Geometry, Vibration Frequencies, Normal Coordinates and IR Absorption Intensities of [6]-Radialene

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SCF-MO calculations, using the MINDO/3-FORCES method, are reported for the equilibrium geometry, vibration frequencies and IR absorption intensities of 6-radialene, considering the planar and chair form. The chair conformation is found to be more stable. The C=C stretching frequencies of the chair form are found to be higher than those of the planar ones. The $=CH_2$ bending frequencies of the planar form are higher than those of the chair form. Also the PM3 method was used for the calculation of the vibration frequencies. Its results are compared with those of the MINDO/3-FORCES method.

Key words: [6]-Radialene; Vibration Frequencies; MINDO/3-FORCES.

1. Introduction

The radialene molecules (3R, 4R, 5R and 6R, Fig. 1) form a class of cyclic hydrocarbons $(CH)_{2n}$ possessing n ring atoms and n exocyclic double bonds. Since 1962 [1] these molecules attracted much attention because of their unique properties. Thus [6]-radialene may be considered as hexamethylene cyclohexane in which all ring carbons are sp^2-hybridized.

The synthesis and characterization of [6]-radialene were performed applying different experimental techniques [2 – 3]. Due to its instability, caused by its quick polymerization at room temperature, it was not possible to find its geometry applying X-ray diffraction. Much attention was paid to its derivatives [4 – 6]. Theoretical studies on them, using the ab initio method, were done by Galasso [7] and Tyutyulkov et al. [8]. Kubba studied theoretically the vibration spectrum of [3]-radialene, applying the MINDO/3-FORCES method [9].

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

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

$$\sum_j L_j(F_{ij} - M_{ij}\lambda) = 0. \qquad (1)$$

The solution of this equation yields both the 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 (APP) values, the

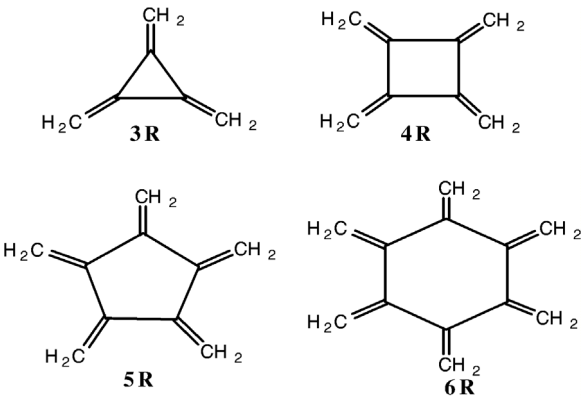

Fig. 1. [3]-, [4]-, [5]- and [6]-radialene molecules.

υ_{10}, A_{2u}, 246 υ_{42}, E_{1u}, 355

Fig. 2. DRAW.MOL graphical representation of two vibration modes of [6]-radialene; left: out of-plane; right: in-plane.

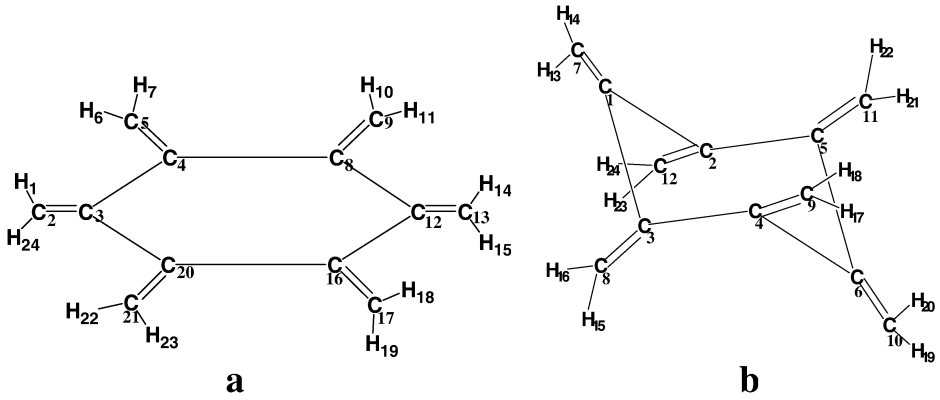

Fig. 3. Equilibrium structure of (a) the planar conformation (D_{3h}) and (b) the chair conformation (D_{3d}) of the 6R molecule as calculated by MINDO/3-FORCES and PM3 methods.

partial contribution of each atom to the molecular vibration [10]. The coefficients L allow a graphical description of the vibration modes in the molecule when introduced in the DRAW.MOL routine developed by Abed et al. [13] (Fig. 2).

