

Theoretical and Spectroscopic investigations of conformations, rotational barriers and scaled vibrations of 2,3-dimethyl hexane

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Abstract: The 2,3-dimethyl hexane conformational isomerism has been investigated in detail, based on HF, Post-HF and DFT calculations at different basis set. The effect of size of basis, ZPE, thermal contributions, electronic correlation and optimization methods on the conformational stability was discussed. The rotational barriers from the most stable conformer to the lowest energy secondary conformers and their correspondent inversion barriers at both HF and MP2 methods using 6-31G* basis set have also been approached. A normal mode calculation of the most and less-stable conformers using a scaled ab initio force field in terms of non-redundant local symmetry coordinates have been made to elucidate the conformational dependence of the vibrational spectra.

Keywords: Ab initio; Functional density theory; Conformational isomerism; Vibrational spectra; normal modes calculation; Scaled ab initio local symmetry force field.

Introduction

Branched alkanes having a chain length exceeding 7 carbons are commonly found in conventional petroleum as hydrocarbon fuels and Fischer-Tropsch (FT) chemical reaction. Before studying the combustion of real fuels based on their oxidation under specific conditions of temperature and pressure inside the combustion chamber, it's essential to locate the steric zones hindering the abstraction of the hydrogen radicals during the oxidation for isolated molecule. Such study can also be focused towards understanding the relationship of permeation and selectivity with structure of organic polymer membranes as well as copolymer network interaction^{1,2}. Because of the rotational isomerism problem, manifested by flexible molecules such as dimethyl hexanes, it's necessary to identify the right computational method for modeling their conformations and reproducing their thermochemical and vibrational properties as sources of confirmation^{3,4}. Further, a special interest is given to dimethyl hexanes conformational and vibrational analyses owing to their use for development of therapeutical macromolecules force fields.

To the best of our knowledge, neither quantum chemical calculations, nor the vibrational analysis study of 2,3-dimethylhexane has been reported yet. This deficiency observed in the literature encouraged us to carry out a complete assignment of the observed rich infrared and Raman spectra of this molecule after determining the most stable conformer and the secondary ones.

We first considered the effect of the correction of the zero-point vibrational energy (ZPE) which is the vibrational energy at 0K, and the thermal correction (CT) on the internal energy (E) of the calculated conformations. Second, we studied the sensitivity of the internal energy to the basis set taking into account the d polarization functions on carbon atoms without (6-31G*) and with p polarization on hydrogen atoms (6-31G**), the optimization method (HF and MP2) and the electron correlation of DFT and Post-HF methods. The rotational barriers from the most stable conformer to the lowest energy secondary conformers and their correspondent inversion barriers at both HF and MP2 methods using 6-31G* basis set have also been approached.

On the other hand, as the relationship between a vibrational spectrum and the corresponding structure, is not direct, the GF empirical formalism of Wilson^{5,6} was used.

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Moreover, the scaling of the ab initio force field and the optimization of its scale factors were performed in order to provide a good agreement between the calculated and observed frequencies. Indeed, the ab initio calculated frequencies are relatively larger than the corresponding experimental values. This is partly due to neglect of anharmonicity and partly of the approximative nature of quantum mechanical methods (degree of neglect of electron correlation and basis set truncation). A normal mode calculation of the most and less-stable conformers of 2,3-DMH using this force field in terms of non-redundant local symmetry coordinates has been made. Contrary to our approach where about fourteen scaling factors were used for matching the computed frequencies with experimental ones without taking into account the vibrational infrared and Raman intensities, recently, just one scaling factor is considered for the assignment, but largely facilitated by a substantial effort towards modeling the vibrational intensities⁷⁻⁹. After providing all computational details, the calculation results will be discussed explicitly.

Computational details

To understand the extension of basis set, the electron correlation and the optimization effects on the relative stability, we have performed the MP2, MP3 and MP4 (DQ) energy calculations at both HF and MP2 optimized geometry with different basis set. LDA level and various gradient correction schemes (B3P86, B3PW91, BLYP, B3LYP) were also carried out. Geometry optimizations at HF/6-31G* and B3LYP/6-31G* were followed by frequencies calculations at the same levels to obtain ZPE and thermal contributions in the total internal energy E_{tot} , in addition to enthalpy H (no scaling vibrational frequencies was applied) knowing that¹⁰:

$$E_{tot} = E + E_{ZPE} + CT$$

$$CT = N_0 \sum_i \frac{h\nu_i}{\left[1 - \exp\left(-\frac{h\nu_i}{kT}\right)\right]} + 3RT$$

$$E_{ZPE} = N_0 \sum_i \frac{1}{2} h\nu_i$$

where N is the Avogadro number, R the gas constant, and for one mole of an ideal gas:

$$H = E + E_{ZPE} + N_0 \sum_i \frac{h\nu_i}{\left[1 - \exp\left(-\frac{h\nu_i}{kT}\right)\right]} + 4RT$$

The carbon positions for each isomer are well known by evaluating the three central C-C bonds

$\tau_1 = \text{C1-C2-C3-C4}$, $\tau_2 = \text{C2-C3-C4-C5}$ and $\tau_3 = \text{C3-C4-C5-C6}$. The torsional angle τ_1 is taken to be positive if, when looking from C2 along C2-C3 bond, C4 is in the clockwise sense with respect to C1. The initial configuration and backbone torsional angles, as well as the numbering of the carbon atoms, are shown in Fig.1. In order to explore widely the space of configurations and generate a maximum of combination of terminal group positions, we have assigned 180° , $+60^\circ$ and -60° to each of τ_1 , τ_2 and τ_3 . Each conformation among twenty seven possible conformations obtained was then optimized at HF/6-31G using the method of complete relaxation without any symmetry constraint.

