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Vibration Frequencies , Normal Coordinates and IR Absorption Intensities of 1-; 1,2-; 1,3- and 1,2,3- Methylene Cyclobutane Dirivatives

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Abstract

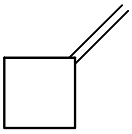
SCF-MO calculations of the vibration frequencies and IR absorption intensities, applying the MINDO/3-FORCES method, are reported for the four molecules, mono-, di- (1,2- and 1,3-), and 1,2,3-trimethylene cyclobutane. In addition, normal coordinate analysis of all vibration modes is described for each molecule. The obtained results allow interesting correlations between the frequencies of similar modes as calculated for the different methylene cyclobutanes.

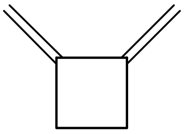
الخلاصة

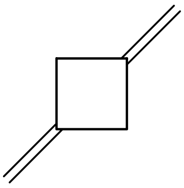
تم حساب ترددات اهتزاز و شدة امتصاص الاشعة تحت الحمراء باسلوب MINDO/3-FORCES لجزيئات احادي و ثنائي(1,2- و1,3-) وثلاثي (1,2,3-) مثلين سايكلوبيوتان الاربع، اضافة الى تصنيف جميع الانماط الاهتزازية(3N-6) العائدة لهذه الجزيئات تماثليا و تكافؤيا. تضمنت النتائج التي تم الحصول عليها علاقات مهمة تربط بين الانماط الاهتزازية المتشابهة في التصنيف التكافؤي للجزيئات الاربع و المختلفة في عدد مجاميع المثلين.

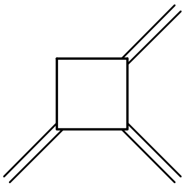
Introduction

The molecules for which calculations were done, are cyclobutane derivatives in which one, two or three CH_2 groups are replaced by one, two or three **$C=CH_2$** to form **mono-, di-** and **tri-**methylene cyclobutane as shown below:


MCB


1,2-DMCB


1,3-DMCB


1,2,3-TMCB

Monomethylene cyclobutane **(MCB)** was synthesized and characterized by different researh groups [1,2]. Theoretical calculations, applying the ab initio method were also performed for this molecule [3]. The two isomers **1,2-** and **1,3**-dimethylene-cyclobutane **(1,2- DMCB and 1,3- DMCB)** were synthesized and characterized by different research groups too[4,5]. Dewar et al. studied the equilibrum geometries and heats of formation of these two isomers applying the MINDO/3 method [6]. An x-ray diffraction measurement for 1,2 dimethylene cyclobutane showed that the molecule is planar with C_{2V} symmetry [7]. Little work was done for trimethylene cyclobutane **(TMCB)** as might be found on studying the literature, obviously due to the fact that this molecule dimerizes quickly at room temperature. Williams and Sharkey [5] could isolate it and characterize its IR spectrum at -80C^o.

The present study is based on the MINDO/3-FORCES method, as described and applied for many other molecules by Shanshal et al. [8]. In this method the force constants are estimated applying Pulay's FORCES method [9]. Applying the so evaluated force constants to the Wilson's Secular equation [10];

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

and solving the equation, one obtains both vibration frequencies **($\lambda = 4\pi^2c^2 \nu^2$)** and vibration mode's eigenvector coefficients (L_j). These coefficients allow the graphical description of the vibration modes of each atom in the molecule when introduced to the DRAW.MOL routine developed by Shanshal et al. [11]. The same coefficients are used to evaluate the partial participation (APP) values [12] of each atom in each vibration mode too. PM3 program [13] were applied for the calculations of the vibration frequencies for these molecules present too.

Results and Discussion

In the present study, the equilibrium geometry of each molecule was calculated, minimizing the total energy of the molecule as a function of all its 3N cartesian coordinates. The calculated geometry values are listed in Table 1.

It is found that the calculated heat of formation value (ΔH_f kJ/mol.) decreases as the number of substituted methylene groups increases:

MCB > 1,3- DMCB > 1,2- DMCB > TMCB
71.57 kJ/ mol 176.54 kJ/ mol 177.96 kJ/ mol 284.34 kJ/ mol

1,2-DMCB is found slightly less stable than 1,3-DMCB. A possible reason is the different repulsion energies between the adjacent atoms of the two exo-methylene groups. These results are in quantitative agreement with those of the PM3 method when applied to the same problem as shown in Table 2.

The calculated vibration frequencies, these were scaled applying the following scaling factors [15]: 0.87 ($C=CH_2$ str.), 0.85 (ring CH_2 str.), 0.88 (C=C str.), 1.06 ($C=CH_2$ sciss.), 1.05 (ring CH_2 sciss.), 1.06 ($=CH_2$ sciss. +

ring str.), 1.05 (ring CH_2 sciss. + ring str.), and no scaling for others.

For methylene cyclobutane (MCB), $\mathbf{C_{2V}}$, (fig.1), the total number of fundamental vibrations is 33. According to the group theoretical argumentation [16] the vibration modes are classified into the following irreducible representations:

$\mathbf{11\,A_1 + 5A_2 + 9B_1 + 8B_2}$

Where $\mathbf{A_1}$, $\mathbf{B_1}$ and $\mathbf{B_2}$ vibration modes are Raman and IR active, while $\mathbf{A_2}$ modes are Raman active only. Our treatment based on the MINDO/3-FORCES method yielded all these vibration modes correctly. The scaled frequency values are listed in Table 2 together with the calculated IR absorption intensities as well as the frequency values obtained by and PM3 method. Fig. 2. shows the graphical representation of some vibration modes of (MCB) molecule as drawn through the DRAW. MOL. routine.

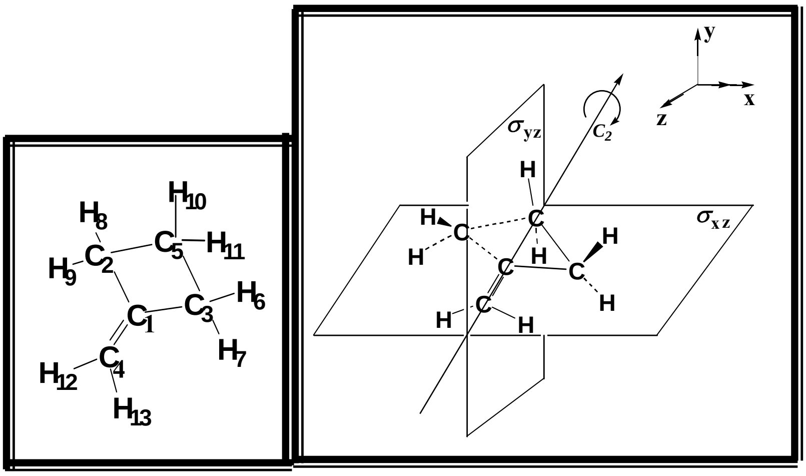


Fig. 1: Equilibrium geometry of methylene-cyclobutane (MCB, C_{2V}) as calculated applying MINDO/3-FORCES and PM3 methods.

Table 1. MINDO/3-FORCES calculated geometric values of methylene-cyclobutane, length (A°)/ angle (deg.).

