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

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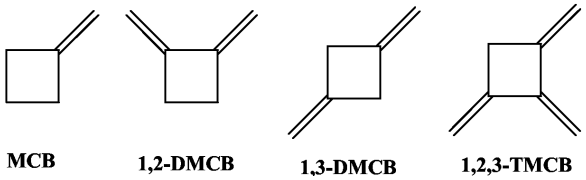
SCF-MO calculations of the vibration frequencies and IR absorption intensities, applying the MINDO/3-FORCES method, are reported for the four molecules, mono-, di- (1,2- and 1,3-), and 1,2,3-trimethylene cyclobutane. Normal coordinate analysis of all vibration modes is described for each molecule. The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

Key words: Methylene Cyclobutanes; Vibrations; Normal Coordinates.

1. Introduction

Monomethylene cyclobutane (MCB) was synthesized and characterized by different investigators [1, 2]. Theoretical calculations, applying the ab initio method, were also performed for this molecule [3]. The two isomers of 1,2- and 1,3-dimethylene cyclobutane (1,2-DMCB and 1,3-DMCB) were synthesized and characterized by other authors too [4, 5]. Applying the MINDO/3 method, Bingham et al. [6] studied the equilibrium geometries and heats of formation of the two isomers. X-ray diffraction of 1,2-dimethylene cyclobutane shows that both molecules are planar with C_{2v} symmetry [7]. Little work has been done on trimethylene cyclobutane (TMCB), since this molecule dimerizes quickly at room temperature. Williams and Sharkey were able to isolate it and characterize its IR spectrum at -80 °C [5].



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

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

and solving (1), one obtains vibration frequencies ($\lambda = 4\pi^2c^2\nu^2$) and vibration mode eigenvector coefficients (L_j). These coefficients allow the graphical description of the vibration modes of all atoms in the molecule, when introduced to the DRAW.MOL routine developed by Abed et al. [11]. The same coefficients are used to evaluate the atomic partial participation (APP) values [12] of each atom in each vibration mode too.

The molecules, for which calculations were done, are the cyclobutane derivatives in which one, two or three CH_2 groups are replaced by $C{=}CH_2$ groups to form mono-, di- (1,2- and 1,3-) and trimethylene cyclobutane, as shown above.

2. Results and Discussion

In the present study the equilibrium geometry of each molecule was calculated, minimizing its total energy 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 (ΔH_f in 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

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

This work		Other work	
Bond lengths, bond angles and dihedral angles	MINDO/3-FORCES	exptl. [13a]	calcd. [13b]
(=C-H vinyl)	1.100	1.104	1.089
(C_2-H_8), (C_3-H_6), (C_2-H_9), (C_3-H_7)	1.115	1.104	1.105
(C_5-H_{10}), (C_5-H_{11})	1.113	1.104	1.105
(C=C)	1.330	1.331	1.333
(C_1-C_2), (C_1-C_3)	1.522	1517	1520
(C_2-C_5), (C_3-C_5)	1.524	1.565	1.553
(C=C-C)	135.2	—	—
$\measuredangle(C_2C_1C_3)$	89.7	—	—
$\measuredangle(C_1C_3C_5)$, $\measuredangle(C_1C_2C_5)$	90.4	—	—
$\measuredangle(C_2CC_3)$	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	—	—
φ(C=C-C-C)	180.0	—	—
φ(CCCC ring)	0.00	—	—

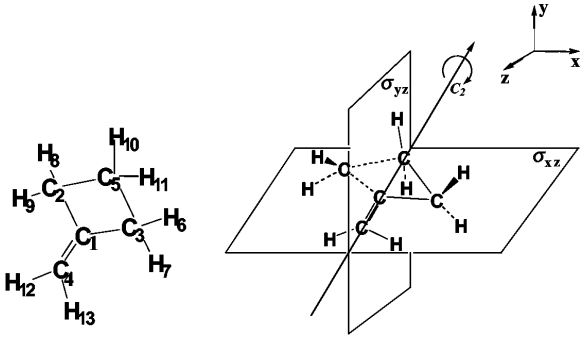


Fig. 1. Equilibrium structure for a methylene cyclobutane molecule (MCB) with C_{2v} symmetry as calculated by MINDO/3-FORCES and PM3 methods.

