.
ν_{109}	A''	2953	44.09	224.9	2956	26.12	6.344	2964	2972			$\nu_{\text{CH}_2}(83) + \nu_{\text{CH}}(7)$	Asymm. CH ₂ str.
ν_{110}	A'	2953	9.071	17.30	2956	24.26	346.3	2964	2972			$\nu_{\text{CH}}(94)$	CH str.
ν_{111}	A'	2954	14.93	349.0	2957	4.26	147.0	2965	2973			$\nu_{\text{CH}}(88)$	CH str.
ν_{112}	A''	2955	27.12	45.15	2958	7.293	34.21	2966	2975			$\nu_{\text{CH}}(96)$	CH str.
ν_{113}	A'	2959	180.6	51.00	2962	197.4	46.45	2970	2979			$\nu_{\text{CH}_2}(66) + \nu_{\text{CH}_2}(19)$ (Me)	Asymm. CH ₂ str. (Pip., Me)
ν_{114}	A''	2962	30.31	35.82	2966	32.51	33.36	2973	2982			$\nu_{\text{CH}_2}(92)$	Asymm. CH ₂ str.
ν_{115}	A'	2968	65.66	89.54	2970	59.35	81.48	2978	2986			$\nu_{\text{CH}_2}(62)$ (Me) + $\nu_{\text{CH}}(29)$	Asymm. CH ₂ str. (Pip., M)
ν_{116}	A''	3406	0.503	62.19	3360	5.423	65.76	3389	3343			$\nu_{\text{NH}}(100)$	NH str.
ν_{117}	A'	3406	0.151	304.7	3360	0.938	301.1	3389	3343	3242 w	3242 w	$\nu_{\text{NH}}(100)$	NH str.
σ		28.98		24.02			27.10		23.43				

Pip., piperidine; M, methylene, scis, scissoring; rock, rocking; twist, twisting; wagg, wagging; asymm., asymmetric; symm., symmetric; str., stretching; tors, torsion; bend, bending; def., deformation; vs, very strong; s, strong; m, medium; w, weak; vw, very weak, IR: IR intensities (KM/mol), Ra, Raman scattering activities (A^{*4}/AMU).

^a Scaling factor: 0.9668.

^b Scaling factor: 0.9603.

^c Scaling factor: 0.9961.

^d Scaling factor: 0.9919.

^e Total energy distribution calculated B3LYP/6-311 G(d,p) level.

