Geometry, Vibration Frequencies, Normal Coordinates and IR Absorption Intensities of 6-Radialine

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الخلاصة

تضمن البحث حسابات نظرية شبه تجريبية بأسلوب MINDO/3-FORCES لدراسة و تحديد طاقات وترددات و شدد حزم الأشعة تحت الحمراء مع تصنيف الأنماط الاهتزازية تكافؤيا و تماثليا عند الأشكال الهندسية الفراغية المتوازنة و الأكثر استقرارا لجريئة 6-Radialine وفقا لنتائج الحساب و هما شكل الكرسي الذي يمتلك التماثل(D_{3d}) و الشكل المستوي الذي يمتلك التماثل (D_{3h}) حيث و جد أن شكل الكرسي هو الشكل الهندسي الفراغي الأكثر استقرارا من الشكل المستوي ويمتلك حرارة التكوين الأقل، كما أن ترددات المط للآصرة المزدوجة في شكل الكرسي (ν(C=C) str.) أعلى من نظيرتها في الشكل المستوي في حين وجد أن ترددات الانحناء لمجموعة المثلين ($=CH_2$) في الشكل المستوي أعلى منها لشكل الكرسي. تم إجراء مقارنات لجميع الأنماط الاهتزازية الأخرى عند الشكلين المستقرين طاقيا. كم تم إعادة الحساب باستخدام برنامجي MINDO/3 و PM3 لأجل المقارنة و التأكد من صحة النتائج.

Abstract

SCF-MO calculations, using MINDO/3-FORCES method, of the equilibrium geometry of 6-Radialine considering the two conformations, planar and chair, as well as the vibration frequencies and IR absorption intensities for each conformer are reported. The chair conformation is found to be more stable. The C=C str. frequencies of the chair form are found to be higher than those of the planar, the $=CH_2$ bending frequencies of the planar form are higher than those of the chair form. PM3 method was used too for the calculation of the vibration frequencies. The results are compared with the MINDO/3-FORCES results.

Introduction

Radialene molecules **(3R, 4R, 5R and 6R fig. 1)** form a class of cyclic hydrocarbons **(CnHn)** possessing n ring atoms and n exocyclic double bonds. Since 1962 [1] these molecules attracted much attention due to their unique properties. So, 6-Radialine may be considered as hexamethylene cyclohexane in which all ring carbons are sp2- hybridized (fig. 2).

The synthesis and characterization of 6-Radialene were performed applying different techniques [2-3]. Due to its instability, polymerizing quickly at room temperature, it was not be possible to estimate its geometry applying x-ray diffraction. Much attention was paid to its derivatives [4-6]. Theoretical studies using ab initio method were done by Galasso [7] and Tyutyulkov et al [8] for it. Kubba studied theoretically the vibration spectrum of 3-Radialene, applying the MINDO/3-FORCES method [9].