1,2-DMCB is less stable than 1,3-DMCB. A possible reason for that is the different repulsion energies between the adjacent atoms of the two exo-methylene groups. This result is in quantitative agreement with those of the PM3 method when applied to the same problem [14].

The calculated vibration frequencies 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.)], 1.20 (=CH_2 twist.), 1.06 (=CH_2 sciss. + ring str.), 1.05 [ring (CH_2 sciss.) + ring str.], and 1.00 for others.

For monomethylene cyclobutane (MCB), C_{2v} (Fig. 1), the total number of fundamental vibrations ($3N-6$) is 33. These are classified into the following irreducible representations:

$$11A_1 + 5A_2 + 9B_1 + 8B_2,$$

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

	Symmetry and description	MINDO/3-FORCES Scaled frequency [cm^{-1}]	Intensity A [km/mol]	PM3 Frequency [cm^{-1}]	expt. [16] Frequency [cm^{-1}]
A_1					
ν_1	=CH_2 sym.str.	3069	21.30	3130	3070
ν_2	ring (CH_2 sym.str.) (5)	2907	69.63	3035	2935
ν_3	ring (CH_2 sym.str.) (2,3,5)	2931	1.02	3025	—
ν_4	C=C str.	1669	0.56	1890	1665
ν_5	ring str. + ring (δCH_2 sciss.)	1422	0.23	1395	1395
ν_6	δ (=CH_2) (sciss.) + ring str.	1406	1.75	1335	1385
ν_7	δ (=CH_2) (sciss.) + ring δ CH_2) (sciss.)	1400	0.24	1315	—
ν_8	ring (δ CH_2) (sciss.) + ring str.	1338	27.03	1280	—
ν_9	ring str. + ring (δ CH_2) (sciss.)	1198	8.87	1122	1175
ν_{10}	ring (δ CH_2 sciss.) + ring def.	1007	5.87	965	990
ν_{11}	ring (δ CCC)	578	0.06	610	—
A_2					
ν_{12}	ring (CH_2 asym.str.)	2900	0.01	3020	—
ν_{13}	ring (δ CH_2 rock.)	1041	0.00	1126	—
ν_{14}	ring (γ CH_2 twist.) + (=CH_2 twist.)	929	0.00	970	—
ν_{15}	ring (δ CH_2 rock.) + (=CH_2 twist.)	744	0.00	806	—
ν_{16}	γ (=CH_2 twist.) + ring(δ CH_2 rock.)	686	0.00	612	—
B_1					
ν_{17}	=CH_2asym.str.	3080	1.02	3025	3082
ν_{18}	ring (CH_2 sym.str.) (2,3)	2905	0.56	1890	2900
ν_{19}	ring (δ CH_2 sciss.) (2,3) + ring str.	1423	0.23	1395	—
ν_{20}	ring str. + ring (δ CH_2 sciss.) (2,3)	1274	1.75	1335	1228
ν_{21}	ring str. + ring (γ CH_2 wag.) (2,3)	1225	0.24	1315	—
ν_{22}	ring (γ CH_2 wag.) + ring str.	1134	1134	1133	1150
ν_{23}	ring (γ CH_2 wag.) + ring str.	1044	3.40	1123	1055
ν_{24}	δ (=CH_2 rock.) + ring def.	868	0.84	1002	870
ν_{25}	δ (=CH_2 rock.) + ring def.	339	0.26	307	—
B_2					
ν_{26}	ring (CH_2 asym.str.)	2918	119.23	3045	—
ν_{27}	ring (CH_2 asym.str.)	2895	33.87	3017	2870
ν_{28}	ring(γ CH_2 twist.)	1057	0.08	1107	—
ν_{29}	ring puck. + ring (δ CH_2 rock.)	980	4.07	1008	—
ν_{30}	γ (=CH_2 twist.)	870	1.26	913	—
ν_{31}	ring (γ CH_2 rock.)	692	3.00	709	715
ν_{32}	ring puck. + ring (δ CH_2 rock.)	397	0.01	416	—
ν_{33}	ring puck. + ring (δ CH_2 rock.)	143	0.00	228	—