THIS WORK		OTHER WORK	
Bond length, bond angles and Dihedral angles	**MINDO/3-FORCES**	**exptl. [17a]**	**calcd. [17b]**
(=C-H vinyl)	1.100	1.104	1.089
$(C_2\text{-}H_8),(C_3\text{-}H_6),(C_2\text{-}H_9),(C_3\text{-}H_7)$	1.115	1.104	1.105
$(C_5\text{-}H_{10}),(C_5\text{-}H_{11})$	1.113	1.104	1.105
C=C	1.330	1.331	1.333
$(C_1\text{-}C_2)$, $(C_1\text{-}C_3)$	1.522	1517	1520
$(C_2\text{-}C_5)$, $(C_3\text{-}C_5)$	1.524	1.565	1.553
C=C-C	135.2	——	——
$<C_2C_1C_3$	89.7	——	——
$<C_1 C_3 C_5$, $< C_1C_2C_5$	90.4	——	——
$<C_2CC_3$	89.6	——	——
<HC=C	124.7	——	——
<HCC	115.7	——	——
φ HC=CC	0.00	——	——
$\varphi H_6C_3C_1C_2$, $\varphi H_8C_2C_1C_3$	119.4	——	——
φC=C-C-C	180.0	——	——
φCCCC ring	0.00	——	——

Table 2: Calculated vibration frequencies and IR absorption intensities for methylene-cyclobutane, compared with available experimental frequencies.

Symmetry and description		MINDO/3-FORCES		PM3	expt.[18]
		Scaled Freq. cm-1	Intensity A km/mol	Freq. cm^{-1}	Freq. cm^{-1}
A_1					
υ_1	$=CH_2$ sym.str.	3069	21.30	3130	3070
υ_2	ring CH_2 sym.str.(5)	3907	69.63	3035	2935
υ_3	ring CH_2 sym.str.(2,3,5)	2931	1.02	3025	-------
υ_4	C=C str.	1669	0.56	1890	1665
υ_5	ring str.+ ring (δ CH_2 sciss.)	1422	0.23	1395	1395
υ_6	δ ($=CH_2$ sciss.) + ring str.	1406	1.75	1335	1385
υ_7	δ ($=CH_2$ sciss.)+ ring(δ CH_2 sciss.)	1400	0.24	1315	-------
υ_8	ring (δ CH_2 sciss.) + ring str.	1338	27.03	1280	-------
υ_9	ring (δ CH_2 sciss.)	1198	8.87	1122	1175
υ_{10}	ring(δ CH_2 sciss.) + δ ring(CCC)	1007	5.87	965	990
υ_{11}	ring (δ CCC)	578	0.06	610	-------
A_2					
υ_{12}	ring CH_2 asym.str.	2900	0.01	3020	-------
υ_{13}	ring (δ CH_2 rock)	1041	0.00	1126	-------
υ_{14}	ring(γ CH_2 twist.) + γ ($=CH_2$ twist.)	929	0.00	970	-------
υ_{15}	Ring(δ CH_2 rock.) + γ ($=CH_2$ twist.)	744	0.00	806	-------
υ_{16}	γ ($=CH_2$ twist.) + ring (δ CH_2 rock.)	686	0.00	612	-------
B_1					
υ_{17}	$=CH_2$ asym.str.	3080	1.02	3025	3082
υ_{18}	ring CH_2 sym.str.(2,3)	2905	0.56	1890	2900
υ_{19}	ring (CC str.)+ring(δ CH_2 sciss.)	1423	0.23	1395	-------
υ_{20}	ring str.+ ring(δ CH_2 sciss.) (2,3)	1274	1.75	1335	1228
υ_{21}	ring str.+ ring(γ CH_2 wag.)(2,3)	1225	0.24	1315	-------
υ_{22}	ring (γ CH_2 wag.) + ring str.	1134	1134	1133	1150

Table 2: Continued

υ_{23}	ring (γ CH_2 wag.) + ring str.	1044	3.40	1123	1055
υ_{24}	δ (= CH_2 rock.) + δ ring (def.)	868	0.84	1002	870
υ_{25}	δ (= CH_2 rock.) + δ ring (def.)	339	0.26	307	-------
B_2					
υ_{26}	ring CH_2 asym. str.	2918	119.23	3045	-------
υ_{27}	ring CH_2 asym.str.	2895	33.87	3017	2870
υ_{28}	ring(γ CH_2 twist.)	1057	0.08	1107	-------
υ_{29}	γ ring (puck.) + ring(δ CH_2 rock.)	980	4.07	1008	960
υ_{30}	γ (= CH_2 twist.)	870	1.26	913	-------
υ_{31}	Ring (γ CH_2 rock.)	692	3.00	709	715
υ_{32}	γ ring (puck.)+ring (δ CH_2 rock.)	397	0.01	416	-------
υ_{33}	γ ring(puck.) + ring (δ CH_2 rock.)	143	0.00	228	-------

scaling factors [13]: 0.87 (C= CH_2 str.), 0.85 (ring CH_2 str.), 0.88 (C=C str.), 1.06 (C= CH_2 sciss.), 1.05 (ring CH_2 sciss.), 1.06 (= CH_2 sciss. + ring str.), 1.05 (ring CH_2 sciss. + ring str.).