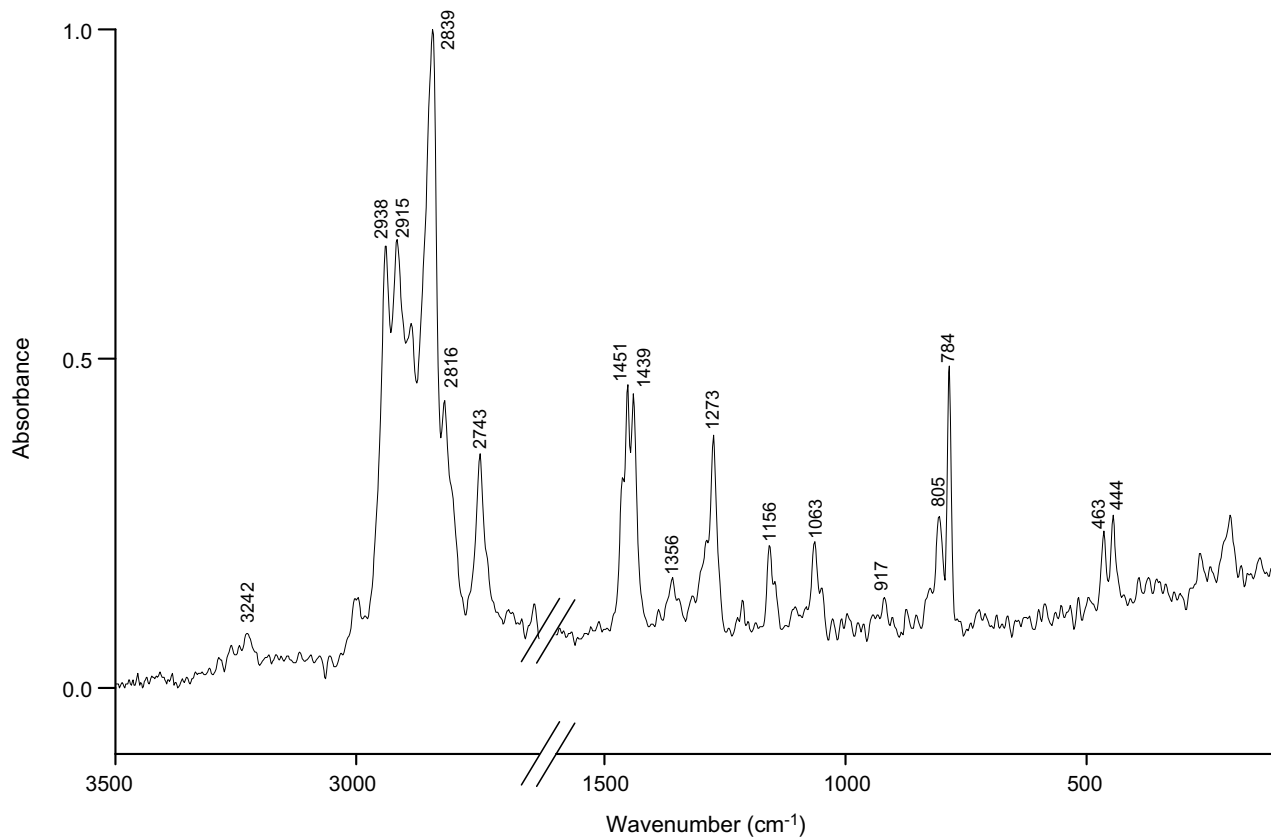


Fig. 3. Raman spectrum of 1,3-bis(4-piperidyl)propane molecule.