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

2. Results and Discussion

The MINDO/3-FORCES treatment of [6]-radialene showed that the chair form is more stable than the planar form. It is known that this method overestimates the H_f values of cyclic planar unsaturated molecules by approximately 40% [16]. Considering this factor, the calculated H_f values are 94 kcal/mol for the planar and 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 gradient value (dE/dq_i) acceptable for the geometry optimization process in MINDO/3-FORCES is $\leq 10^{-5}$ au/au, which is lower than the acceptable gradient value in PM3, we prefer the relative order of stability as predicted by the MINDO/3-FORCES method. The evaluation of the relative stability of the chair over the planar form agrees with the experimental findings reported in [17].

The evaluation of 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 chair conformation of the 6R molecule; length (Å), angle (deg.).

Bonds lengths 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 Table 1 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. This is seen through the values of the bond angles of the planar form (HCH 107.4°) compared to those of the chair form (HCH 109.9°) (Fig. 3). The C-C-C angles of the planar form are 120°, those of the chair form are smaller (113.0°), obviously due to the bigger strain of the chair form.

The planar conformation of [6]-radialene is of D_{6h} symmetry. Its total number of fundamental vibrations $(3N-6)$ is 66, classified into the following irreducible representations:

$$\text{in-plane: } 4A_{1g}+3A_{2g}+4B_{1u}+4B_{2u}+8E_{2g}+2A_{2u}+7E_{1u},$$
$$\text{out of-plane: } B_{1g}+3B_{2g}+3E_{1g}+A_{1u}+2A_{2u}+4E_{2u},$$

where A_{1g}, E_{1g}, E_{2g}, are Raman active and IR inactive, while A_{2u}, E_{1u} are IR active and Raman inactive. It is

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

Symmetry and description		MINDO/3-FORCES Frequency [cm^{-1}]	Intensity [km/mol]	PM3 Frequency [cm^{-1}]	Expt. [17] Frequency [cm^{-1}]
In-plane:					
A_{1g}					
ν_1	=CH_2 sym.str.	3091	0.00	3152	–
ν_2	C=C str.	1631	0.00	1744	–
ν_3	δ (=CH_2 sciss.)	1463	0.00	1402	–
ν_4	δ ring breathing	660	0.00	716	–
A_{2g}					
ν_6	=CH_2 sym.str.	3080	0.00	3120	–
ν_7	δ (=CH_2 rock.) + ring(δ CCC)	973	0.00	1105	–
ν_8	ring (δ CCC) + δ (=CH_2 rock.)	524	0.00	638	–
B_{1u}					
ν_{12}	=CH_2 sym.str.	3086	0.00	3138	–
ν_{13}	C=C str.	1643	0.00	1762	–
ν_{14}	δ (=CH_2 sciss.)	1406	0.00	1413	–
ν_{15}	δ ring (CCC)	572	0.00	590	–
ν_{23}	γ(=CH_2 wag.)	874	0.00	920	–
B_{2u}					
ν_{19}	=CH_2 sym.str.	3089	0.00	3138	–
ν_{20}	ring str.	1426	0.00	1468	–
ν_{21}	δ (=CH_2 rock.)	895	0.00	970	–
ν_{22}	δ (=CH_2 rock.)	451	0.00	638	–
E_{1u}					
ν_{26}	=CH_2 sym.str.	3089	71.79	3148	3090
ν_{27}	=CH_2 asym.str.	3083	75.02	3140	2920
ν_{28}	C=C str.	1614	2.41	1723	1652
ν_{29}	δ (=CH_2 sciss.)	1450	12.46	1436	1390
ν_{30}	δ ring (CCC)	1109	2.67	1205	1061
ν_{31}	δ (=CH_2 rock.) + ring (δ CCC)	819	1.53	936	–
ν_{32}	δ (=CH_2 rock.) + ring (δ CCC)	355	1.18	440	–
E_{2g}					
ν_{33}	=CH_2 sym.str.	3087	0.00	3133	–
ν_{34}	=CH_2 asym.str.	3084	0.00	3130	–
ν_{35}	C=C str.	1626	0.00	1714	–
ν_{36}	ring str. + δ (=CH_2 sciss.)	1367	0.00	1484	–
ν_{37}	ring str. + δ (=CH_2 sciss.)	1307	0.00	1363	–
ν_{38}	δ (=CH_2 rock.)	880	0.00	949	–
ν_{39}	δ (=CH_2 rock.)	413	0.00	537	–
ν_{40}	ring (δ CCC)	391	0.00	438	–