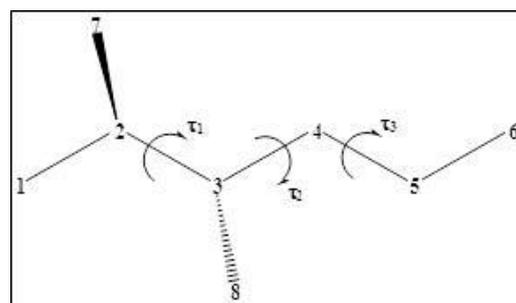


Figure 1. Numbering of the carbon atoms and definition of the torsional angles for 2,3-DMH

Normal mode calculations were carried out using the Wilson GF method. Force constants were obtained in Cartesian coordinates and transformed in term of non-redundant local symmetric coordinates in order to be transferred unchanged between conformers of each molecule. Indeed, the vibrational results of n-pentane and n-hexane obtained with these scale factors defined in terms of local symmetry coordinate (scale ab initio local symmetry force field SALSFF) were found slightly better than those obtained in terms of internal coordinates¹¹. The complete force field in Cartesian coordinates was determined by ab initio molecular orbital calculations at HF/6-31G after optimizing the equilibrium geometries at the same level of theory. According to Mirkin and Krimm vibrational analysis on a series of n-alkanes and some branched alkanes (less than 6 carbons)^{11,12}, it showed that HF/6-31G gives more accurate results (eigen vectors and interaction force constants) than HF/6-31G* and equivalent to MP2/6-31G*. All the above computations were performed using the Gaussian 2003 program package¹³, the program GAR2PED was used to obtain a potential energy distribution from a Gaussian archive record¹⁴.

Results and discussion

The 2,3-dimethyl hexane is the most rich molecule in the series of dimethyl hexanes in term of conformation. The most stable conformer A ($\tau_1=68, \tau_2=163, \tau_3=-176$) (HF/6-31G optimized geometry) has a six carbons chain in trans

configuration ramified by two adjacent methyl groups on the same side as presented in Fig. 2. The same figure shows also all 3D secondary conformers with their Newman projections within a relative internal energy range of 1 kcal/mol, which are:

B($\tau_1=-70, \tau_2=163, \tau_3=-177$), C($\tau_1=64, \tau_2=58, \tau_3=172$), D($\tau_1=167, \tau_2=159, \tau_3=180$) and E($\tau_1=-176, \tau_2=-61, \tau_3=-178$). The two conformers B and C are very close to A (difference of about 0.2 kcal/mol). Another group of conformers with extremely close energies contains D and E conformers while the relative energies of conformations destabilized by Syn-pentane interaction¹⁵ exceed 1.8 kcal/mol. It should be noted that the conformer D is less stable

than conformer A, even both branching methyls are not on the same side with respect to the trans main chain.

Regarding ZPE, thermal contribution to internal energy and enthalpic energy, they have an effect barely perceptible on the HF/6-31G* conformational stability ordering and no effect on B3LYP/6-31G* one¹⁶ (Tab. 1). Furthermore, the correlation of the relative energies of 2,3-DMH conformers obtained at various methods using different basis sets are discussed in more detail in Figure 3, Tab. 2 and Tab. 3 collected the post-HF and DFT results only at 6-31G**.

Table 1. ZPE and thermal contribution in relative energies and relative enthalpies (kcal/mol) for 2,3-DMH conformers calculated with HF and B3LYP/6-31G* methods.

Conf.	HF/6-31G*			B3LYP/6-31G*		
	ΔE	$\Delta(E+ZPE)$	ΔH	ΔE	$\Delta(E+ZPE)$	ΔH
A	0	0 (164.90) ^(a)	0 (172.10) ^(b)	0	0 (154.90) ^(a)	0 (162.39) ^(b)
B	0.11	0.13 (164.92)	0.11 (172.10)	0.13	0.10 (154.88)	0.10 (162.35)
C	0.19	0.31 (165.02)	0.23 (172.14)	0.22	0.19 (154.87)	0.17 (162.34)
D	0.82	0.92 (164.99)	0.83 (172.11)	0.58	0.56 (154.88)	0.54 (162.35)
E	0.81	1.06 (165.14)	0.90 (172.19)	0.80	0.78 (154.88)	0.73 (162.32)
F	1.02	1.21 (165.09)	1.11 (172.18)	0.86	1.01 (154.05)	0.95 (162.47)
G	1.10	1.21 (165.09)	1.11 (172.22)	1.03	1.10 (154.97)	1.03 (162.38)
H	1.17	1.38 (165.18)	1.22 (172.20)	1.06	1.09 (154.93)	1.06 (162.39)
I	1.74	1.37 (165.09)	1.27 (172.23)	1.38	1.52 (154.05)	1.44 (162.45)

E+ZPE is the internal energy taking account ZPE correction at 0K;

H is the enthalpy taking account the thermal contribution at 298K and 1atm.

^{a, b} Data in parentheses are respectively values of unscaled zero point energy and thermal contribution in hartree.

Table 2. Electronic energy (hartree) of the most stable conformer A and the relative energies (kcal/mol) of secondary conformers for different ab initio methods, with HF (a) and MP2 (b) optimization, involving 6-31G** basis set.

Conformer	Level of calculation			
	HF//HF ^a	MP2//HF	MP3//HF	MP4 (DQ)//HF
A	-313.45798	-314.63630	-314.72697	-314.73199
B	0.12	0.03	0.04	0.04
C	0.18	-0.09	-0.01	-0.02
D	0.84	0.61	0.62	0.66
E	0.82	0.19	0.34	0.33
	HF//MP2 ^b	MP2//MP2	MP3//MP2	MP4(DQ)//MP2
A	-313.45729	-314.63694	-314.72728	-314.73239
B	0.12	0.01	0.03	0.03
C	0.29	-0.19	-0.06	-0.07
D	0.81	0.63	0.62	0.67
E	0.88	0.13	0.31	0.31

Table 3. Electronic energy (hartree) of the most stable conformer A and the relative energies (kcal/mol) of secondary conformers for DFT methods, involving 6-31G** basis set.