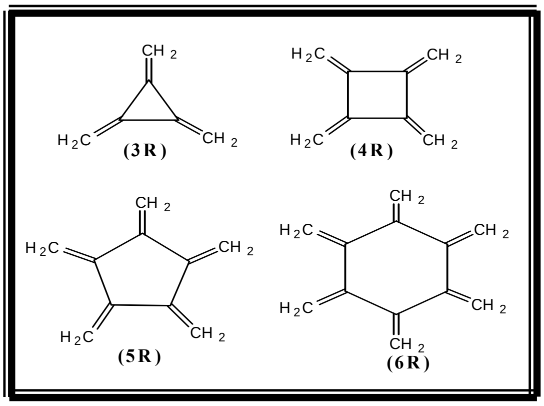


Fig. 1: 3, 4, 5 and 6-Radialene molecules

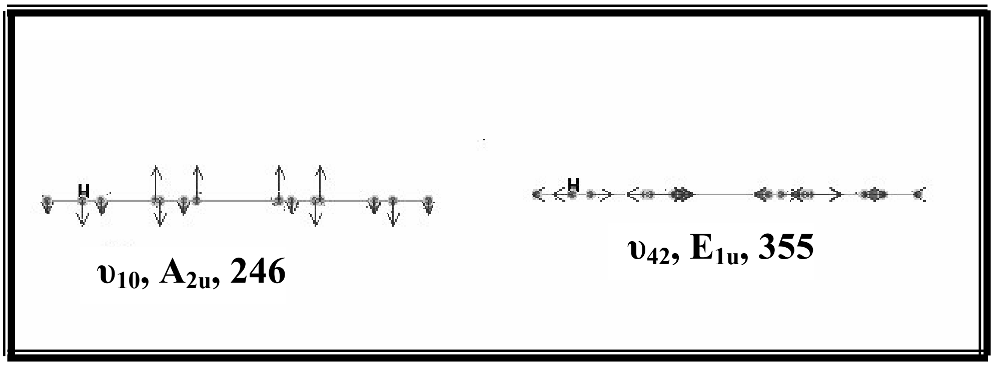


Fig 2. DRAW. MOL graphical representation of two vibration modes of 6-Radialene (planar-form), (a) out of plane; (b) in-plane.

The present study is based on the MINDO/3-FORCES method, which was developed and applied to the treatment of organic molecules by Shanshal et al. [10]. Such a treatment yields the equilibrium geometry and energy values for the molecules, in addition to their fundamental vibration frequencies **(3N-6)** and IR absorption intensities.

MINDO/3-FORCES method adopts the Pulay forces method to calculate the force constants of molecules [11], which are introduced then to the Wilson secular equation of the following form [12];

$$\sum_{j} L_j \ (F_{ij} - M_{ij}\,\lambda) = 0 \ldots\ldots\ldots (1)$$

Solution of this equation yields both vibration frequencies **($\lambda = 4\pi^2 c^2 \nu^2$)** and vibration mode eigenvector coefficients (L), which are utilized in evaluating the atomic partial participation values **(APP)** (the partial contribution of each atom to the molecular vibration) [10]. The same coefficients (L) allow a graphical description of the vibration modes in the molecule when introduced to the DRAW.MOL routine developed by Shanshal et. al [13] (fig. 2).

In the present work Dewar's MINDO/3 program [14] and PM3 [15] method were used too, for the calculation of the vibration frequencies for the two conformers of 6-Radialene. Both Dewar's MINDO/3 and MINDO/3-FORCES programs yielded similar results.

Results and discussion

MINDO/3-FORCES treatment for 6-radialene showed that the chair form is more stable than the planar**.** It is known [16] that this method overestimates the **ΔH_f** values of cyclic planar unsaturated molecules by a ratio of approximately 40%. Considering this factor the calculated ΔH_f values are (ΔH_f = 94 kcal/mol) for the planar and (ΔH_f = 81 kcal/mol) for the chair form. The PM3 [15] treatment yields for the same molecule 95 kcal/mol for the planar and 98 kcal/mol for the chair form. However due to the fact that the lowest gradiant value (d^2E_{ii}/dq_i^2) acceptable for the geometry optimization process in MINDO/3-FORCES is $\leq 10^{-5}$ au/au, which is lower than the acceptable gradiant value in PM3, we prefered the relative stability order as predected by the MINDO/3-FORCES method. The evaluation of the relative stability of the chair over the planar form comes in agreement with experimental findings reported before [17].

The treatment for the vibration frequencies was carried out for the equilibrium geometry of each conformer after minimizing its total energy as a function of all its **3N** cartesian coordinates. The equilibrium geometric values for the two conformers are listed in (Table 1).

Table 1. MINDO/3-FORCES calculated geometric parameters for the planar and the chair conformations of 6R molecule, length (A°)/ angle (deg.).

Bonds length and angles	MINDO/3-FORCES **Planar form**	MINDO/3-FORCES **Chair form**
(C-H)	1.100	1.100
(C=C)	1.352	1.343
(C-C)	1.521	1.520
< H-C-H	107.4	109.9
< H-C=C	126.3	125.1
< C=C-C	120	123.4
< C-C-C	120	113.0

The values in the table Show similar C=C and C-C bond lengths for both conformations. The unusual small values of HCH bond angles may be attributed to the strain caused by the crowding of the HCH groups, which seems to be of bigger conformational influence in the planar than in the chair form, as shown through the bond angles of the planar form (HCH

107.4°) compared with those of the chair form (HCH 109.9°), (Fig. 3). The C-C-C angles of the planar form are trigonal (120°), those of the chair form are smaller (113.0°), obviously due to the strain of the chair form.