γ : in-plane

δ : out of plane

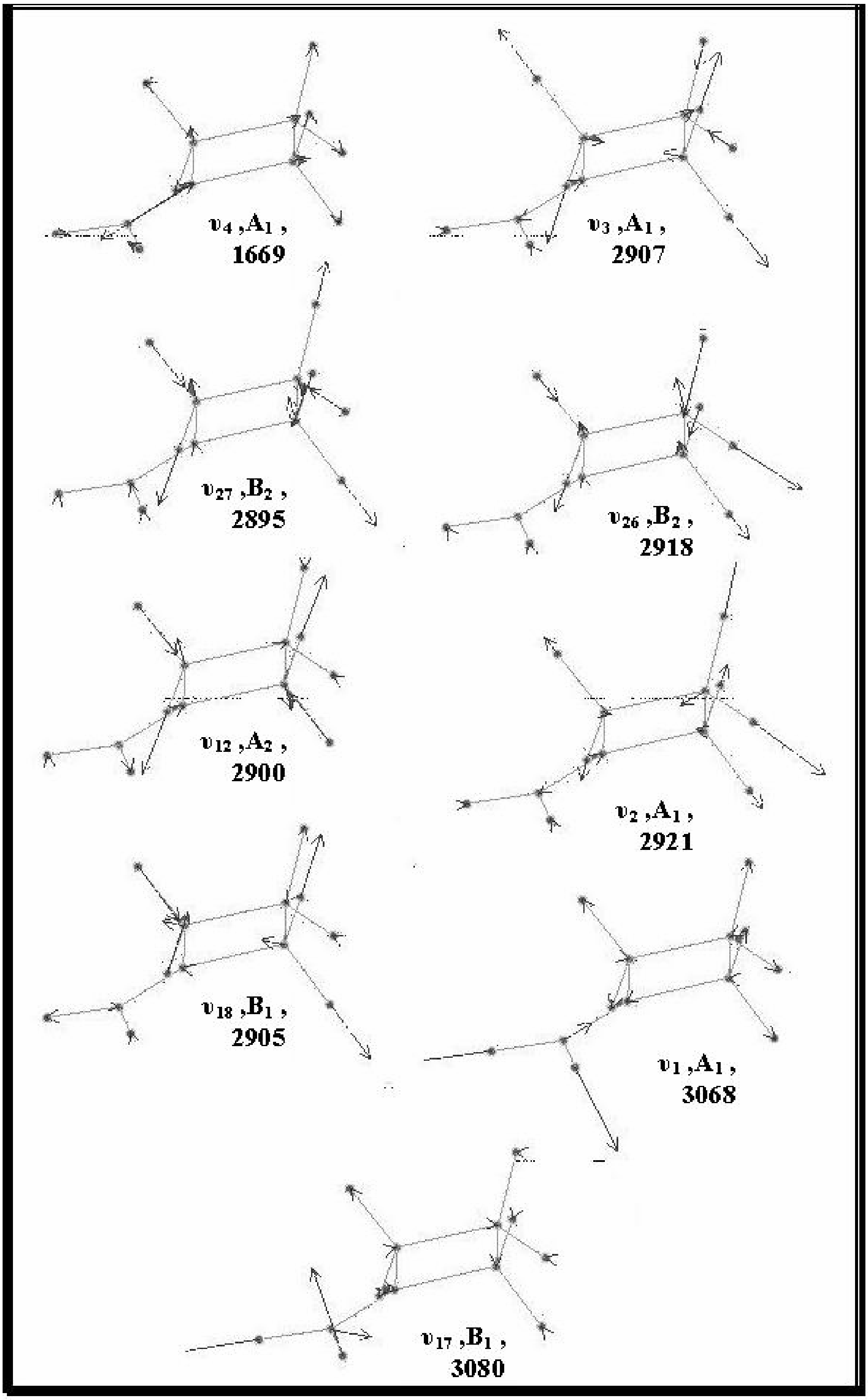


Fig. 2. The graphical representation of some vibration modes of (MCB) molecule as drawn through the DRAW. MOL. routine.

For 1,2- dimethylene cyclobutane, with C_{2V} symmetry (fig.3), the calculated geometry values are listed in table 3. It possess 36 vibration modes. These are classified into the following irreducible representations:

$$\mathbf{12\ A_1 + 7A_2 + 11B_1 + 6B_2}$$

The corresponding scaled frequencies for all these modes are listed in table 4.

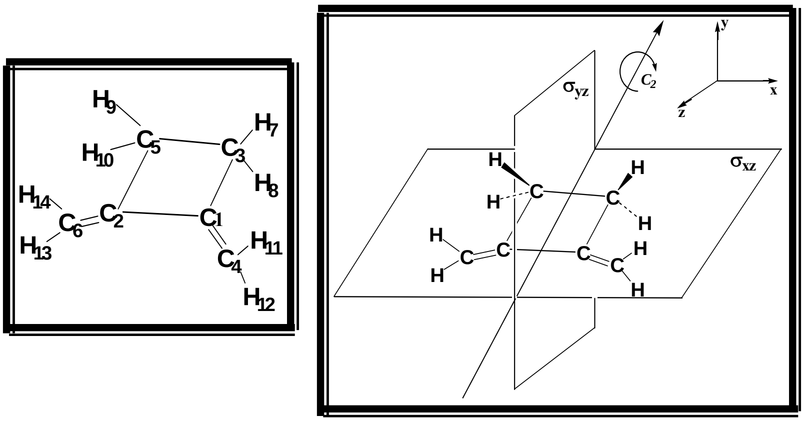


Fig. 3: Equilibrium geometry for 1,2-bis (methylene) cyclobutane (DMCB) molecule with C_{2V} symmetry as calculated by MINDO/3-FORCES and PM3 methods.

Table 3. MINDO/3-FORCES calculated geometric parameters of 1.2-bis methylene cyclobutane, length (A°)/ angle (deg.).

THIS WORK		OTHER WORK	
Bond lengths, angles and Dihedral angles	MINDO/3-FORCES	exptl. [19]	Calcd. [20]
(=C-H vinyl)	1.100	1.111	1.100
(C=C)	1.332	1.343	1.332
(C_1-C_2)	1.518	1.486	1.518
(C_1-C_2),(C_2-C_5)	1.522	1.530	1.522
(C_3-C_5)	1.523	1.575	1.523
(C-H ring)	1.114	1.122	1.114
$< C_1 C_3 C_5$, $< C_2C_5C_3$	89.9	——	90.1
$< C_2 C_1 C_3$, $< C_1C_2C_5$	90.1	91.5	——
$< H_7 C_3 H_8$, $< H_9C_5H_{10}$	103.9	——	104.0
$< H_7 C_3 C_5$, $< H_8C_3C_5$	115.7	110.3	——
$< H_{11} C_4 H_{12}$, $< H_{13}C_6H_{14}$	110.5	——	110.5
$< C_4 C_1 C_2$, $< C_6C_2C_1$	135.6	——	135.6
$< C_4 C_1 C_3$, $< C_6C_2C_5$	134.3	133.8	——
$< H_{11} C_4 C_1$, $< H_{12}C_4C_1$	125.1	123.7	——
$\varphi\ H_{12}C_4C_1C_2$	0.0	——	——
$\varphi\ C_4C_1C_3 C_5$	180.0	——	——
$\varphi\ C_1C_2C_5 C_3$	0.00	——	——

Table 4: Calculated vibration frequencies and IR absorption intensities for 1,2-bis methylene-cyclobutane, compared with available experimental frequencies.