Conformer	Level of calculation					
	SVWN//SVWN	B3P86//B3P86	B3PW91//B3PW91	BLYP//BLYP	B3LYP//B3LYP	B3LYP//HF
A	-313.97364 ^(a)	-316.94203	-315.62087	-315.49803	-315.73336	-315.73215
B	0.13	0.14	0.13	0.12	0.13	0.15
C	-0.25	0.16	0.20	0.24	0.21	0.23
D	0.20	0.53	0.57	0.52	0.57	0.61
E	-0.03	0.65	0.77	0.89	0.79	0.80

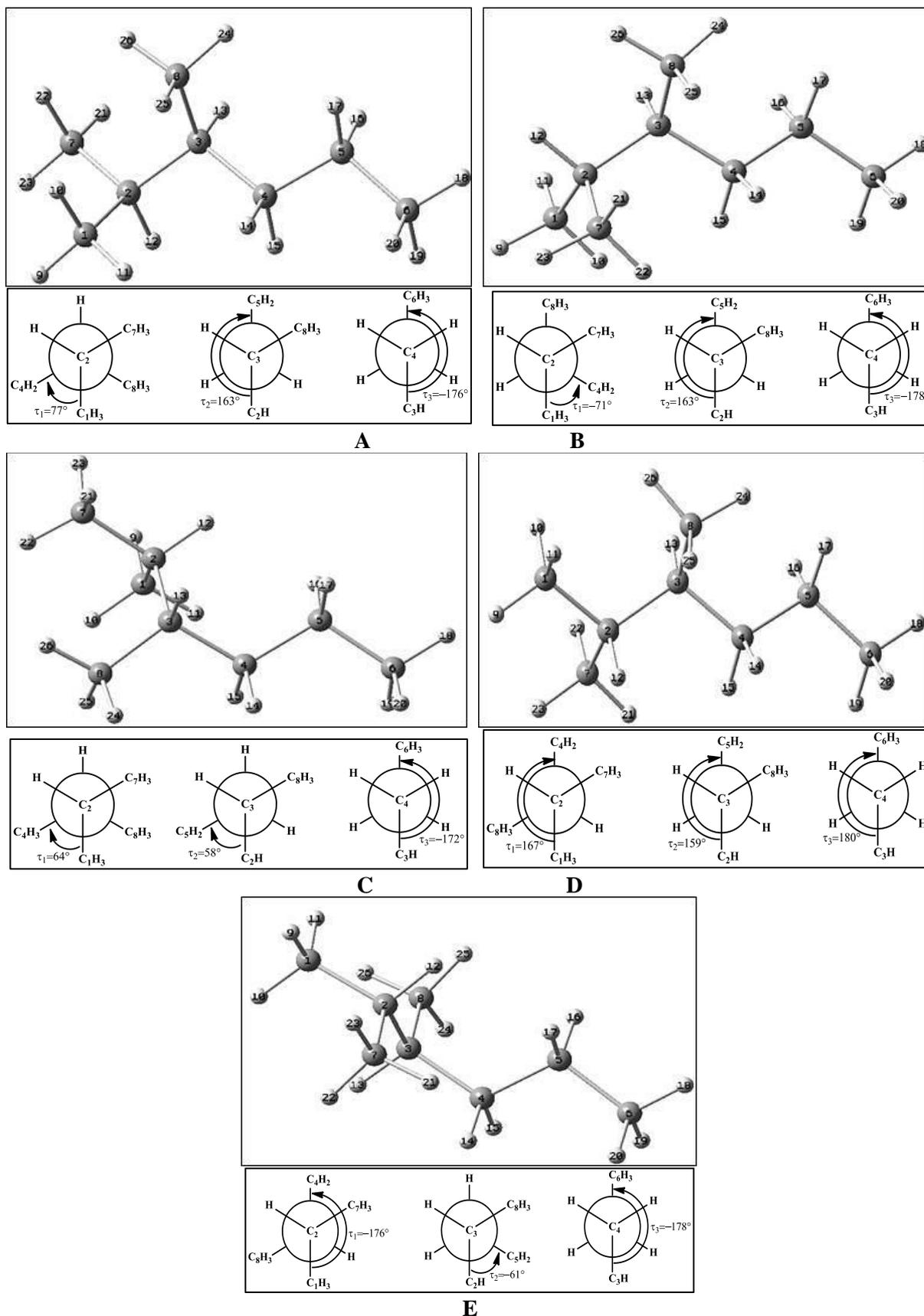


Figure 2. Stable conformations of 2,3-DMH

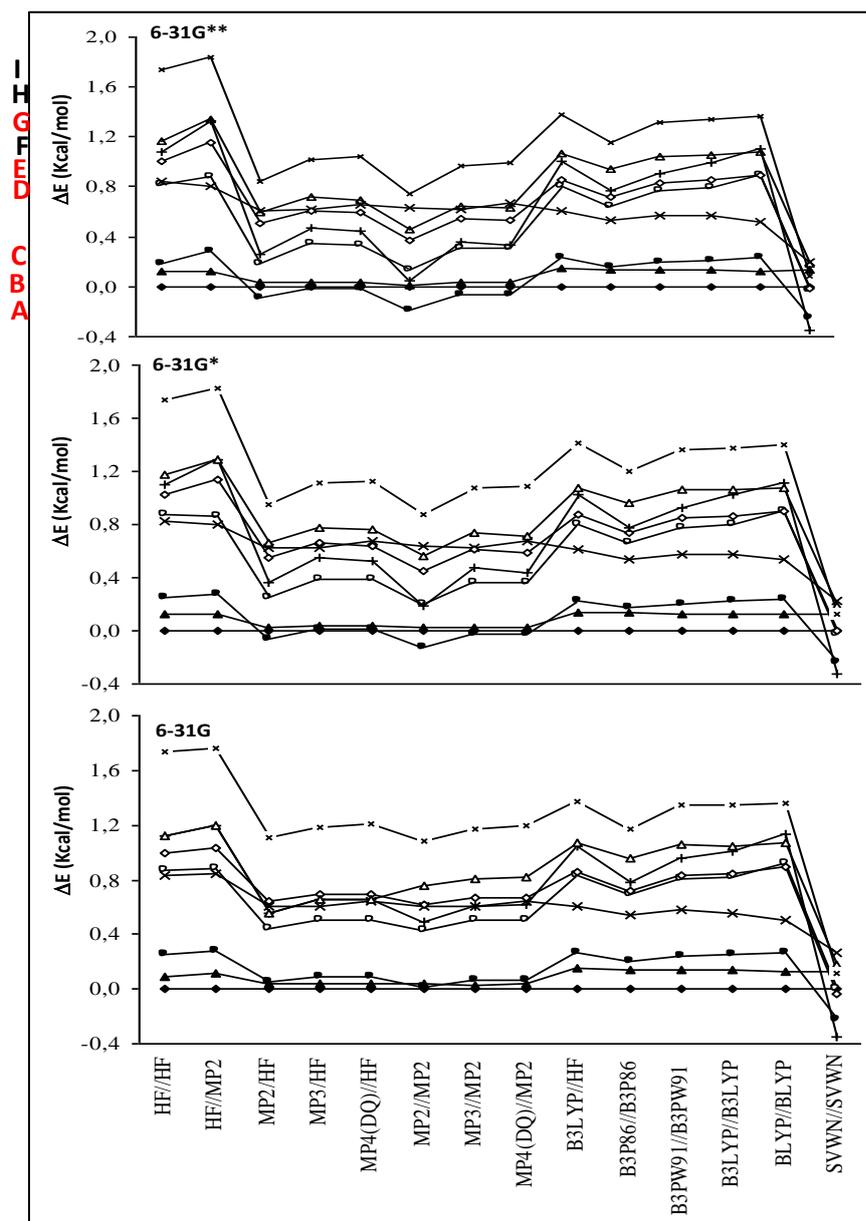


Figure 3. The correlation of the relative energies of 2,3- DMH conformers (A-I) obtained at various methods using 6-31G, 6-31G* and 6-31G** basis sets.