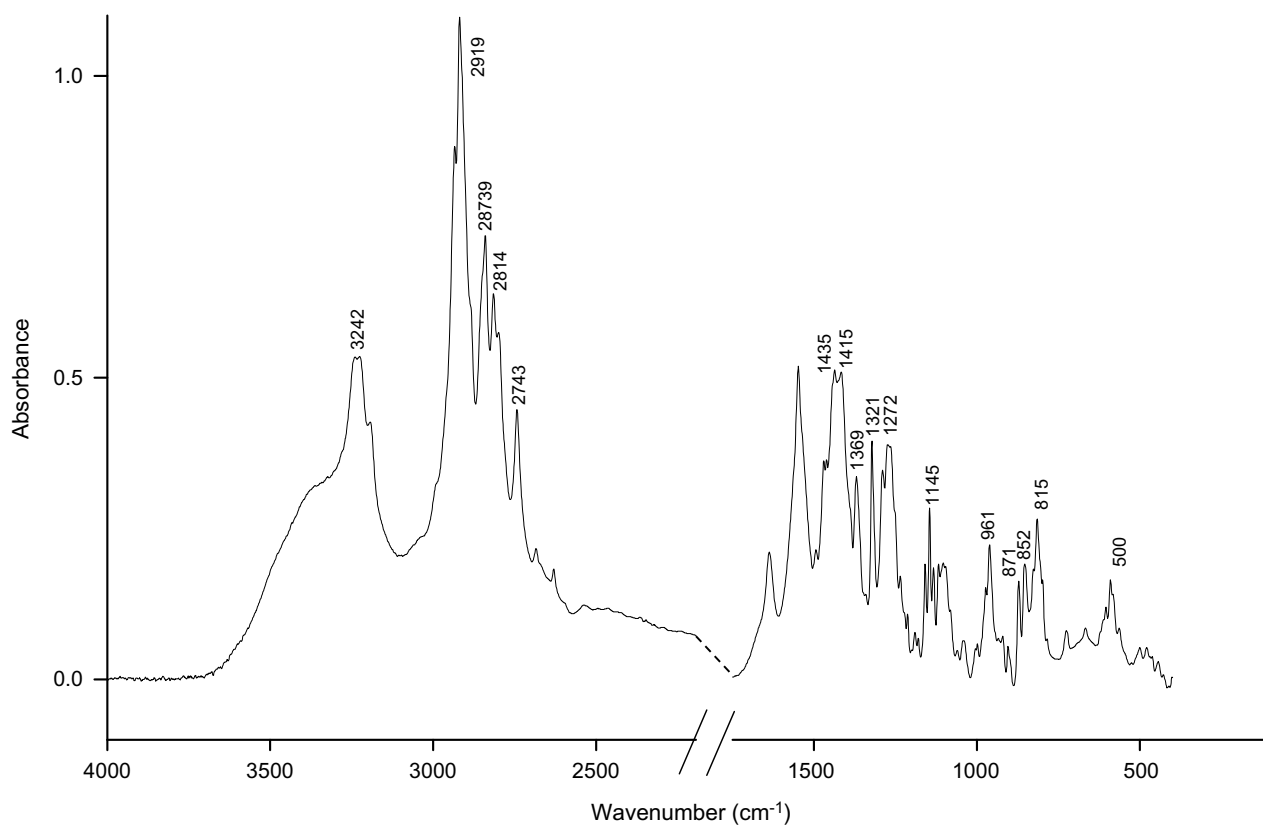


Fig. 4. The infrared spectrum of 1,3-bis(4-piperidyl)propane molecule.