The planar conformation of 6-Radialene is of $\mathbf{D_{6h}}$ symmetry. Its total number of fundamental vibrations (3N-6) is **66,** classified into the following irreducible representations;

(a)- In-plane: $4A_{1g} + 3A_{2g} + 4B_{1u} + 4B_{2u} + 8E_{2g} + 2A_{2u} + 7E_{1u}$

(b)- Out of plane: $B_{1g} + 3B_{2g} + 3E_{1g} + A_{1u} + 2A_{2u} + 4E_{2u}$

where $\mathbf{A_{1g}}$, $\mathbf{E_{1g}}$, $\mathbf{E_{2g}}$, are Raman active and IR inactive, while $\mathbf{A_{2u}}$, $\mathbf{E_{1u}}$ are IR active and Raman inactive. It is clear that mutual exclusion holds because of the center of symmetry in the molecule. Table 2 includes the calculated vibration frequencies of the planar conformation. All vibration frequencies are scaled applying the following scaling factors [9]:
0.875 (CH_2 str.), 0.93 (C=C str.); 1.06 (CH_2 sciss); 1.115 (CH_2 twist.).

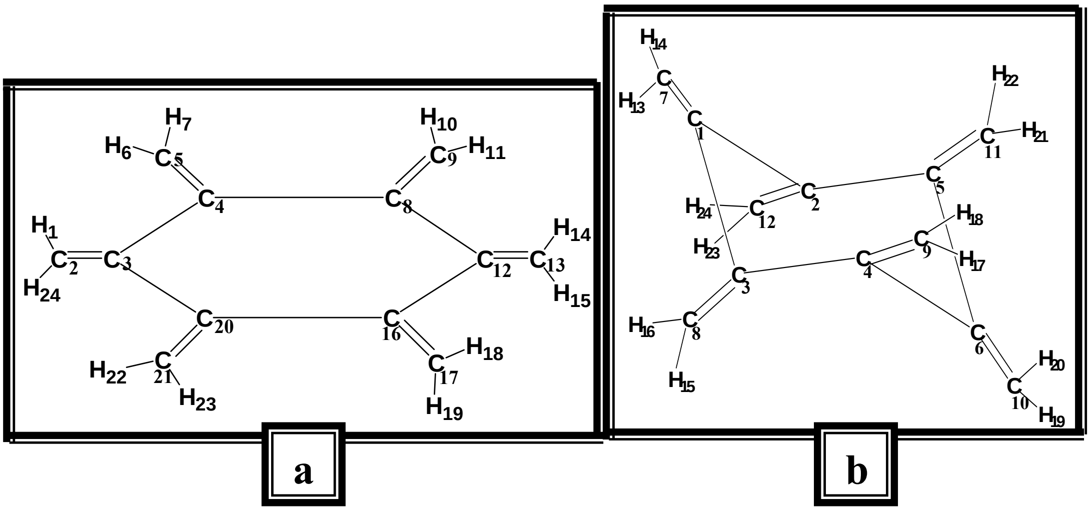


Fig. 3: Equilibrium geometry for (a) planar conformation (D_{3h}) and (b) chair conformation (D_{3d}) of 6R molecule as calculated by MINDO/3-FORCES and PM3 methods.

Inspection of the frequency values in Table 2 reveals the following relations:

νsym (=CH_2 str.) > νasym (=CH_2 str.)

δ(=CH_2 sciss.) > δ(=CH_2 rock.)

γ (=CH_2 (wag.)) > γ (=CH_2 (twist.))

Fig. 4. shows the graphical representation of some vibration modes of 6R (planar conformation) as drawn through the DRAW. MOL. Routine [13].