Table 5. Values (kcal/mol) of possible rotational barriers from the most stable conformer to the lowest energy secondary conformers and their correspondent inversion (in parentheses) barriers for 2,3-DMH.

	A→B	A→D	A→C
HF/6-31G*	8.76 (8.65)	3.78 (2.96)	2.01 (1.84)
MP2/6-31G*	8.64 (8.63)	4.05 (3.44)	2.15 (2.28)

As can be seen, HF and DFT (other than LDA) give relative energies values higher than MPn, except for D conformer. In the same way, the stability ordering was modified by MPn calculations as E became more stable than D and G more stable than F. The basis set extension consolidates this change, giving in addition, C more stable than A at 6-31G**. We noticed also that the optimization method has no effect on stability ordering, even it affects substantially MP2 relative energies of the secondary conformers like C, E, F and G. For

instance, a decrease going until 0.2 kcal/mol is observed for G at 6-31G**. Except for LDA where the relative energy values are very weak, the conformational stability ordering for DFT methods is similar to HF. Increase going until about 0.3 kcal/mol is observed from B3P86 to BLYP for G conformer at 6-31G* or at 6-31G**. As an illustration, the three central torsional angles values for the optimized conformers A-E at MP2/MP2/6-31G** and B3LYP/B3LYP/6-31G** were collected in Table 4.

In reality, the differences observed between HF, post HF and DFT are due to the fact that HF method neglects static and dynamic correlation, DFT functionals associate a portion of exact HF exchange to an ab initio or empirical exchange and correlation while the explicitly correlated methods like MPn use anti bonding configurations. In addition, the DFT functionals investigated here for comparison, are doubtful in the evaluation of van der Waals interactions which play a prominent role during the conformers determination, especially when some conformers possess congested structures^{17,18}.

On another aspect, the rotational barriers from the most stable conformer A to the lowest secondary conformers and their correspondent inversion barriers have been evaluated at both HF and MP2 methods using 6-31G* basis set, the optimization methods were respectively HF and MP2. In n-butane, the experimental value is 3.62 kcal/mol¹⁹ with calculated values being 3.49²⁰ and 3.31 kcal/mol^{21,22}. In their work, Mirkin et al. found a good agreement between experimental values and MP2/6-31G* rotational barriers which were relatively larger than HF/6-31G* or HF/6-31G ones^{18,23}. Concerning 2,3-DMH, the one-dimensional rotation from A leads to the following conformational changes:

Around C2C3 bond:

A ($\tau_1=68$, $\tau_2=163$, $\tau_3=-176$) \rightarrow B ($\tau_1=-70$, $\tau_2=163$, $\tau_3=-177$)

A ($\tau_1=68$, $\tau_2=163$, $\tau_3=-176$) \rightarrow D ($\tau_1=167$, $\tau_2=159$, $\tau_3=180$).

Around C3C4 bond:

A ($\tau_1=68$, $\tau_2=163$, $\tau_3=-176$) \rightarrow C ($\tau_1=64$, $\tau_2=58$, $\tau_3=172$)

For the latter for example, the torsion angle τ_2 was kept at constant value from 45° to 190°, in 5° intervals, all the other bond lengths and angles were optimized. (Fig. 4).

According to the collected values in Tab. 5, MP2/6-31G* rotational barriers corresponding to A \rightarrow C and A \rightarrow D transitions are larger than HF/6-31G* ones, the difference has reached for the latter about 0.3 kcal/mol, this difference is more important for the inversion rotational barrier since it reaches 0.5 kcal/mol. However, MP2/6-31G* rotational barrier for A \rightarrow B transition decreases slightly while its inversion rotational barrier remains unchanged. Moreover, the high values of A \rightarrow B rotational barrier and its inversion are due to the strong interaction of the C1C2C7 isopropyl group with the C4C3C8 group. Unfortunately, there are no experimental values for these barriers.

During the refinement of the ab initio normal modes frequencies, the 2,3-DMH scale factors of HF/6-31G force constants were optimized in order to obtain the lowest rms deviation. Their values

collected in Tab. 6 are almost the same as those obtained by Mirkin and Krimm for n-alkanes and some congested branched alkanes^{11,12}, the most important difference does not exceed 10% and concerns CCC bending and CC torsion. Raman and IR frequencies in liquid phase as well as the calculated frequencies at HF/6-31G level are listed in Tab. 7. The PED (contributions $\geq 10\%$) for the most stable conformer A is given, except when its band doesn't exist, in which case the PED listed is for the existing lowest energy conformer. On the whole, the computed scaled frequencies are in good agreement with the experimental data leading rms deviation, not exceeding 6 cm⁻¹ for frequencies below 1500 cm⁻¹. As the molecule 2,3-DH contains 4 CH₃, 2CH₂ and 2 CH, its different vibration modes are subdivided in two groups. The first group (18 modes) contains 8 degenerate asymmetric stretching CH₃as (in plane and out of plane), 4 symmetric stretching CH₃ss, 2 asymmetric stretching CH₂as, 2 symmetric stretching CH₂ss and 2 CH stretching (CHs). All these modes are pure, except CH₂ss and CHs, characterized by the predominant contribution of one to the other. The second group contains, as pure modes or in combination, 8 degenerate asymmetric deformations CH₃ab (in plane and out of plane), 5 symmetric deformations CH₃sb, 8 degenerate rocking CH₃r (in plane and out of plane), 2 CH₂tw twisting, 2 CH₂ro rocking, 4 CCH defCH (in plane and out of plane) deformations as well as all related CC stretching and CCC deformations.