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.).

Inspection of the frequencies in Table 2 reveals the following relations:

$$\begin{aligned} \nu\,\mathrm{sym}(=\mathrm{CH_2\,str.}) &> \nu\,\mathrm{asym}(=\mathrm{CH_2 str.}),\\ \delta\,(=\mathrm{CH_2\,sciss.}) &> \delta\,(=\mathrm{CH_2\,rock.}),\\ \gamma(=\mathrm{CH_2\,wag.}) &> \gamma(=\mathrm{CH_2\,(twist.)}). \end{aligned}$$

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

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

Table 2 (continued).

Symmetry and description		MINDO/3-FORCES Frequency [cm^{-1}]	Intensity [km/mol]	PM3 Frequency [cm^{-1}]	Expt. [17] Frequency [cm^{-1}]
Out of-plane:					
A_{1u}					
ν_5	γ(=CH_2 twist.)	645	0.00	665	–
A_{2u}					
ν_9	γ(=CH_2 wag.)	877	11.81	915	897
ν_{10}	γC=CH_2 wag.)	246	0.01	327	–
B_{1g}					
ν_{11}	γ(=CH_2 twist.)	628	0.00	597	–
B_{2g}					
ν_{16}	γ(=CH_2 wag.)	1001	0.00	949	–
ν_{17}	ring puck.	762	0.00	770	–
ν_{18}	γ(C=CH_2 wag.)	3	0.00	15	–
E_{1g}					
ν_{23}	γ(=CH_2 wag.)	874	0.00	920	–
ν_{24}	γ(=CH_2 twist. + γ(CC)	607	0.00	674	–
ν_{25}	γ(CC)	318	0.00	415	–
E_{2u}					
ν_{41}	γ(=CH_2 wag.)	870	0.00	936	–
ν_{42}	ring puck.	701	0.00	773	–
ν_{43}	γ(CC) + γ(=CH_2 twist.)	486	0.00	528	–
ν_{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.).

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

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

$$\begin{aligned} \nu\,\mathrm{asym}(=\mathrm{CH_2\,str.}) &> \nu\,\mathrm{sym}(=\mathrm{CH_2\,str.})\\ &\text{(in contrast to that of the planar form)}\\ \delta\,(=\mathrm{CH_2\,sciss.}) &> \delta\,(=\mathrm{CH_2\,rock.}),\\ \gamma(=\mathrm{CH_2\,wag.}) &> \gamma(=\mathrm{CH_2\,twist.}). \end{aligned}$$

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

Inspection of the frequencies in Tables 2 and 3 reveals the following interesting results:

a) ν(C=C str.) chair ($1654\ cm^{-1}$) > ν(C=C str.) planar ($1614\ cm^{-1}$),

b) δ (=CH_2 sciss.) planar ($1450\ cm^{-1}$) > δ (=CH_2 rock.) chair ($1421\ cm^{-1}$),

c) γ(=CH_2 wag.) planar ($877\ cm^{-1}$) > γ(=CH_2 twist.) chair ($869\ cm^{-1}$).