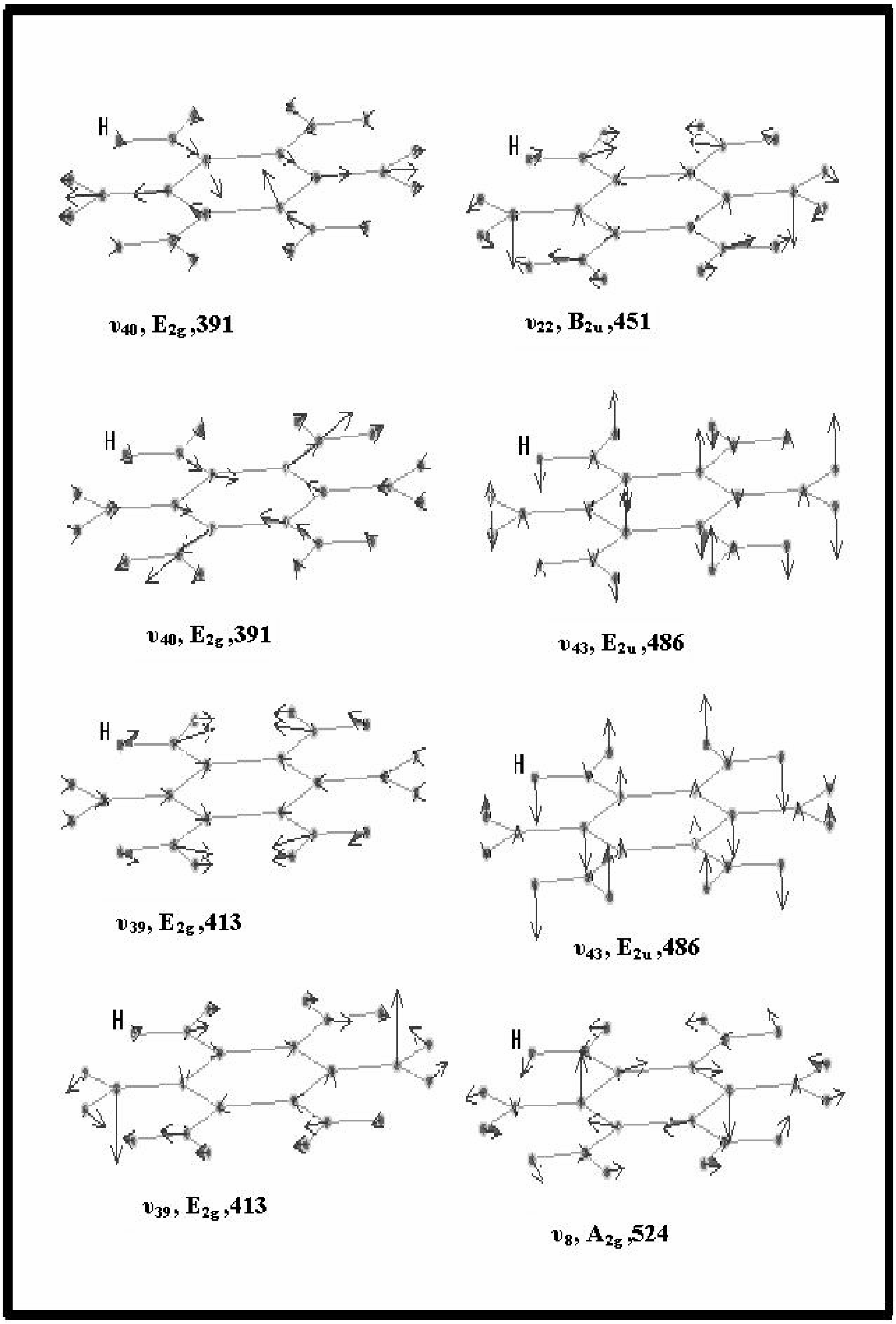
Table 2: **Calculated vibration frequencies and IR absorption intensities for planar conformation of 6R molecule.**