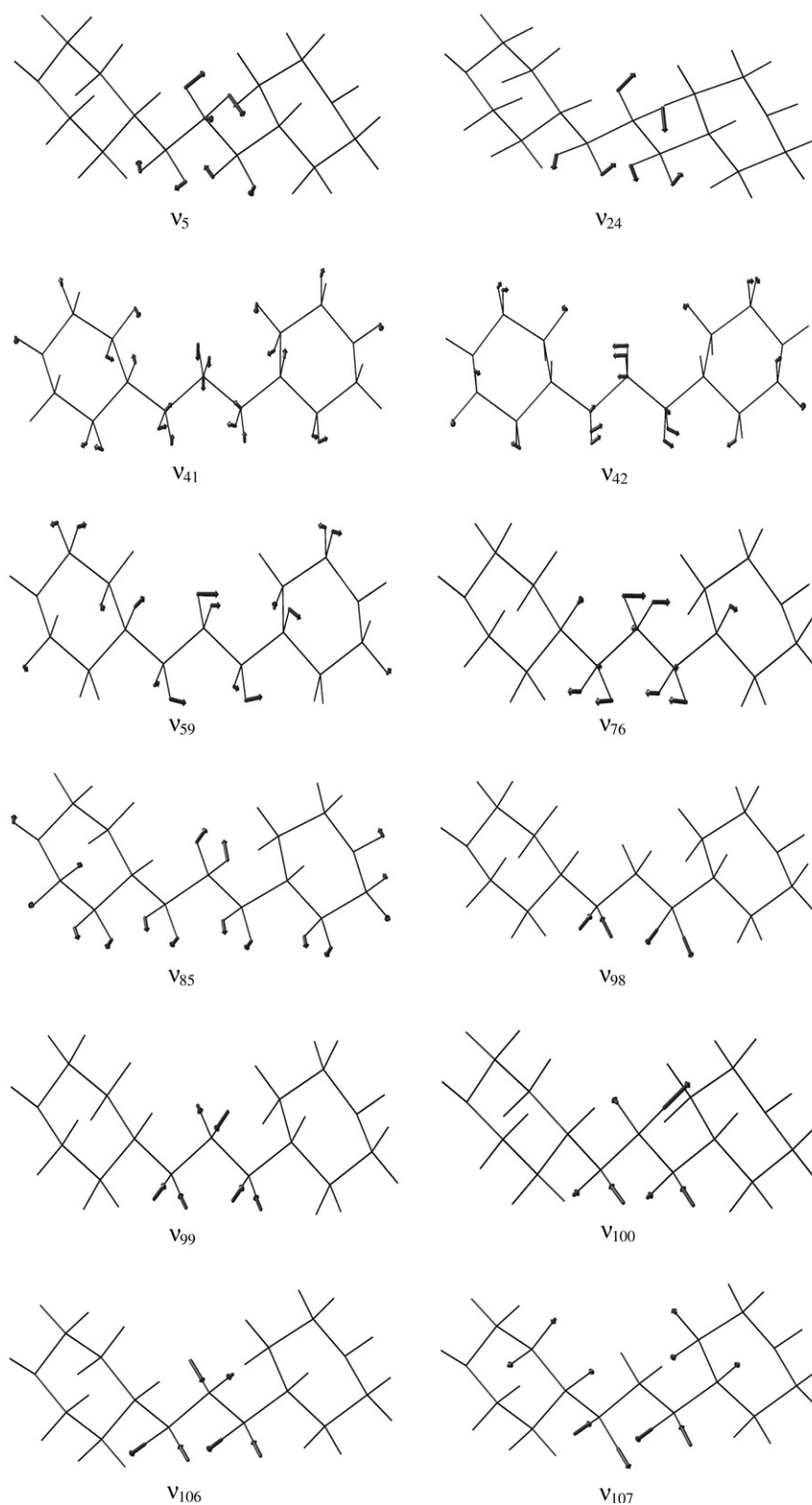


Fig. 5. Some raw methylene vibrations of TMDP (B3LYP/6-311 G(d,p) method).

On account of the fact that 1,3-bis(4-piperidyl) propane has been examined, reassignments of some vibrational modes are proposed. The good agreement between the frequencies calculated by B3LYP/6-31

G(d), and experimental results indicates that the density functional methods are reliable and provides valuable information for understanding the vibrational spectra of molecule.

Table 4

Theoretically calculated optimized energy (a.u.), dipole moment (D), zero-point vibrational energies (kcal/mol), rotational constants (GHz), entropies (cal/mol K) for 1,3-bis(4-piperidyl)propane (in TT conformation)

	B3LYP		BLYP		HF	
	6-311 G(d,p)	6-31 G(d)	6-311 G(d,p)	6-31 G(d)	6-311 G(d,p)	6-31 G(d)
Optimized energy (a.u)	−620.714430419	−620.546968481	−620.344420349	−620.162145120	−616.469966975	−616.320263037
Dipole moment (Debye)	1.672	1.908	1.615	1.871	1.870	1.937
E_{HOMO} (eV)	−6.019	−5.830	−4.746	−4.507	−9.782	−9.718
E_{LUMO} (eV)	1.074	2.274	0.546	2.483	4.206	6.148
$\Delta E_{\text{H-L}}$ (eV)	7.093	8.104	5.292	6.990	13.988	15.866
Zero-point energy (kcal/mol)	240.02264	242.18830	233.02464	234.87877	256.36497	259.30688
Rotational constants (GHz)	1.86613	1.86014	1.84032	1.83151	1.89443	1.89362
	0.16942	0.16940	0.16622	0.16646	0.17005	0.17008
	0.15876	0.15870	0.15585	0.15600	0.15943	0.15945
<i>Entropy (callmol K)</i>						
Total	127.911	127.146	129.319	128.591	123.006	122.628
Translational	41.933	41.933	41.933	41.933	41.933	41.933
Rotational	33.126	33.130	33.177	33.180	33.103	33.104
Vibrational	52.852	52.083	54.209	53.478	47.970	47.591

Acknowledgements

This work was supported by the Research Fund of The Gazi University Project No. 30/2005-01. We thank the central laboratory of METU for Raman spectra of molecule and Gazi University Art and Science Faculty Department of Chemistry for Infrared spectra of molecule.

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