Based on the HF/6-31G scaled ab initio vibrational computations for the conformer A (Tab. 7), CH₃ab was located as pure mode from 1386 to 1367 cm⁻¹ and combined with CH₂b from 1466 to 1443 cm⁻¹, CH₃sb appears from 1386 to 1367 cm⁻¹, essentially alone or, to a lesser extent, combined with CH₂wa while HCC deformation DefCH of the two tertiary carbons appears alone or combined with CH₂wa from 1354 to 1262 cm⁻¹. As an illustration, DefCH contributes predominantly in the calculated modes 1350 (51%) and 1342 (52%), observed respectively at 1354 and 1337 cm⁻¹ while it contributes with CH₂wa and/or C2C3 stretching from 1320 to 1260 cm⁻¹. Furthermore, the CC stretching acts within the range 1200-720 cm⁻¹, essentially in combination with CH₃r and CH₂ro, knowing that the latter mainly concerns the lower limits. The most important modes involving predominately CC contributions were calculated at 1055 (56%), 1005 (53%) and 756 (56%) and observed at 1051, 1009 and 776 cm⁻¹ respectively. Concerning the CCC deformation, it appears in 550-280 cm⁻¹ interval, except for the deformation mode of the central skeleton, to which contribute C2C3C4, C3C4C5 and C4C5C6 deformation coordinates, calculated at 148 like CC torsions, which are located globally in the range 260-30 cm⁻¹

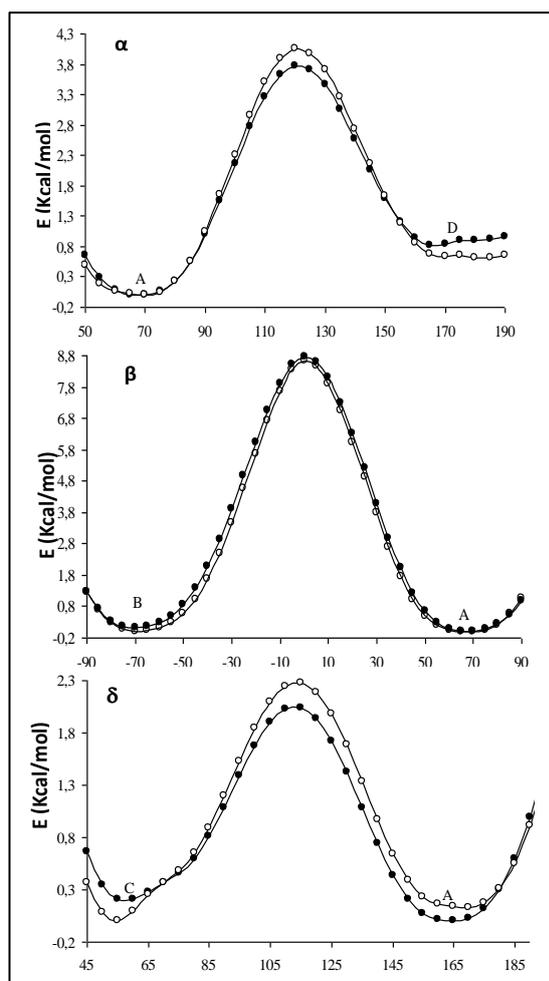


Figure 4 HF/6-31G* (•) and MP2/6-31G* (○) rotational barriers for:
 (α): A (~70,~160,~180) → D (~170,~160,~180)
 (β): B (~70,~160,~180) → A (~70,~160,~180)
 (δ): C (~60,~60,~170) → A (~70,~160,~180)

Table 6 Local symmetry coordinates scale factors for HF/ 6-31G constants and B3LYP/6-31G constants of conformers of 2,3-DMH.

Symmetry coordinates	HF/ 6-31G	B3LYP/6-31G
CCs	0.871	0.976
CH ₃ s	0.830	0.909
CH ₂ s	0.815	0.900
CHs	0.825	0.916
CH ₃ sb	0.760	0.891
CH ₃ ab	0.780	0.897
CH ₃ r	0.771	0.909
CH ₂ sb	0.768	0.893
CH ₂ ro	0.809	0.889
CH ₂ wa	0.775	0.894
CH ₂ tw	0.784	0.914
CCCb	0.825	0.936
Def CH	0.763	0.925
CCt	0.979	1.112

In order to complete our conformational analysis, the normal modes of secondary conformers based on the same HF/6-31G scaled ab initio force field as the conformer A were determined. We have noticed that all the observed frequencies were reproduced by the vibrational mode calculation of A, B, C and D conformers, together. Indeed, almost all bands are common of these conformers, however certain bands were found specific to secondary conformers such as:

- the observed bands 1146 and 1124 cm⁻¹ which correspond to modes due essentially to methyl rocking, the former was calculated at 1139 for C, 1153 for D while the latter was calculated at 1132 for A, 1129 for B. Thus, the band 1146 was reproduced by normal mode calculation for C and D while normal mode calculation of A and B reproduce 1124 cm⁻¹ observed band. This situation was also found for (868, 861) observed pair of bands.
- the observed bands 789 and 776 cm⁻¹ which is due essentially to CC stretching, the former was calculated at 784 for D while the latter was calculated at 756, 754 and 752 for A, B and C respectively. The same situation was found for (1039, 1031) and (740, 719) observed pairs of bands.
- the observed bands 1146 and 1124 cm⁻¹ which correspond to modes due essentially to methyl rocking, the former was calculated at 1139 for C and 1153 for D, and the latter was calculated at 1132 for A and 1129 for B. This situation was also found for (868, 861) pair of bands.
- the observed bands 995, 981 and 971 cm⁻¹, due essentially to methyl rocking, were calculated respectively at 991 for C, 980 and 986 for A and B, and at 968 for D.

For comparison, the B3LYP/6-31G vibrational analysis was also performed (Tab. 8), its rms (4.5 cm⁻¹) was found comparable to HF/6-31G one (5.7 cm⁻¹) for no CH stretching. Moreover, the frequencies predicted by HF/6-31G and B3LYP/6-31G rarely differ by more than 5 cm⁻¹. Furthermore, both the two methods reproduce, almost the same potential energy distribution for all normal modes, essentially for the predominant contributions, except the mode observed at 995 assigned to C conformer, calculated by HF/6-31G at 991 as methyl rocking and by B3LYP/6-31G at 995 as CC stretching. In terms of conformational analysis, B3LYP/6-31G gives the same list of pair of bands sensitive to conformational stability. It should be noted, however, that the most important difference between the two methods was found in the values of the scale factors. The increase of scale factors of B3LYP/6-31G compared to HF/6-31G ones can sometimes reach up to 20 % such as the scale factors of the CH₂wa and CCC deformation (Tab. 6).