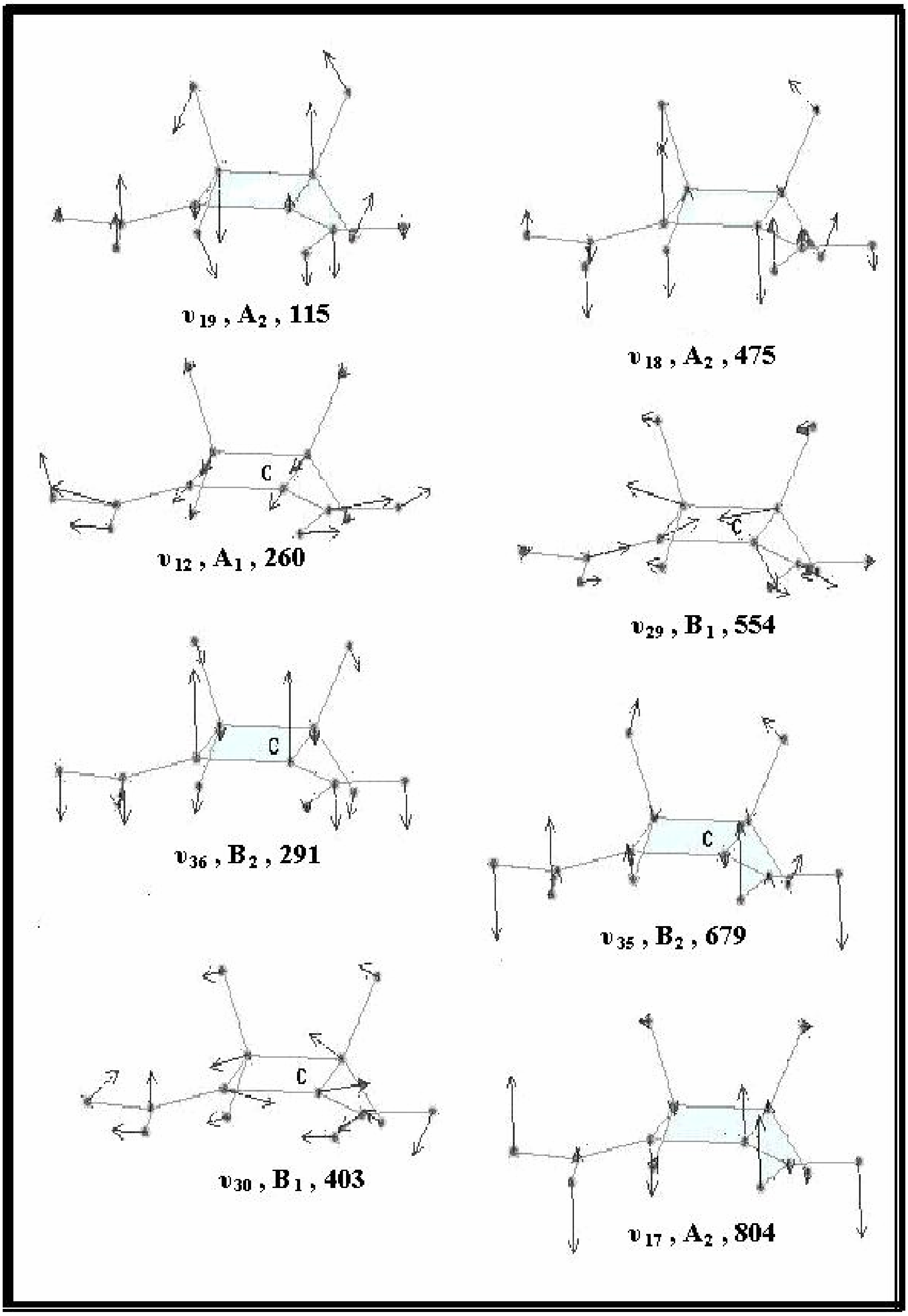
Symmetry and description		MINDO/3-FORCES		PM3	expt.[ ]
In-plane		Freq. cm^{-} Scaled	Intensity A km/mol	Freq. cm^{-1}	Freq. cm^{-1}
A_1					
υ_1	=CH_2 sym.str.(1,2)	3081	44.01	3143	3080
υ_2	=CH_2 sym.str.(1,2)	3069	13.15	3129	3065
υ_3	ring CH_2 sym.str.	2913	88.24	3037	2925
υ_4	C=C str.	1683	0.29	1902	1640
υ_5	ring str.+ ring δ CH_2 (sciss.)	1390	2.46	1406	1380
υ_6	δ(=CH_2 (sciss.))(1,2) + ring str.	1416	3.81	1372	——
υ_7	ring str. + ring δ CH_2 (sciss.)	1266	15.89	1290	1240
υ_8	ring str.	1212	0.49	1259	——
υ_9	ring δ CH_2 (sciss.) + ring str.	1136	5.83	1107	1125
υ_{10}	ring (def.)+ring δ CH_2(sciss.)	939	1.74	996	——
υ_{11}	δ(=CH_2(rock.))(1,2)+ring(def.)	828	0.53	884	——
υ_{12}	δ(=CH2(rock.))(1,2)+ring(def.)	260	0.15	315	——
A_2					
υ_{13}	=CH_2 sym.str.(1,2)	2896	0.00	3027	——
υ_{14}	=CH_2 sym.str.(1,2)	1046.	0.00	1103	——
υ_{15}	ring CH_2 sym.str.	939.	0.00	997	——
υ_{16}	C=C str.	865.	0.00	923	——
υ_{17}	ring str.+ring δ CH_2 (sciss.)	804.	0.00	723	——
υ_{18}	δ(=CH_2 (sciss.))(1,2) + ring str.	475.	0.00	531	——
υ_{19}	ring str.+ring δ CH_2 (sciss.)	115.	0.00	208	——
B_1	ring str.				
υ_{20}	ring δ CH_2 (sciss.) + ring str.	3079.	34.62	3142	——
υ_{21}	ring (def.) + ring δ CH_2(sciss.)	3067.	27.94	3120	——
υ_{22}	δ(=CH_2(rock.))(1,2)+ring(def.)	2906.	50.28	3031	2890
υ_{23}	δ(=CH2(rock.))(1,2)+ring(def.)	1617.	0.37	1851	——

Table 4: Continued

υ_{24}	ring δ CH_2 sciss. + ring str.	1406	8.20	1362	——
υ_{25}	ring δ CH_2(sciss.)+ δ(=CH_2 (sciss.))(1,2)	1382	0.02	1350	——
υ_{26}	ring str.+ ring δ CH_2(sciss.)	1233	11.60	1273	——
υ_{27}	ring δ CH_2(sciss.) + ring(def.)	1138	2.84	1138	——
υ_{28}	δ =CH_2(rock.)(1,2) + ring(def.)	876	0.00	926	——
υ_{29}	ring(def.) + CC=C (def.)	554	0.41	618	——
υ_{30}	ring (def.) + δ(=CH_2 (rock.))(1,2)	403	0.81	512	——
B_2					
υ_{31}	ring CH_2 asym.str.(rock.)	2909	109.30	3037	2930
υ_{32}	ring δ CH_2(rock.) + ring(puck.)	970.	1.97	1022	950
υ_{33}	γ (=CH2(wag.))(1,2)	870.	4.07	929	880
υ_{34}	ring δ CH_2(rock.) + ring(puck.)	717	2.75	803	725
υ_{35}	γ (=CH_2(twist.))(1,2)+ring δ CH_2(rock.)	679	0.11	619	——
υ_{36}	γ (C=C) + ring(puck.)	291	0.03	415	——

scaling factors [13]: 0.87 (C=CH_2 str.), 0.85 (ring CH_2 str.), 0.88 (C=C str.), 1.06 (C=CH_2 sciss.), 1.05 (ring CH_2 sciss.), 1.20 (=CH_2 twist.), 1.06 (=CH_2 sciss. + ring str.), 1.05 (ring CH_2 sciss. + ring str.), and 1.00 for others.

Fig. 4. shows the graphical representation of some vibration modes of 1,2-dimethylene cyclobutane C_{2v} as drawn through the DRAW. MOL. routine.



ν_{19} , A_2 , 115

ν_{18} , A_2 , 475

ν_{12} , A_1 , 260

ν_{29} , B_1 , 554

ν_{36} , B_2 , 291

ν_{35} , B_2 , 679

ν_{30} , B_1 , 403

ν_{17} , A_2 , 804

Fig. 4. Graphical representation of some vibration modes of 1.2,bis, methylene cyclobutane as drawn through the DRAW. MOL routine.