Symmetry and description		**MINDO/3-FORCES**		**PM3**	**Expt.[17]**
In-plane		Scaled Freq.cm^{-1}	Intensity km/mol	Freq.cm^{-1}	Freq.cm^{-1}
A$_{1g}$					
υ_1	$=CH_2$ sym.str.	3091	0.00	3152	------
υ_2	C=C str	1631	0.00	1744	------
υ_3	δ ($=CH_2$ (sciss.))	1463	0.00	1402	------
υ_4	δ ring (breathing)	660	0.00	716	------
A$_{2g}$					
υ_6	$=CH_2$ sym.str.	3080	0.00	3120	------
υ_7	δ ($=CH_2$(rock.))+ring(δ ccc)	973	0.00	1105	------
υ_8	ring(δ ccc)+δ ($=CH_2$(rock.))	524	0.00	638	------
B$_{1u}$					
υ_{12}	$=CH_2$ sym.str.	3086	0.00	3138	------
υ_{13}	C=C str	1643	0.00	1762	------
υ_{14}	δ ($=CH_2$ (sciss.))	1406	0.00	1413	------
υ_{15}	δ ring (CCC)	572	0.00	590	------
B$_{2u}$					
υ_{19}	$=CH_2$ sym.str.	3089	0.00	3138	------
υ_{20}	ring str.	1426	0.00	1468	------
υ_{21}	δ ($=CH_2$ (rock.))	895	0.00	970	------
υ_{22}	δ ($=CH_2$ (rock.))	451	0.00	638	------
E$_{1u}$					
υ_{26}	$=CH_2$ sym.str.	3089	71.79	3148	3090
υ_{27}	$=CH_2$asym.str.	3083	75.02	3140	2920
υ_{28}	C=C str	1614	2.41	1723	1652
υ_{29}	δ ($=CH_2$ (sciss.))	1450	12.46	1436	1390
υ_{30}	δ ring (CCC)	1109	2.67	1205	1061
υ_{31}	δ ($=CH_2$(rock.))+ring(δ ccc)	819	1.53	936	------
υ_{32}	δ ($=CH_2$(rock.))+ ring (δ ccc)	355	1.18	440	------

Table 2: Continued

E_{2g}					
υ_{33}	$=CH_2$ sym.str	3087	0.00	3133	------
υ_{34}	$=CH_2$ asym.str	3084	0.00	3130	------
υ_{35}	C=C str	1626	0.00	1714	------
υ_{36}	ring str $+\delta$ ($=CH_2$ (sciss.)).	1367	0.00	1484	------
υ_{37}	ring str $+\delta$ ($=CH_2$ (sciss.)).	1307	0.00	1363	------
υ_{38}	δ ($=CH_2$ (rock.))	880	0.00	949	------
υ_{39}	δ ($=CH_2$ (rock.))	413	0.00	537	------
υ_{40}	ring (δ CCC)	391	0.00	438	------
	Out of plane				
A_{1u}					
υ_{5}	γ ($=CH_2$ (twist.))	645	0.00	665	------
A_{2u}					
υ_{9}	γ ($=CH_2$ (wag.))	877	11.81	915	897
υ_{10}	γ $C=CH_2$ (wag.)	246	0.01	327	------
B_{1g}					
υ_{11}	γ ($=CH_2$(twist.))	628	0.00	597	------
B_{2g}					
υ_{16}	γ ($=CH_2$(wag.))	1001	0.00	949	------
υ_{17}	ring (puck.)	762	0.00	770	------
υ_{18}	γ $C=CH_2$ (wag.)	3	0.00	15	------
E_{1g}					
υ_{23}	γ ($=CH_2$(wag.))	874	0.00	920	------
υ_{24}	γ ($=CH_2$(twist.)) $+\gamma$ (CC)	607	0.00	674	——
υ_{25}	γ (CC)	318	0.00	415	------
E_{2u}					
υ_{41}	γ ($=CH_2$ (wag.))	870	0.00	936	------
υ_{42}	ring (puck.)	701	0.00	773	------
υ_{43}	γ (CC) + γ ($=CH_2$ (twist.))	486	0.00	528	------
υ_{44}	γ (C=C).	4	0.00	17	------

scaling factors: 0.875 (CH_2 str.), 0.93 (C=C str.); 1.06 (CH_2 sciss); 1.115 (CH_2 twist.).



υ_{40}, E_{2g} ,391

υ_{22}, B_{2u} ,451

υ_{40}, E_{2g} ,391

υ_{43}, E_{2u} ,486

υ_{39}, E_{2g} ,413

υ_{43}, E_{2u} ,486

υ_{39}, E_{2g} ,413

υ_{8}, A_{2g} ,524

Fig. 4. The graphical representation of some vibration modes of 6R (planar conformation) as drawn through the DRAW. MOL. routine.