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.)], 1.20 (=CH_2 twist.), 1.06 (=CH_2 sciss. + ring str.), 1.05 [ring (CH_2 sciss. + ring str.)], and 1.00 for others. δ: in-plane. γ: out of-plane.

where the A_1, B_1 and B_2 modes are Raman and IR active, while the A_2 mode is 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 the MINDO/3 and PM3 method. Figure 2 shows the graphical representation of some vibration modes of the MCB molecule as drawn through the DRAW. MOL routine.

For 1,2-dimethylene cyclobutane with C_{2v} symmetry (Fig. 4), the calculated geometry values are listed in Table 3. Its number of normal vibration modes is 36, which are classified into the following irreducible rep-

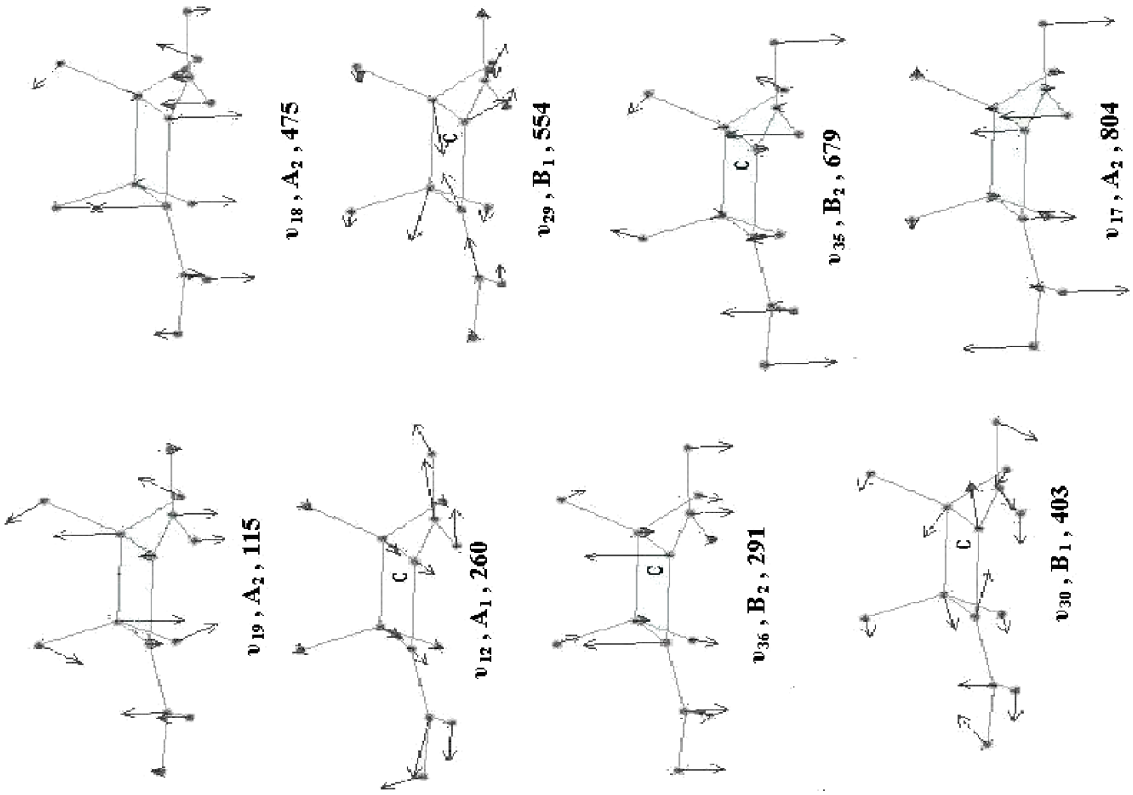


Fig. 3. The graphical representation of some vibration modes of the 1,2-dimethylene cyclobutane molecule as drawn through the DRAW.MOL routine.