As for 1,3-dimethylene cyclobutane(DMCB), D_{2h}, (fig. 5) the calculated geometric values are listed in table 5. Its total number of vibrations (3N-6) is 36. These are classified into the following irreducible representation:

$\mathbf{7A_g + 3B_{1g} + 3B_{2g} + 5B_{3g} + 2A_u + 5B_{1u} + 6B_{2u} + 5B_{3u}}$

where $\mathbf{A_g}$, $\mathbf{B_{1g}}$, $\mathbf{B_{2g}}$ and $\mathbf{B_{3g}}$ modes are Raman and IR inactive; $\mathbf{B_{1u}}$, $\mathbf{B_{2u}}$ and $\mathbf{B_{3g}}$ modes are IR active only; and $\mathbf{A_u}$ mode is Raman and IR inactive, since $\mathbf{D_{2h}}$ group includes a center of symmetry; and the rule of mutual exclusion holds. The corresponding scaled frequencies and IR intensities are listed in table 6.

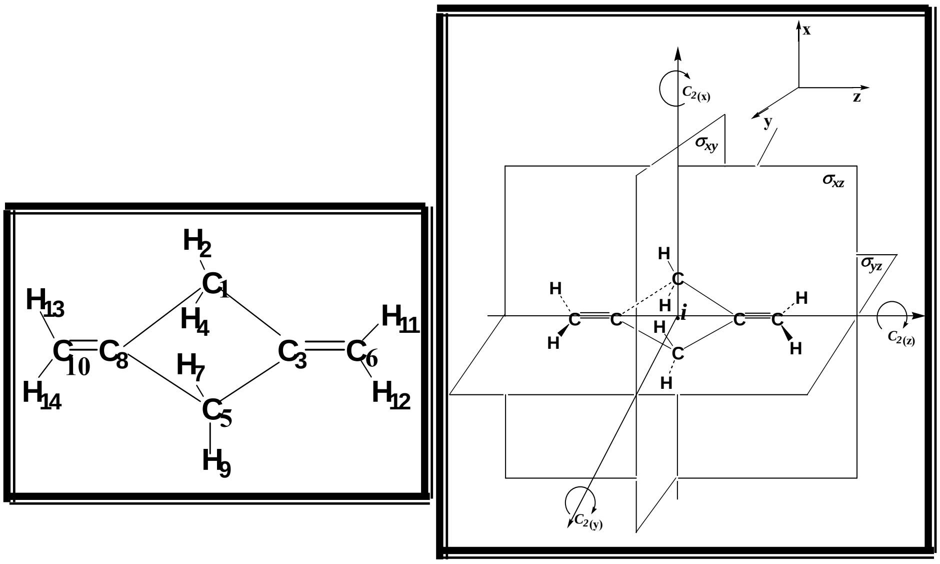


Fig. 5: Equilibrium geometry for 1,3-bis methylene cyclobutane (DMCB) molecule with D_{2h} symmetry as calculated applying both MINDO/3-FORCES and PM3 methods.

Fig. 6 shows the graphical representation of some vibration modes of 1,3-bis methylene cyclobutane as drawn through the DRAW. MOL. routine.

Table 5. MINDO/3-FORCES calculated geometric values of 1,3-bis methylene cyclobutane molecule, length (A°)/ angle (deg.).

THIS WORK		OTHER WORK
Bonds length, Bond angles and Dihedral angles	**MINDO/3-FORCES**	**calcd.[20]**
(C-H vinyl)	1.100	1.100
(C-H ring)	1.115	1.115
(C=C)	1.330	1.330
(C-C ring)	1.521	1.521
< C1 C3 C6 , < C1C8C10	135.3	——
< C3 C5 C8 , < C3C1C8	90.7	——
< C1 C3 C5 ,< C1C8C5	89.3	89.3
< HC1H , <HC5H	104.1	104.0
< HC=C	124.7	——
< HC6H ,< HC10H	110.5	110.6
< HC-C	115.7	——
φ HC=C-C	0.0	——
φ C=C-C	180	——
φ HC-C-C	119.3	——
φ C=C-C-C	180.0	——
φ CCCC ring	0.0	——

Table (6): Calculated vibration and IR absorption frequencies for 1,3-bis methylene cyclobutane (DMCB) molecule, compared with available experimental frequencies.

Symmetry and description		**MINDO/3-FORCES**		**PM3**	**expt.[17]**
In-plane		Freq. cm$^-$ Scaled	Intensity A km/mol	Freq. cm^{-1}	Freq. cm^{-1}
A_g					
υ_1	=CH_2 sym.str.	3068.	0.00	3131	——
υ_2	ring CH_2 sym.str.	2899	0.00	3019	——
υ_3	C=C str.	1693.	0.00	1933	——
υ_4	δ =CH_2(sciss.) + ring δ CH_2(sciss.) + ring (breathing)	1436	0.00	1397	——
υ_5	δ =CH_2(sciss.)+ ring δ CH_2(sciss.)	1392.	0.00	1368	——
υ_6	ring (breathing) +ring δ CH_2 (sciss.)	1105	0.00	1104	——
υ_7	ring (breathing)	531.	0.00	622	——
A_u					
υ_8	ring γ CH_2(twist.)	954.	0.00	1016	——
υ_9	γ (=CH_2(twist.))	711.	0.00	687	——
B_{1g}					
υ_{10}	ring CH_2 asym.str.	2891	0.00	3011	——
υ_{11}	ring γ CH_2(twist.)+ γ (=CH_2(twist.))	962.	0.00	867	——
υ_{12}	γ (=CH_2(twist.))+ring δ CH_2(rock.)	664.	0.00	679	——
B_{1u}					
υ_{13}	=CH_2 sym. Str.	3068.	49.74	3130	3060
υ_{14}	C=C str.	1650.	1.60	1897	1650
υ_{15}	δ (=CH_2(sciss.)) + ring(def.)	1416.	2.55	1390	——
υ_{16}	ring γ CH_2(wag.)+ δ (=CH_2(sciss.))	1226.	48.86	1277	1220
υ_{17}	ring γ CH_2(wag.)	927.	6.48	1009	——
B_{2g}					
υ_{18}	ring γ CH_2(twist.) + ring(puck.)	1028.	0.00	1106	——
υ_{19}	γ (=CH_2(wag.))	871.	0.00	953	——
υ_{20}	ring(puck.) + γ (=CH_2(wag.))	379.	0.00	454	——