Comparison of the calculated frequencies with the few available experimental ones, shows the better

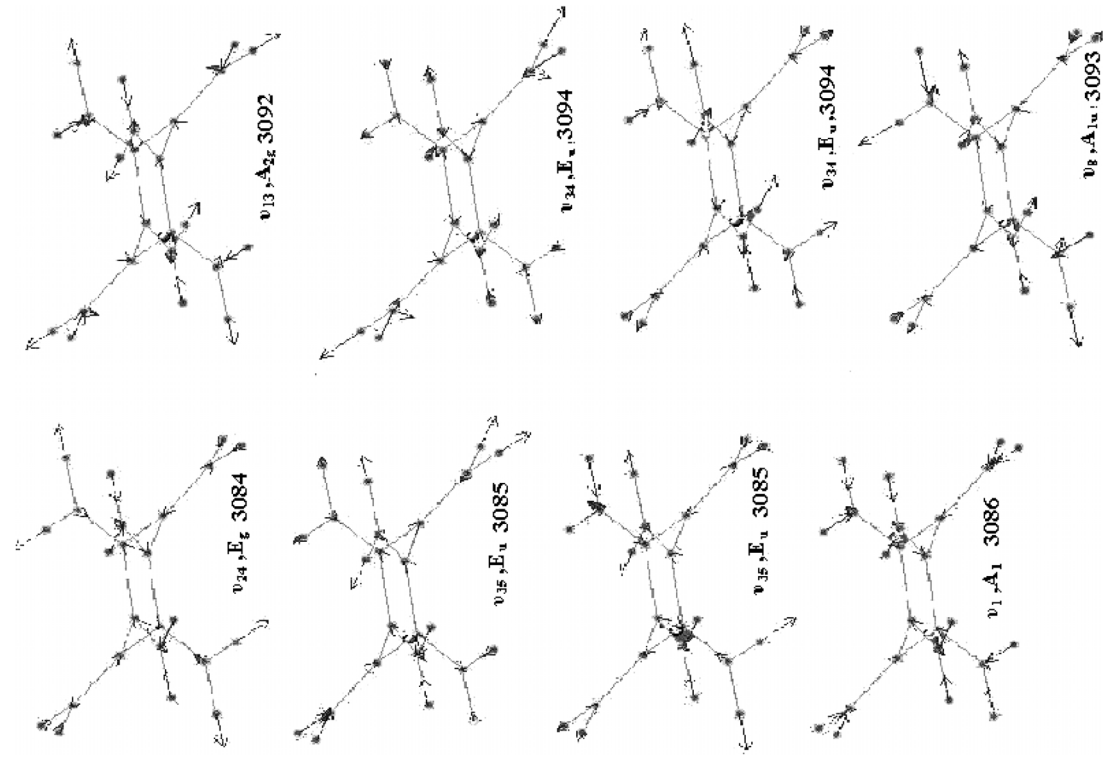

Fig. 5. Graphical representation of some vibration modes of the 6R molecule (chair conformation) as drawn through the DRAW.MOL routine.