Table 7. Observed and calculated HF/6-31G frequencies (cm^{-1}) of 2,3 DMH.

v(obs)	v(Calc)				Potential energy distribution (PED) ^{a,b}
	A	B	C	D	
*	1477	1474	1475	1486	C8H3ab1(58)-C7H3ab2(18)
1466	1473	1472	1473	1475	C1H3ab2(45)C8H3ab2(14)C7H3ab2(13)C7H3ab1(11)
1466	1472	1469	1472	1469	C1H3ab1(37)-C7H3ab1(32)C8H3ab2(19)
1466	1468	1467	1468	1468	C6H3ab1(53)-C5H2b(16)
1466	1465	1464	1465	1466	C8H3ab2(24)-C8H3ab1(23)-C7H3ab2(14)-C6H3ab1(12)-C1H3ab1(10)
1466	1463	1463	1463	1464	C6H3ab2(90)
1466	1459	1463	1459	1460	C7H3ab2(35)-C1H3ab2(17)C8H3ab2(16)-C1H3ab1(15)
1458	1456	1455	1455	1455	C5H2b(45)C6H3ab1(25)-C4H2b(21)
1458	1455	1455	1453	1454	C7H3ab1(45)-C1H3ab2(19)C1H3ab1(14)
1443	1445	1445	1447	1445	C4H2b(61)C5H2b(24)
1386	1386	1385	1385	1385	C1H3sb(41)C7H3sb(35)C8H3sb(17)
1377	1380	1379	1377	1378	C6H3sb(37)-C8H3sb(28)
1377	1375	1376	1375	1376	C6H3sb(47)C8H3sb(34)
1367	1368	1368	1368	1369	C7H3sb(38)-C1H3sb(37)
1367	1363	1365	1365		C4H2wa(23)-C5H2wa(21)-C7H3sb(12)
1354	1350	1350	1353	1354	DéfC3H(22)-DéfC2H(19)-DéfC2H(10)
1337	1342	1342	1344	1340	DéfC3H(25)DéfC2H(15)-DéfC2H(12)-C5H2wa(11)
*			1321	1327	DéfC2H(20)-C5H2wa(19) C2C3s(11)
1308	1315	1316		1309	C5H2wa(29)DéfC2H(21)C4H2wa(18)
1308	1302	1308	1315	1302	DéfC2H(25)DéfC3H(22) C2C3s(13)
1295	1292	1292	1287	1293	C5H2tw(54)-C4H2tw(25)
1262	1265	1266	1276	1263	DéfC3H(32)C4H2wa(21)-DéfC2H(13)
1231	1241	1247	1240	1238	C4H2tw(21)C5H2tw(19)-C6H3r2(17)-C5H2ro(11)
*	1197	1203	1200	1184	C2C3s(12),
1186	1179	1178	1179	1178	C1H3r1(13)C7H3r2(11)-C8H3r1(11)
1160	1162	1164	1166	1158	C7H3r1(12)-C3C4s(11)C7C2C3b(10)
1146			1139	1153	C1H3r2(19)-C8H3r2(18)-C3C4s(10)
1124	1132	1129			C1H3r2(19)-C8H3r2(18) C2C7s(11)
1074	1076	1072	1085	1080	C6H3r1(24)-C4C5s(16)
1051	1055	1051	1055	1075	C4C5s(21)-C5C6s(19)-C3C4s(16)
1039	1043		1037	1040	C5C6s(21)-C8H3r2(10)
1031		1031			C8H3r2(24)-C5C6s(11)-C1H3r2(11)
1009	1005	1013	998	1003	C5C6s(24) C3C8s(18)-C3C4s(11)
995			991		C8H3r1(28)
981	980	986			C8H3r1(23)-C4H2tw(14) C3C8s(11)
971				968	C8H3r1(33)C7H3r1(16)
942	951	947	954	949	C7H3r1(37)-C1H3r2(17)-C1C2s(15)
937	933	942	941	948	C8H3r2(25)C1H3r2(17) C2C3s(13)-C3C4s(12)-C2C7s(10)
918	912	904	913	909	C7H3r2(41)-C1H3r1(27)DéfC2H(11)
896	899	897	895	902	C6H3r1(20) C4C5s(15) C1C2s(10) C5C6s(10)
868		868	872		C6H3r1(14)C4H2ro(11)-C8H3r1(11)
861	863			864	C4H2ro(19)-C6H3r2(15)-C8H3r1(14)
850	845	850	856	845	C6H3r2(16) C3C8s(15)-C4H2ro(14)
789				784	C2C3s(23)
776	756	754	752		C2C3s(29) C1C2s(16) C3C8s(11)
740	740	745		738	C5H2ro(50)-C4H2ro(22)-C6H3r2(13)
719			710		C2C3s(30)C4H2ro(15)
552	552	547	552		C1C2C3b(26)-C2C3C8b(26)C7C2C3b(12)