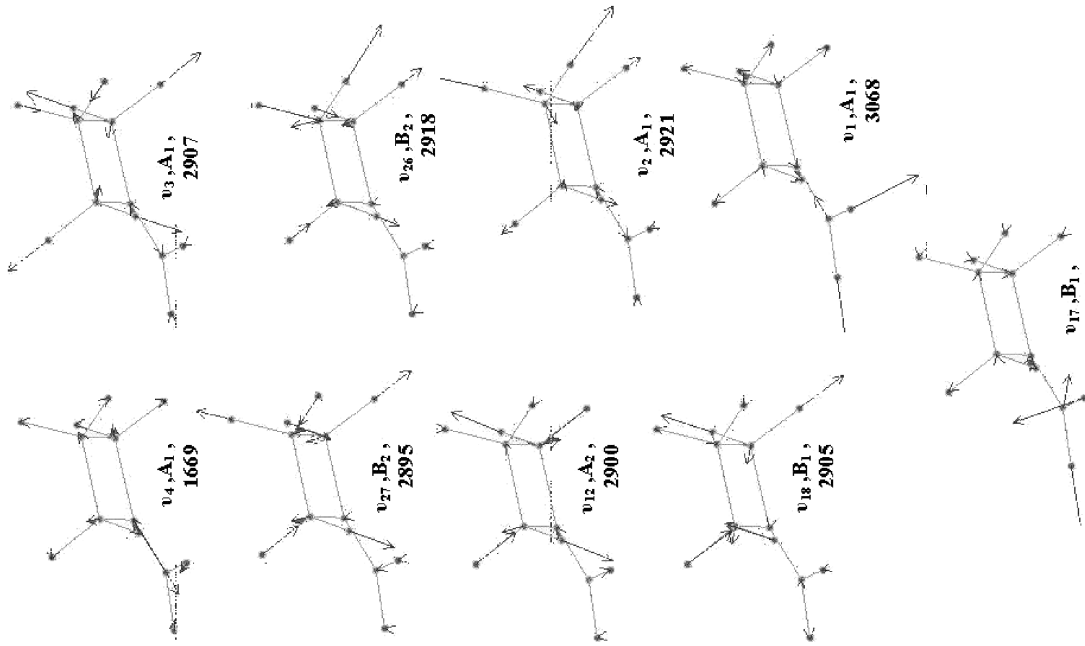


Fig. 2. Graphical representation of some vibration modes of the MCB molecule as drawn through the DRAW.MOL routine.

Table 3. MINDO/3-FORCES calculated geometric values of 1,2-dimethylene cyclobutane; length (Å), angle (deg.) and dihedral angle (deg.).

This work		Other work	
Bond lengths, angles and dihedral angles	MINDO/3-FORCES	exptl. [17]	calcd. [18]
(=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
$\measuredangle(C_1C_3C_5)$, $\measuredangle(C_2C_5C_3)$	89.9	—	90.1
$\measuredangle(C_2C_1C_3)$, $\measuredangle(C_1C_2C_5)$	90.1	91.5	—
$\measuredangle(H_7C_3H_8)$, $\measuredangle(H_9C_5H_{10})$	103.9	—	104.0
$\measuredangle(H_7C_3C_5)$, $\measuredangle(H_8C_3C_5)$	115.7	110.3	—
$\measuredangle(H_{11}C_4H_{12})$, $\measuredangle(H_{13}C_6H_{14})$	110.5	—	110.5
$\measuredangle(C_4C_1C_2)$, $\measuredangle(C_6C_2C_1)$	135.6	—	135.6
$\measuredangle(C_4C_1C_3)$, $\measuredangle(C_6C_2C_5)$	134.3	133.8	—
$\measuredangle(H_{11}C_4C_1)$, $\measuredangle(H_{12}C_4C_1)$	125.1	123.7	—
$\varphi(H_{12}C_4C_1C_2)$	0.0	—	—
$\varphi(C_4C_1C_3C_5)$	180.0	—	—
$\varphi(C_1C_2C_5C_3)$	0.00	—	—