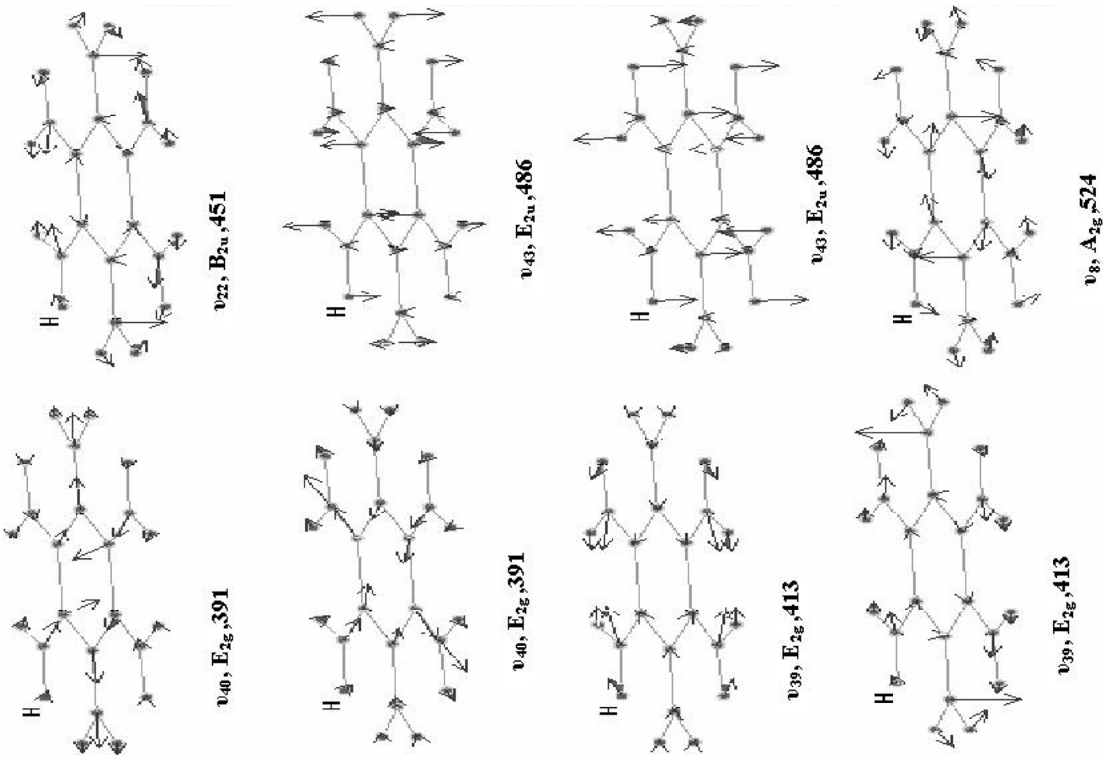

Fig. 4. Graphical representation of some vibration modes of the 6R molecule (planar conformation) as drawn through the DRAW.MOL routine.

Table 3. Calculated vibration frequencies and IR absorption intensities for the chair conformation of the 6R molecule.1

Symmetry and description	MINDO/3-FORCES		PM3	Expt. [17]	Symmetry and description	MINDO/3-FORCES		PM3	Expt. [17]
In-plane	Scaled frequency [cm^{-1}]	Intensity [km/mol]	Frequency [cm^{-1}]	[cm^{-1}]	In-plane	Scaled frequency [cm^{-1}]	Intensity [km/mol]	Frequency [cm^{-1}]	[cm^{-1}]
A_{1g}					E_g				
ν_1 =CH_2 sym.str.	3086	0.00	3134	–	ν_{23} =CH_2 asym.str.	3095	0.04	3138	–
ν_2 C=C str.	1827	0.00	1880	–	ν_{24} =CH_2 sym.str.	3084	0.00	3135	–
ν_3 δ(=CH_2 sciss.)	1424	0.00	1347	–	ν_{25} C=C str.	1659	0.00	1854	–
ν_4 γ(=CH_2 wag.)	877	0.00	1033	–	ν_{26} δ(=CH_2 sciss.) + ring str.	1428	0.00	1465	–
ν_5 ring puck.	764	0.00	818	–	ν_{27} ring str. + δ(=CH_2 sciss.)	1274	0.00	1298	–
ν_6 ring puck.	692	0.00	709	–	ν_{28} δ(=CH_2 rock.)	865	0.00	1007	–
ν_7 γ(C=CH_2 wag.)	104	0.00	104	–	ν_{29} γ(=CH_2 twist.)	991	0.01	926	–
A_{1u}				–	ν_{30} γ(=CH_2 twist.)	741	0.00	666	–
ν_8 =CH_2 asym.str.	3094	26.87	3137	–	ν_{31} ring puck.	523	0.00	524	–
ν_9 ring str.	1372	0.00	1551	–	ν_{32} δ(=CH_2 rock.) + ring (δ CCC)	295	0.00	335	–
ν_{10} δ(= CH_2 rock.)	872	0.00	940	–	ν_{33} γ(C=CH_2 wag.)	225	0.00	274	–
ν_{11} δ(=CH_2 twist.)	724	0.00	561	–	E_u				
ν_{12} δ(=CH_2 rock.)	281	0.00	342	–	ν_{34} =CH_2 asym.str.	3094	102.34	3139	3090
A_{2g}					ν_{35} =CH_2 sym.str.	3085	47.28	3134	2920
ν_{13} =CH_2 asym.str.	3092	0.00	3139	–	ν_{36} C=C str.	1677	0.08	1858	1652
ν_{14} δ(=CH_2 rock.) + δ ring	963	0.00	1054	–	ν_{37} δ(=CH_2 sciss.)	1421	13.51	1350	1390
ν_{15} γ(=CH_2 twist.)	681	0.00	619	–	ν_{38} ring (δ CCC)	1092	0.81	1193	–
ν_{16} γ(ring CCC) + (=CH_2 twist.)	463	0.00	540	–	ν_{39} γ(=CH_2 wag.)	869	5.51	1019	897
A_{2u}					ν_{40} δ(=CH_2 rock.) + ring puck.	825	1.00	873	–
ν_{17} =CH_2 sym.str.	3084	29.74	3137	3090	ν_{41} δ(ring puck.) + γ(=CH_2 twist.)	689	1.51	732	764
ν_{18} C=C str.	1654	0.69	1856	1652	ν_{42} γ(=CH_2 twist.) + ring puck.	625	1.19	554	–
ν_{19} δ(=CH_2 sciss.)	1401	11.44	1307	1390	ν_{43} δ(=CH_2 rock.) + ring puck.	293	0.62	336	–
ν_{20} γ(=CH_2 twist.)	992	21.90	1007	1061	ν_{44} γ(C=CH_2 wag.)	70	0.04	63	–
ν_{21} γ(ring puck.)	677	1.69	699	764					
ν_{22} γ(C=CH_2 wag.)	172	0.27	194	–					