Table 6: Continued

B_{2u}					
υ_{21}	$=CH_2$ asym.str.	3080.	82.82	3139	3070
υ_{22}	ring CH_2 sym.str.	2895.	134.72	3028	2890
υ_{23}	ring str.+ ring δ CH_2(sciss)	1337.	18.17	1392	1330
υ_{24}	ring str.+ ring δ CH_2 (sciss.)	1246.	1.12	1293	1235
υ_{25}	δ ($=CH_2$(rock.)) + ring(def.)	864.	2.68	921	860
υ_{26}	ring (def.) + δ ($=CH_2$(rock.))	267.	0.22	363	——
B_{3g}					
υ_{27}	$=CH_2$ asym. Str.	3080	0.00	3140	——
υ_{28}	ring str.+ ring γ CH_2(wag.)	1225.	0.00	1276	——
υ_{29}	ring γ CH_2(wag.) + ring (def.)	1118.	0.00	1193	——
υ_{30}	δ ($=CH_2$(rock.)) + ring γ CH_2 (wag.)	876.	0.00	933	——
υ_{31}	ring (def.) + δ ($=CH_2$(rock.))	396.	0.00	467	——
B_{3u}					
υ_{32}	ring CH_2 asym. Str.	2891.	70.88	3006	2885
υ_{33}	ring (puck.) + ring δ CH_2(rock.)	940.	940.	942	1008
υ_{34}	γ ($=CH_2$(wag.))	868.	868.	868	923
υ_{35}	ring (puck.) + ring δ CH_2 (rock.)	410.	410.	412	493
υ_{36}	ring (puck.) + γ ($=CH_2$(wag.))	95.	95.	97	215

scaling factors [13]: 0.87 ($C=CH_2$ str.), 0.85 (ring CH_2 str.), 0.88 (C=C str.), 1.06 ($C=CH_2$ sciss.), 1.05 (ring CH_2 sciss.), 1.20 ($=CH_2$ twist.), 1.06 ($=CH_2$ sciss. + ring str.), 1.05 (ring CH_2 sciss. + ring str.), and 1.00 for others.

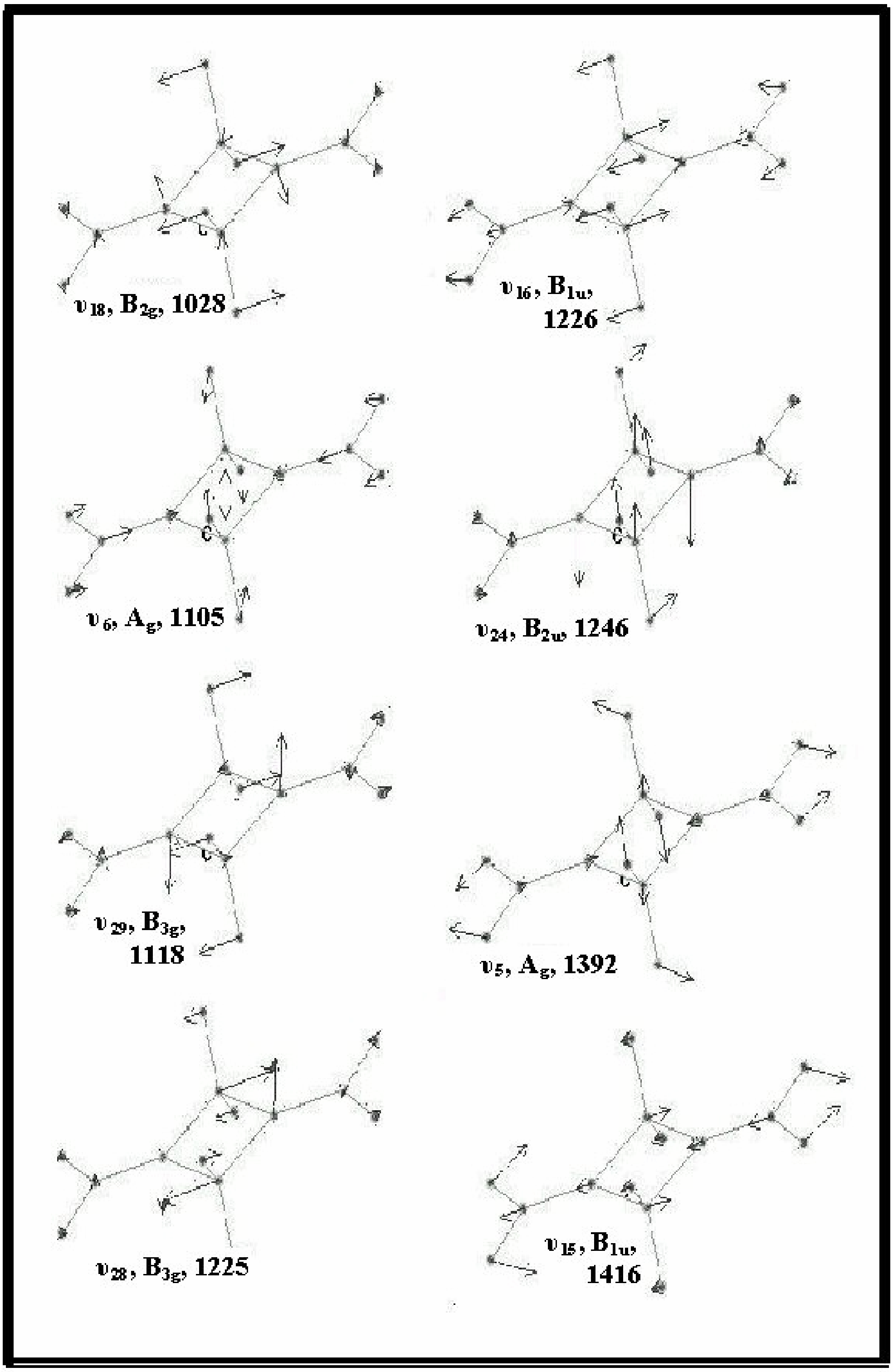


Fig. 6. Graphical representation of some vibration modes of 1.3-bis methylene cyclobutane as drawn through the DRAW. MOL routine.

Finally MINDO/3-FORCES treatment was done for trimethylene cyclobutane, the resulting geometric parameters, C_{2V} symmetry (fig. 7), are listed in table 7. Its 39 fundamental vibrations are classified into the following irreducible representations:

$$\mathbf{14A_1 + 5A_2 + 12B_1 + 8B_2}$$

Its corresponding scaled frequencies and IR absorption intensities as yielded by the MINDO/3-FORCES treatment are listed in table 8.

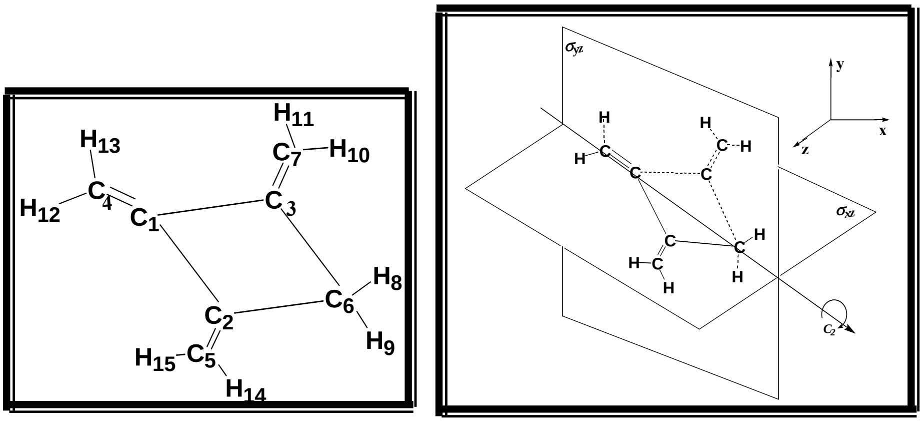


Fig. 7: Equilibrium geometry for 1, 2, 3 -Tis (methylene) cyclobutane (TMCB) molecule with C_{2V} symmetry as calculated by MINDO/3-FORCES and PM3 methods.