v(obs)	v(Calc)				Potential energy distribution (PED) ^{a,b}
	A	B	C	D	
513			518	513	C2C3C4b(28)C7C2C3b(12)-C4C5C6b(11)
504	501				C8C3C4b(21)C2C3C4b(18)C7C2C3b(16)-C4C5C6b(15)
482		477			C1C2C3b(24)C2C3C8b(21)C8C3C4b(15)
460				464	C2C3C8b(30)-C1C2C3b(16)C1C2C7b(11)
444		440			C8C3C4b(21)-C3C4C5b(13)-C1C2C7b(13)
428	423			420	C1C2C7b(48)
402			405		C8C3C4b(27)-C1C2C7b(23)-C4C5C6b(13)
402			400		C1C2C7b(40)C3C4C5b(15)C8C3C4b(13)
*				384	C1C2t(18)C3C8t(17)-C2C3C8b(13)C8C3C4b(11)
365		362		374	C1C2C7b(21)C7C2C3b(17)-C8C3C4b(16)
335	344			339	C8C3C4b(44)C4C5C6b(18)C1C2C7b(13)
313	305	324	318	307	C7C2C3b(30)C4C5C6b(21)-C1C2C7b(12) C3C4s(11)
*	291	284	292		C2C3C8b(29)C7C2C3b(21)-C3C4C5b(18)
*	284	267	275		C1C2C3b(46)C2C3C8b(19)
*	259	250	262	272	C1C2t(58)C3C8t(27)
*	245	242	250	263	C5C6t(61)C2C7t(17)
*	237	231	241	253	C2C7t(59)-C5C6t(23)
*	207	217	211	227	C3C8t(49)-C1C2t(31)-C2C7t(12)
*	148	156	166	173	C3C4C5b(31)-C2C3C4b(29)-C4C5C6b(17)
*	94	94	117	96	C4C5t(49)-C3C8t(14)
*	74	74	80	65	C3C4t(36)-C2C3t(26)
*	36	48	42	54	C3C4t(34)C2C3t(31)C3C8t(15)C4C5t(10)

a Potential energy distribution (contribution ≥ 10) for A conformer, except when no A band is given, in which case the PED is for the existing secondary conformer.

b CH₃sb, totally symmetric bending of CH₃; CH₃ab1 (CH₃ab₂), in plane (out of plane) degenerate bending of CH₃; CH₃r1 (CH₃r₂), in plane (out of plane) degenerate rocking of CH₃; CH₂b, scissoring of CH₂; CH₂tw, twisting of CH₂; CH₂ro, rocking of CH₂; CH₂wa, wagging of CH₂; Def CH (Def 'CH), in plane (out of plane) deformation CCH; CCCb, CCC deformation; CCs, CC stretching; CCt, CC torsion.

Conclusion

In light of this work, we can conclude that ZPE, thermal contribution to internal and enthalpic energies have an effect barely perceptible on the HF/6-31G* conformational stability ordering and no effect on B3LYP/6-31G* one. Further, the stability ordering was modified by MPn calculations and the basis set extension, while the optimization method has no effect. MP2/6-31G* rotational barriers corresponding to A \rightarrow C and A \rightarrow D transitions are larger than HF/6-31G* ones. However, MP2/6-31G* rotational barrier for A \rightarrow B transition decreases slightly. Concerning the vibrational analysis, HF/6-

31G as well as B3LYP/6-31G led to the same sensitive pair of bands to conformational stability. Even the difference between the optimized HF/6-31G and B3LYP/6-31G scale factors can sometimes reach up to 20 % , their obtained rms deviation were found comparable.

Regarding its simplicity and its ab initio character, the scaled ab initio force field of branched hexanes seems to be complete and useful as a basis for the development of spectroscopically accurate molecular mechanics energy function for the derived polymers.

Table 8. Observed and calculated B3LYP/6-31G frequencies (cm⁻¹) of 2,3 DMH.

v(obs)	v(Calc)				Potential energy distribution (PED) ^{a,b}
	A	B	C	D	
1466	1476	1474	1472	1483	C8H3ab1(52)-C7H3ab2(11)
1466	1472	1472	1472	1475	C1H3ab2(26)C7H3ab2(20)C7H3ab1(14)
1466	1471	1470	1470	1468	C1H3ab1(42)C8H3ab2(23)-C7H3ab1(22)
1466	1470	1466	1468	1466	C6H3ab1(27)-C5H2b(23)C1H3ab2(16)
1466	1463	1463	1463	1461	C8H3ab2(32)-C8H3ab1(18)-C1H3ab1(17)-C7H3ab2(11)
1466	1461	1462	1462	1461	C6H3ab2(88)

1466	1457	1461	1456	1457	C6H3ab1(51)C5H2b(28)-C4H2b(14)
1458	1454	1455	1454	1454	C7H3ab2(31)-C1H3ab2(20)C8H3ab1(12)C4H2b(10)
1458	1451	1453	1450	1451	C7H3ab1(40)C1H3ab1(19)-C7H3ab2(17)
1443	1446	1443	1444	1446	C4H2b(44)C5H2b(17)C1H3ab2(14)-C8H3ab2(13)
1386	1387	1386	1396	1385	C1H3sb(35)C8H3sb(29)C7H3sb(28)
1377	1380	1381	1381	1380	C6H3sb(56)
1377	1375	1377	1373	1376	C8H3sb(45)C6H3sb(25)-C1H3sb(11)
1367	1367	1367	1369	1367	C1H3sb(36)-C7H3sb(27)
1367	1363	1364	1363		C7H3sb(25)
1354	1351	1354	1355	1352	C5H2wa(31)-DéfC2H(13)-C4H2w(13)
1337	1342	1337	1342	1335	DéfC2H(19)-DéfC3H(19)-DéfC3H(15)
*			1328	1326	DéfC3H(23)DéfC2H(14)DéfC2H(12)
1308	1317	1310		1312	C5H2wa(27)C4H2w(20)DéfC2H(17)
1308	1298	1307	1309	1303	DéfC2H(26)DéfC3H(22)C2C3s(11)
1295	1291	1295	1293	1293	C5H2tw(55)-C4H2tw(30)
1262	1269	1263	1259	1267	DéfC3H(34)C4H2w(21)-DéfC2H(15)
1231	1239	1245	1241	1238	C4H2tw(25)C5H2tw(20)-C6H3r2(16)-C5H2ro(10)
*	1193	1208	1196	1184	C2C3s(14)
1186	1178	1177	1180	1174	C8H3r1(12)-C1H3r1(12)C4H2ro(11)
1160	1162	1163	1166	1158	C7H3r1(12)-C3C4s(11)C7C2C3b(11)
1146			1138	1154	C1H3r2(18)-C8H3r2(18)-C3C4s(11)
1124	1131	1128			C8H3r2(19)-C1H3r2(18)
1074	1076	1074	1079	1078	C6H3r1(24)-C4C5s(15)
1051	1053	1053	1059	1074	C4C5s(21)-C5C6s(18)-C3C4s(16)
1039	1044		1037	1038	C5C6s(25)
1031		1030			C8H3r2(18)-C5C6s(14)
1009	1004	1011	999	1002	C5C6s(24)C3C8s(14)-C3C4s(12)-C8H3r1(10)
995			995		C3C8s(36)
981	980	986			C8H3r1(19)C3C8s(16)-C4H2tw(14)
971				971	C8H3r1(35)C7H3r1(14)
942	952	943	955	951	C7H3r1(37)-C1H3r2(17)-C1C2s(14)
937	928	936	935	941	C8H3r2(21)C1H3r2(14)C2C3s(13)-C3C4s(12)
918	915	901	914	915	C7H3r2(39)-C1H3r1(29)DéfC2H(11)
896	900	896	892	903	C6H3r1(18)C1C2s(15)C4C5s(14)
868		872	874		C4H2ro(21)-C6H3r2(17)C6H3r1(10)
861	864			865	C4H2ro(17)-C8H3r1(14)-C6H3r2(13)
850	845	857	859	847	C6H3r2(17)-C4H2ro(16)C3C8s(15)
789				782	C2C3s(24)
776	756	775	758		C2C3s(31)C1C2s(16)C3C8s(10)
740	742	755		743	C5H2ro(50)-C4H2ro(22)-C6H3r2(13)
719			711		C2C3s(35)C4H2ro(14)
552	556	549	555		C1C2C3b(26)-C2C3C8b(26)C7C2C3b(12)
513			520	516	C2C3C4b(27)C7C2C3b(11)-C4C5C6b(11)
504	503				C8C3C4b(20)C2C3C4b(18)C7C2C3b(16)-C4C5C6b(15)
482		479			C1C2C3b(25)C2C3C8b(21)C8C3C4b(16)
460				463	C2C3C8b(30)C1C2C7b(15)-C1C2C3b(13)
444		440			C8C3C4b(21)-C3C4C5b(13)-C1C2C7b(13)
428	425			423	C1C2C7b(48)
402			404		C8C3C4b(39)C3C4C5b(11)
402			401		C1C2C7b(60)