Scaling factors: 0.875 (CH_2 str.), 0.93 (C=C str.), 1.06 (CH_2 sciss.), 1.115 (CH_2 twist.), 0.112 (rock.).

agreement of the chair form frequencies with the experimental ones. This is true for all vibration modes, and particularly for the frequency 764 cm^{-1}, which seems to be completely absent in the planar form. The comparison of the calculated with the experimental vibration spectra indicates the chair conformation is the stable one 6R.

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[1] P. A. Waitkas, E. B. Sanders, L. I. Peterson, and G. W. Griffin, J. Am. Chem. Soc. **89**, 24 (1962).
[2] A. J. Barkovitch, E. S. Strauss, and P. C. Volhardt, J. Am. Chem. Soc. **99**, 8321 (1977).
[3] H. Hopf and G. Maas, Angew. Chem., Int. Ed. Engl. **31**, 931 (1992).
[4] W. March and J. D. Dunitez, Helv. Chim. Acta **58**, 767 (1975).
[5] G. Wilke, Angew. Chem. **100**, 189 (1988).
[6] A. Stranger, N. Ashkenazi, R. Bose, D. Sieser, and P. Stellberg, Chem. Eur. J. **3**, 208 (1997).
[7] V. Galasso, J. Mole. Struct. Theochem. **281**, 253 (1993).
[8] N. Tyutyulkov, F. Dietz, K. Müllen, M. Baumgarten, and S. Karabunarliev, Chem. Phys. **189**, 83 (1994).
[9] R. M. Kubba, Z. Naturforsch. **56a**, 505 (2001).
[10] a) D. H. Abed and M. Shanshal, Arbeitsbericht des Instituts für Theoretische Chemie, Stuttgart **27**, 389 (1990); b) D. H. Abed, S. F. Al-Saidi, and M. Shanshal, Chim. Acta Turc. **23**, 7 (1995).
[11] P. Pulay, Mol. Phys. **17**, 197 (1969).
[12] E. B. Wilson jr., J. C. Decius, and 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. **9**, 31, 539 (1990).
[14] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Am. Chem. Soc. **97**, 1285, 1294, 1302, 1307 (1975).
[15] a) J. J. P. Stewart, J. Comput. Chem. **10**, 209, 221 (1989); b) R. L. Andrew, Molecular Modelling Principles and Applications, 2nd Ed., Prentice Hall, London 2001.
[16] K. Shimizu, K. Miyamichi, H. Kato, and T. Yonezawa, Nippon Kagaku Zasshi **91**, 206 (1970) (in Japanese).
[17] P. Schiess and M. Heitzmann, Helv. Chim. Acta **61**, 2 (1978).