Figure 8 shows the graphical representation of some vibration modes of 1,2,3 tri- methylene cyclobutane molecule as drawn through the DRAW. MOL. routine.

Table 8. MINDO/3-FORCES calculated geometric parameters of 1,2,3-tris methylene cyclobutane, length (A°)/angle (deg.).

Bonds length, bond angles and Dihedral angles.	MINDO/3-FORCES
$(=C-H)$	1.100
$(C_6-H_8),(C_6-H_9)$	1.115
$(C_1-C),(C_1-C_3)$	1.518
$(C_3-C_6),(C_2-C_6)$	1.520
$(C_2=C_5),(C_3=C_7)$	1.332
$(C_1=C_4)$	1.334
$< H_{14} C_5 H_{15}$, $< H_{11}C_7H_{10}$	110.5
$< H_{14} C_5 C_2$, $< H_{15}C_5C_2$,$< H_{10} C_7 C_3$,$< H_{11}C_7C_3$	125.1
$C_5C_2C_1$,< $< C_7 C_3 C_1$, $< C_5 C_2 C_6$,$< C_7C_3C_6$	134.8
$< H_8C_6 H_9$	103.9
$< H_8 C_6 C_2$, $< H_9C_6C_3$	115.8
$< C_1 C_2 C_6$, $< C_1C_3C_6$	89.7
$< C_2 C_1 C_3$, $< C_2C_6C_3$	90.2
φ $H_8C_6C_2C_5$	60.7
φ $H_8C_6C_3C_7$	-60.7
φ CCCC ring	0.00
φ $C_1C_2C_6H_9$	118.8

Table (8: Calculated vibration and IR absorption frequencies for 1,2,3 tris metlenecyclobutane (DMBC) molecule, compared with available experimental frequencies.

Symmetry and description		MINDO/3-FORCES		PM3	expt.[21]
In-plane		Freq. cm^{-} Scaled	Intensity A km/mol	Freq. cm^{-1}	Freq. cm^{-1}
A_1					
υ_1	=CH_2 asym.str.(2,3)	3080	76.051	3145	3075
υ_2	=CH_2 sym. str. (1,2,3)	3070	4.47	3137	-------
υ_3	=CH_2 sym. str. (1,2,3)	3067	14.93	3133	-------
υ_4	ring CH_2 sym. str.	2900	67.375	3088	2890
υ_5	(C=C) str. (1,2,3)	1703	0.04	1920	-------
υ_6	(C=C) str. (1)	1603	0.14	1805	-------
υ_7	ring δ CH_2 (sciss.)	1420	3.68	1386	-------
υ_8	δ (=CH_2(sciss.)) (1)	1413	10.65	1322	-------
υ_9	δ (=CH_2 (sciss.))(1,2,3) +ring δ CH_2 (sciss.)	1390	0.02	1305	-------
υ_{10}	ring str.+ ring δ CH_2 (sciss.)	1208	1.04	1231	-------
υ_{11}	ring (def.)+ δ (=CH_2 (rock.)) (2,3)	940	0.22	953	-------
υ_{12}	δ (=CH_2 (rock.)) (2,3) +ring (def.)	826	1.42	850	-------
υ_{13}	ring breathing	517	0.21	633	-------
υ_{14}	δ (=CH_2(rock.)) (2,3)+ring (def.)	268	0.33	264	-------
A_2					-------
υ_{15}	ring γ CH_2(twist.)	992	0.00	1032	-------
υ_{16}	γ (=CH_2(wag.)) (2,3)	867	0.00	984	-------
υ_{17}	γ (=CH_2 (twist.)) (1) +ring (puck.)	786	0.00	670	-------
υ_{18}	γ (=CH_2 (twist.)) (1,2,3)	681	0.00	592	-------
υ_{19}	ring (puck .) + γ (=CH_2(twist.))	364	0.00	384	-------
B_1					-------
υ_{20}	= CH_2 asym. str. (1,2,3)	3081	25.41	3145	-------
υ_{21}	=CH_2 asym. str. (1, 2,3)	3079	10.99	3144	-------
υ_{22}	=CH_2 sym. str. (2,3)	3068	46.68	3136	-------

Table 8:Continued

υ_{23}	C=C str.(2,3)	1633	0.89	1720	1644
υ_{24}	δ(=CH_2(sciss.))(2,3)	1413	7.41	1324	-------
υ_{25}	γ(=CH_2(twist.))	1224	11.28	1229	-------
υ_{26}	ring str. +ring γ CH_2 (wag.)	1181	9.79	1211	-------
υ_{27}	ring (def.) +ring γ CH_2 (wag.) +δ(=CH_2 (rock.)) (1,2,3)	1034	1.14	1080	-------
υ_{28}	δ(=CH_2(rock.)) (2,3) +ring γ CH_2 (wag.)	886	0.73	878	-------
υ_{29}	δ(=CH_2(rock.))(1)	829	0.20	851	-------
υ_{30}	ring (def.) +δ(=CH_2(rock.))(1,2,3)	456	0.74	485	-------
υ_{31}	δ(=CH_2(rock.))(1,2,3)	258	0.15	237	-------
B_2					-------
υ_{32}	ring CH_2 asym. str.	2893	64.12	3031	-------
υ_{33}	ring δ CH_2 (rock.) + ring(puck.)	903	5.43	1035	-------
υ_{34}	γ(=CH_2 (wag.))(1)	868	5.92	1007	865
υ_{35}	γ(=CH_2 (wag.)) (1,2,3) +ring δ CH_2 (rock.)	855	0.35	954	-------
υ_{36}	ring (puck.)+ γ(=CH_2(twist.)) (2,3)	694	0.06	727	-------
υ_{37}	ring δ CH_2 (rock.)+ γ(=CH_2(twist.)) (2,3)	504	0.06	559	-------
υ_{38}	ring (puck.) +γ(=CH_2 (wag.)) (1,2,3)	261	0.05	272	-------
υ_{39}	ring (puck.) +ring δ CH_2 (sciss.) + γ(=CH_2 (wag.)) (1,2,3)	77	0.00	106	-------

scaling factors [13]: 0.87 (C=CH_2 str.), 0.85 (ring CH_2 str.), 0.88 (C=C str.), 1.06 (C=CH_2 sciss.), 1.05 (ring CH_2 sciss.), 1.20 (=CH_2 twist.), 1.06 (=CH_2 sciss. + ring str.), 1.05 (ring CH_2 sciss. + ring str.).