The fundamental vibration (3N-6) of the chair form with D_{3d} symmetry are classified into the following irreducible representations;

$$\mathbf{7A_{1g} + 4A_{2g} + 11E_g + 5A_{1u} + 8E_{2g} + 6A_{2u} + 11E_u}$$

where A_{1g} and E_g are Raman active and IR inactive and A_{2u} and E_u are IR active and Raman inactive. The mutual exclusion holds here too, due to the center of symmetry in the molecule. Inspection of the frequency values in table 3 reveals the following relations:

νasym (=CH_2 str.) > νsym (=CH_2 str.) (in contrast to that of the planar form).

δ (=CH_2 (sciss.)) > δ (=CH_2 (rock.))

γ (=CH_2 (wag.)) > γ (=CH_2 (twist.))

Fig. 5. shows the graphical representation of some vibration modes of 6R (chair conformation) as drawn through the DRAW. MOL. routine.

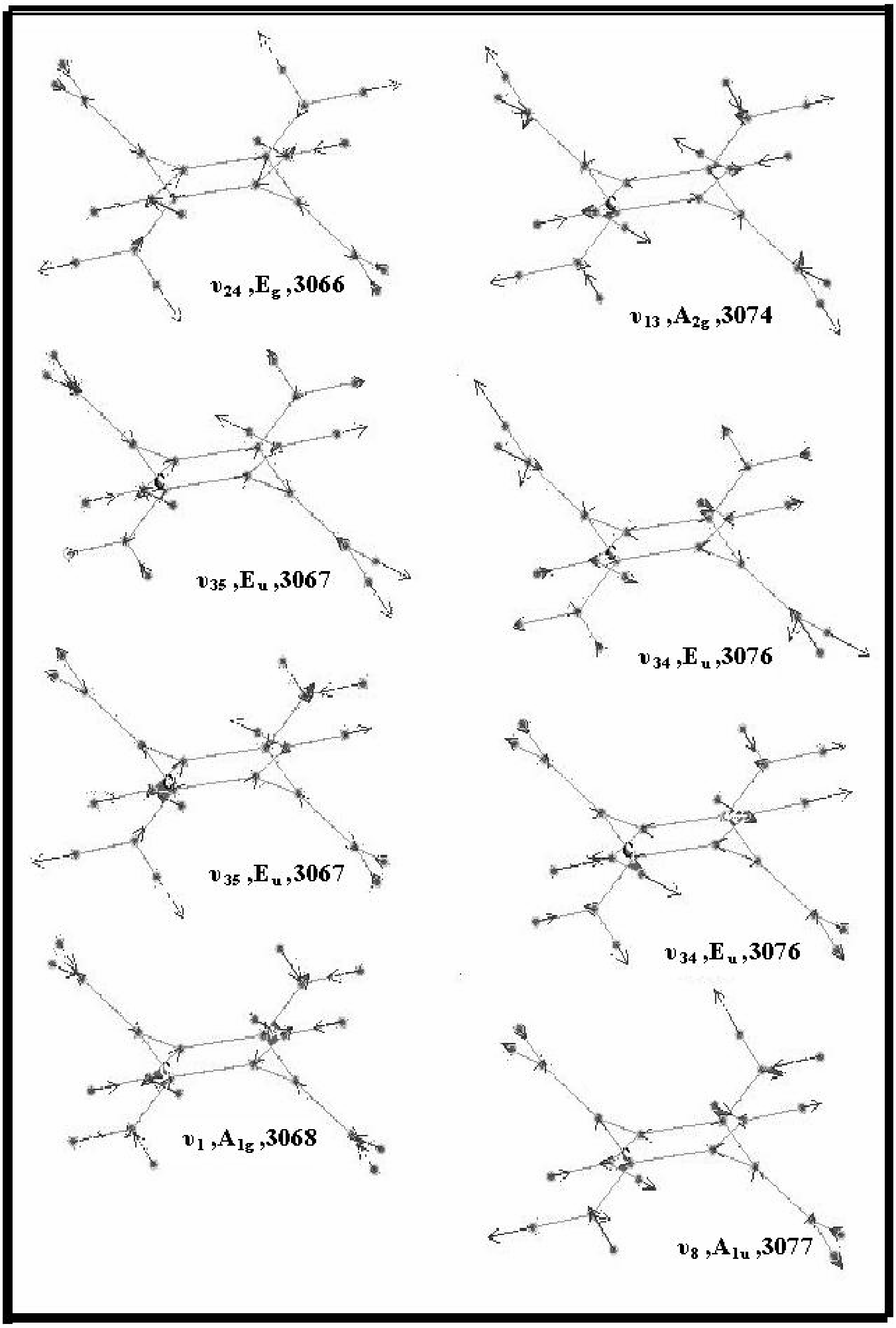


Fig. 5. The graphical representation of some vibration modes of 6R (chair conformation) as drawn through the DRAW. MOL. routine.