*				384	C2C3C8b(18)-C3C8t(12)C2C3C4b(11)-C1C2C7b(11)
365		364		374	C8C3C4b(44)C4C5C6b(18)C1C2C7b(14)
335	347			332	C8C3C4b(44)C4C5C6b(18)C1C2C7b(14)
313	306	326	318	309	C7C2C3b(30)C4C5C6b(21)-C1C2C7b(13)C3C4s(11)
*	293	286	290		C2C3C8b(26)C7C2C3b(21)-C3C4C5b(19)
*	288	272	271		C1C2C3b(46)C2C3C8b(22)
*	257	254	257	260	C1C2t(49)C3C8t(34)
*	245	249	242	258	C5C6t(70)-C1C2t(11)
*	235	240	230	228	C2C7t(61)-C5C6t(15)
*	213	231	212	215	C3C8t(43)-C1C2t(32)-C2C7t(19)
*	149	157	168	162	C3C4C5b(31)-C2C3C4b(28)-C4C5C6b(18)
*	94	99	111	97	C4C5t(37)-C3C4t(19)-C3C8t(14)-C2C3t(12)
*	78	76	74	66	C3C4t(37)-C2C3t(27)C4C5t(10)
*	44	57	37	37	C3C4t(32)C2C3t(32)C4C5t(16)C3C8t(11)

References

- 1- M. Macchione, J.C. Jansen, G. De Luca, E. Tocci, M. Longeri, E. Drioli, *Polymer*, **2007**, 48, 2619.
- 2- Denis Bertina, Sandra Grimaldib, Marie Leblanca, Sylvain R.A. Marqueea, Didier Siria, Paul Tordoa, *J. Mol. Struct.*, **2007**, 811, 255–266.
- 3- Arthur J. LaPlante, Howard D. Stidham, Gamil A. Guirgis, Horace W. Dukes, *J. Mol. Struct.*, **2012**, 1023, 170–175.
- 4- A. Suvitha, S. Periandy, M. Govindarajan, P. Gayathri *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2015**, 138, 900–912.
- 5- E. B. Wilson, J. C. Decius, P. C. Cross, *Molecular Vibrations* (N. Y. : McGraw-Hill, **1955**).
- 6- S. Califano, *Vibrational States* (N. Y. : J. Willey and Sons, **1976**).
- 7- I.A. Shaaban, A.E. Hassan, A.M. Abuelela, W.M. Zoghaieb, T.A. Mohamed, *Journal of Molecular Structure*, **2016**, 1003, 70-81.
- 8- K.Govindarasu, E. Kavitha, *Journal of Molecular Structure*, **2015**, 1088, 70-84.
- 9- S. Subashchandrabose, V. Thanikachalam, G. Manikandan, H. Saleem, Y. Erdogdu, *Spectrochimica Acta Part A*, **2016**, 157, 96–103.
- 10- G. E. Segal (Ed.): *Semiempirical Methods of Electronic Structure Calculation, Part B: Applications*, Vol. 8. Plenum Press, London, New York, **1977**.
- 11- N. G. Mirkin, S. Krimm, *J. Phys. Chem.*, 1993, 97, 13887.
- 12- N. G. Mirkin, S. Krimm, *J. Mol. Struct.*, 2000, 67, 550-551.
- 13- Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
- 14- J.M.L. Martin, C. Van Alsenoy, program GAR2PED, University of Antwerp, **2011**.
- 15- R. W. Hoffman, K. Menzel, *Eur. J. Org. Chem.*, **2001**, 1865.
- 16- E. Koglin; R. J Meier, *Chem. Phys. Lett.*, **1999**, 312, 284.
- 17- J. Miao, S. Hua, S. Li, *Chemical Physics Lett.*, **2012**, 541, 7-11.
- 18- Y. Zhao, D.G. Truhlar, *Theor. Chem. Acc.*, **2008**, 120, 215.
- 19- W.A. Herrebout, B.J. van der Veken, A. Wang, J.R. Durig, *J. Phys. Chem.*, **1995**, 99, 578.
- 20- M.A. Murko, H. Castejon, K.B. Wiberg, *J. Phys. Chem.*, 1996, 100, 16162.
- 21- G.D. Smith, R.J. Jaffe, *J. Phys. Chem.* **1996**, 100, 18 718.
- 22- N.L. Allinger, J.T. Fermann, W.D. Allen, H.F. Schaefer III, *J. Chem. Phys.*, **1997**, 106, 5143.
- 23- M. J. Hafezi, F. Sharif, *J. Mol. Structure Theochem*, **2007**, 814, Issues 1–3, 43.