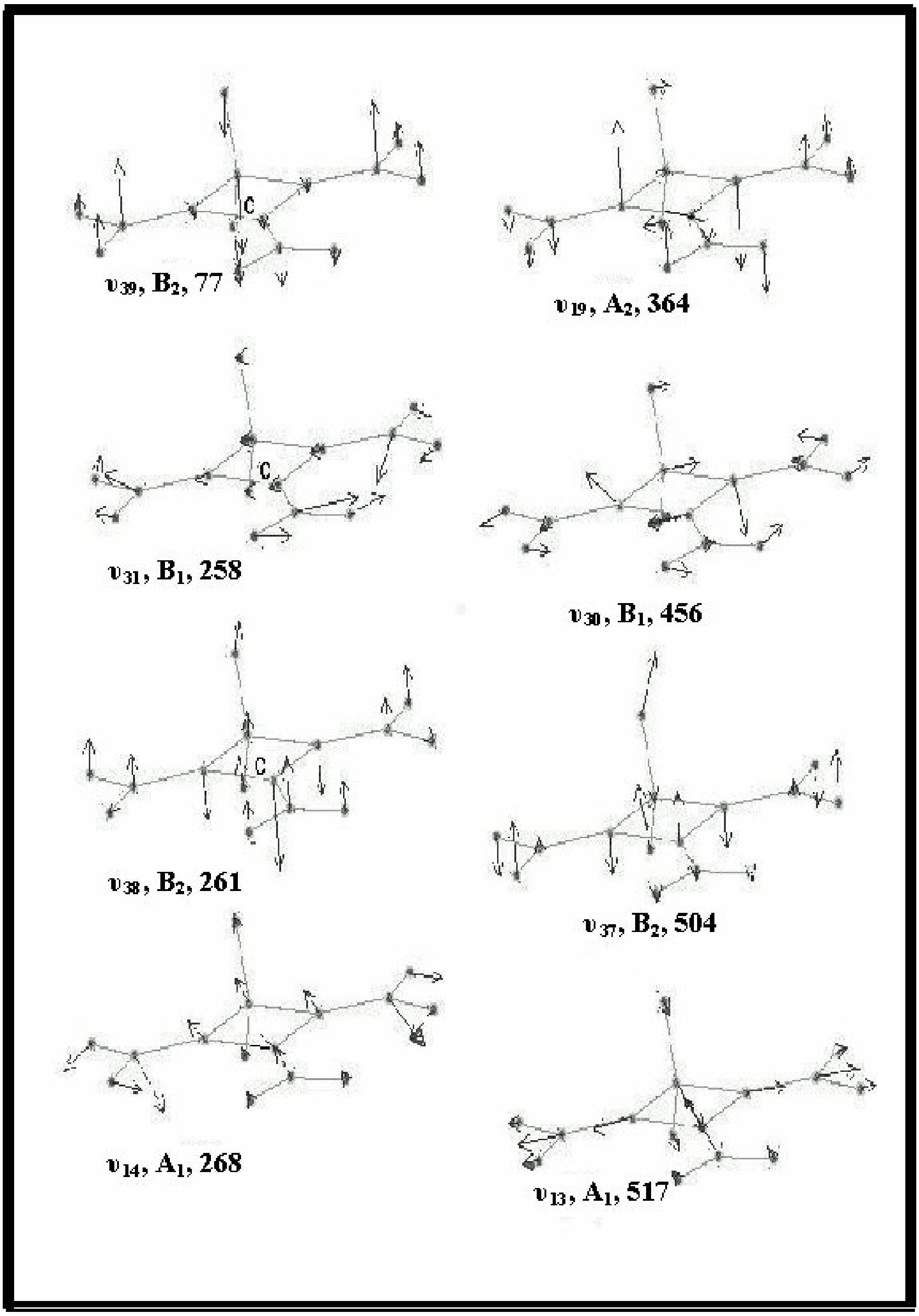


Fig. 8. Graphical representation of some vibration modes of 1,2,3-trimethylene cyclobutane as drawn through the DRAW. MOL routine.

Inspection of the frequency values in table 2, 4, 6 and 8 indicates that all four molecules show the following common relations;

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

1. **the (=CH_2) stretching vibrations are unaffected by the number of methylene groups.**

δ (=CH_2 (sciss.)) > δ (=CH_2 (rock.))
γ (=CH_2 (wag.)) > γ (=CH_2 (twist.))

It was further found that;

2. **the ring CH_2 vibrations depend on the number of methylene groups as follows:**

a. ring CH_2 sym. str. > ring CH_2 sym. str. > ring CH_2 sym. str.
1,2-DMCB MCB TMCB
2913 cm^{-1} 2905cm^{-1} 2900 cm^{-1}

and

ring CH_2 sym. str. > ring CH_2 sym. str.
1,2-DMCB 1,3-DMCB
2913 cm^{-1} 2895cm^{-1}

b. ring CH_2 asym. str. > ring CH_2 asym. str. > ring CH_2 asym. str.
MCB 1,2-DMCB TMCB
2918 cm^{-1} 2910 cm^{-1} 2893 cm^{-1}

and

ring CH_2 asym. str. > ring CH_2 asym. str.
1,2-DMCB 1,3-DMCB
2910 cm^{-1} 2891 cm^{-1}

3-The asym. ringCH_2 stretching frequency decreases as the number of the *exo*- methylene groups increases.

4- The C=C stretching frequency decreases as the number of the same methylene groups increases;

C=C str. > C=C str. > C=C str.
MCB 1,3-DMCB TMCB
1669 cm^{-1} 1650 cm^{-1} 1633 cm^{-1}

the C=C stretching vibration frequency of 1,2-DMCB showing the lowest values 1617 cm^{-1}.

5-The ring stretching frequency decreases as the number of methylene groups increases:

ring str. > ring str. > ring str.
MCB 1,2-DMCB TMCB
1274 cm^{-1} 1266 cm^{-1} 1225 cm-^{1}

the ring stretching frequency of 1,3-DMCB showing the highest value 1337cm^{-1}.

The $=CH_2$ bending frequency decreases as the number of methylene groups increases:

a. $\delta(=CH_{2\,(sciss.)}) > \delta(=CH_{2\,sciss.})\ ;\ \delta(=CH_{2\,sciss.}) > \delta(=CH_{2\,(sciss.)})$

MCB	1,3-DMCB	1,2-DMCB	TMCB
1422 cm^{-1}	1417 cm^{-1}	1416 cm-^{1}	1413 cm-^{1}

b. $\delta(=CH_{2\,(rock.)}) > \delta(=CH_{2\,(rock.)}) > \delta(=CH_{2\,(rock.)})$

MCB	1,2-DMCB	TMCB
868 cm^{-1}	828 cm^{-1}	826 cm-^{1}

and

$\delta(=CH_{2\,(rock.)}) > \delta(=CH_{2\,(rock.)})$

1,3-DMCB	1,2-DMCB
864 cm^{-1}	828 cm^{-1}

The reason for these sequences may be attributed to the crowding strain which makes the scissoring or rocking motion in the same plane more difficult as the number of methylene groups increases.

6-The CH_2 bending vibration frequency increases as the number of methylene groups increases:

ring $\delta(CH_{2\,(sciss.)}) >$ ring $\delta(CH_{2\,sciss.}) >$ ring $\delta(CH_{2\,(sciss.)})$

TMCB	1,2-DMCB	MCB
1421cm^{-1}	1406 cm^{-1}	1338 cm-^{1}

and

ring $\delta(CH_{2\,(rock.)}) >$ ring $\delta(CH_{2\,(rock.)}) >$ ring $\delta(CH_{2\,(rock.)})$

TMCB	1,2-DMCB	MCB
903 cm^{-1}	717 cm^{-1}	692 cm^{-1}

the ring CH_2 rocking frequency of 1,3-DMCB shows the highest value 940 cm^{-1}.

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