Table 3: Calculated vibration frequencies and IR absorption intensities for the chair conformation of 6R molecule.

Symmetry and description		MINDO/3-FORCES		PM3	expt.[17]
In-plane		Scaled Freq.cm^{-}	Intensity (A) km/mol	Freq.cm^{-1}	Freq.cm^{-1}
A_{1g}					
υ_1	$=CH_2$ sym.str.	3086	0.00	3134	------
υ_2	C=C str.	1827	0.00	1880	------
υ_3	δ ($=CH_2$ (sciss.))	1424	0.00	1347	------
υ_4	γ ($=CH_2$ (wag.))	877	0.00	1033	------
υ_5	ring puck.	764	0.00	818	------
υ_6	ring puck.	692	0.00	709	------
υ_7	γ $C=CH_2$ (wag.)	104	0.00	104	------
A_{1u}					------
υ_8	$=CH_2$ asym. str.	3094	26.87	3137	------
υ_9	ring str.	1372	0.00	1551	------
υ_{10}	δ (= CH_2 (rock.))	872	0.00	940	------
υ_{11}	δ ($=CH_2$ (twist.))	724.	0.00	561	------
υ_{12}	δ ($=CH_2$ (rock.))	281	0.00	342	------
A_{2g}					
υ_{13}	$=CH_2$ asym. Str.	3092	0.00	3139	------
υ_{14}	δ ($=CH_2$ (rock.)) + δ ring	963.	0.00	1054.	------
υ_{15}	γ ($=CH_2$ (twist.))	681	0.00	619.	------
υ_{16}	γ ring (CCC) + ($=CH_2$ (twist.))	463	0.00	540.	------
A_{2u}					
υ_{17}	$=CH_2$ sym. Str.	3084	29.74	3137	3090
υ_{18}	C=C str.	1654	0.69	1856	1652
υ_{19}	δ ($=CH_2$ (sciss.))	1401	11.44	1307	1390
υ_{20}	γ $=CH_2$ (twist.)	992	21.90	1007	1061
υ_{21}	γ ring (ring puck.)	677	1.69	699	764
υ_{22}	γ $C=CH_2$ (wag.)	172	0.27	194	------

Table 3: Continued

E_g					
υ_{23}	$=CH_2$ asym. str.	3095	0.04	3138	------
υ_{24}	$=CH_2$ sym. str.	3084	0.00	3135	------
υ_{25}	C=C str.	1659	0.00	1854	------
υ_{26}	δ ($=CH_2$ (sciss.)) + ring str.	1428	0.00	1465	------
υ_{27}	ring str.+ δ ($=CH_2$ (sciss.))	1274	0.00	1298	------
υ_{28}	δ ($=CH_2$ (rock.))	865	0.00	1007	------
υ_{29}	γ ($=CH_2$ (twist.))	991	0.01	926	------
υ_{30}	γ ($=CH_2$(twist.))	741	0.00	666	------
υ_{31}	ring (puck.)	523	0.00	524	------
υ_{32}	δ ($=CH_2$(rock.)) + ring (δ CCC)	295	0.00	335	------
υ_{33}	γ $C=CH_2$ (wag.)	225	0.00	274	------
E_u					
υ_{34}	$=CH_2$ asym. str.	3094	102.34	3139.	3090
υ_{35}	$=CH_2$ sym. str.	3085	47.28	3134.	2920
υ_{36}	C=C str.	1677	0.08	1858	1652
υ_{37}	δ ($=CH_2$ (sciss.))	1421	13.51	1350	1390
υ_{38}	ring (δ ccc)	1092	0.81	1193	------
υ_{39}	γ ($=CH_2$ (wag.))	869	5.51	1019	897
υ_{40}	δ ($=CH_2$ (rock.)) + ring (puck.)	825	1.00	873	------
υ_{41}	δ ring (puck.) + γ ($=CH_2$ (twist.))	689	1.51	732	764
υ_{42}	γ ($=CH_2$ (twist.)) + ring (puck.)	625	1.19	554	------
υ_{43}	δ ($=CH_2$(rock.)) + ring (puck.)	293	0.62	336	------
υ_{44}	γ $C=CH_2$ (wag.)	70	0.04	63	------

scaling factors: 0.875 (CH_2 str.), 0.93 (C=C str.); 1.06 (CH_2 sciss); 1.115 (CH_2 twist.).

Inspection of the frequency values in tables 2 and 3 reveals the following interesting results:

(a) νC=C str. > νC=C str.
Chair (1654 cm^{-1}) Planar (1614 cm^{-1})

(b) δ (=CH_2 (sciss.)) > δ (=CH_2 (rock.))
Planar (1450 cm^{-1}) Chair (1421 cm^{-1})

(c) γ (=CH_2 (wag.)) > γ (=CH_2 (twist.))
Planar (877 cm^{-1}) Chair (869 cm^{-1})

Comparision of the calculated frequency values with the few available experimental frequencies, show the better agreement of the chair form frequencies with the experimental frequency values. This is true for all the vibration modes and particularly for the frequency 764 cm^{-1} which seem to be completely absent in the planar form. The comparison of the calculated and experimental vibration spectra indicates the correct acceptance of a stable chair conformation for 6R.

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References

1- P. A. Waitkas, E. B. Sanders, L. I. Peterson, and G. W. Griffin, ***J. Am. Soc***., 1962, **24(22)**, 89.

2- A. J. Barkovitch, E. S. Strauss, and P. C.Volhardt, ***J. Am. Chem. Soc.,***1977, ***99,*** 8321.

3- H. Hopf and G. Maas, ***Angew. Chem., Int. Ed. Engl.,*** 1992***, 31,*** 931.

4- W. March and J. D. Dunitez, Helv. ***Chim Acta***, 1975, **58**,767.

5- G.Wilke , ***Angew .Chem .,*** 1988, ***100,*** 189.

6- A. Stranger, N. Ashkenazi, R. Bose, D. Sieser and P. Stelliberg, ***Chem, Eur. J. ,*** 1997, ***3 (No.2) ,20***.

7- V. Galasso, ***J. Mole. Struct.,*** 1993***, (Theochem , 281),*** 253.

8- N.Tyutyulkov,F. Dietz. K. Müllen, M. Baumgarten and S. Karabunarliev, ***Chemical Physics 189, 83-97*** (1994).

9- R. M. Kubba, ***Z. Naturforsc.,*** 2001, ***56a,*** 505.

10- A) D. H. Abed and M. Shanshal, ***Arbeitsberich Des Institüts FürTheoretische Chemie, Stüttgart, 27, 389*** (1990). B)-D. H. Abed, S. F. Al-Saidi and M.

Shanshal, ***Chim. Acta Turc.,*** 1995, ***23,*** 7.

11- P. Pulay, ***Mo . phys.,17,197*** (1969).

12- E. B. Wilson, Ir., J. C. Decius, P. C. Cross, **" *Molecular Vibration"***, Mc Graw-Hill, New York, (1955).

13- D. H. Abed, M. B. Mammo, S. F. Al-Saidi and M. Shanshal, ***Iraqi, J. Sci.,*** 1990, ***9 31 ,*** 539.

14- R. C. Bingham, M. J. S. Dewar and D. H. LC, ***J. Am. Chem. Soc.,*** 1975, ***97,*** 1285, 1294, 1302, 1307.

15-(a) J. J. P. Stewart, ***J. Comput . Chem .,*** **10, 209, 221** (1989). (b) R. Leach Andrew, ***"Molecular Modelling Principles and Applications***", Second Edition, Prentice Hall, London,(2001).

16- K. Shimizu, K. Miyamichi, H. Kato, T. Yonezawa, ***Nippon Kagaku Zasshi,*** 1970(Japan), ***91 (2)*** ,206.

17- P. Schiess and M. Heitzmann, ***Helv. Chim. Acta.,*** 1978**, 61,Fasc. 2–Nr.**74.