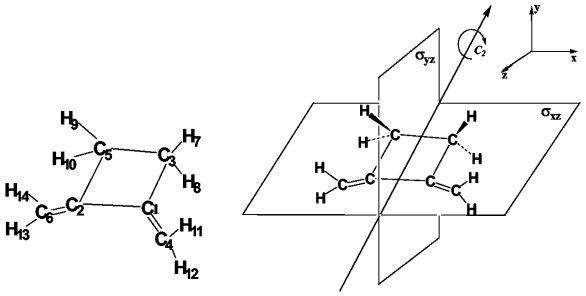


Fig. 4. Equilibrium structure for 1,2-dimethylene cyclobutane (1,2-DMCB) with C_{2v} symmetry as calculated by the MINDO/3-FORCES method.

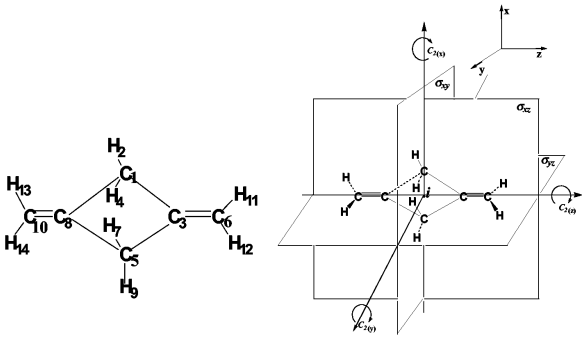


Fig. 5. Equilibrium structure of 1,3-dimethylene cyclobutane (1,3-DMCB) with D_{2h} symmetry as calculated using both MINDO/3-FORCES and PM3 methods.

resentations:

$$12A_1 + 7A_2 + 11B_1 + 6B_2.$$

Table 4. Calculated vibration frequencies and IR absorption intensities for the 1,2-dimethylene cyclobutane molecule, compared with available experimental frequencies.

Symmetry and description		MINDO/3-FORCES		PM3	expt. [13]
	In-plane	Scaled frequency [cm^{-1}]	Intensity A [km/mol]	Frequency [cm^{-1}]	[cm^{-1}]
A_1					
ν_1	$=CH_2$ sym.str. (1,2)	3081	44.01	3143	3080
ν_2	$=CH_2$ sym.str. (1,2)	3069	13.15	3129	3065
ν_3	ring (CH_2 sym.str.)	2913	88.24	3037	2925
ν_4	C=C str.	1683	0.29	1902	1640
ν_5	ring str. + ring (δCH_2 sciss.)	1390	2.46	1406	1380
ν_6	δ(=CH_2 sciss.) (1,2) + ring str.	1336	3.81	1372	—
ν_7	ring str. + ring (δCH_2 sciss.)	1266	15.89	1290	1240
ν_8	ring str.	1212	0.49	1259	—
ν_9	ring (δCH_2 sciss.) + ring str.	1136	5.83	1107	1125
ν_{10}	ring def. + ring (δCH_2 sciss.)	939	1.74	996	—
ν_{11}	δ(=CH_2 rock.) (1,2) + ring def.	828	0.53	884	—
ν_{12}	δ(=CH_2 rock.) (1,2) + ring def.	260	0.15	315	—
A_2					
ν_{13}	$=CH_2$ sym.str. (1,2)	2896	0.00	3027	—
ν_{14}	$=CH_2$ sym.str. (1,2)	1046	0.00	1103	—
ν_{15}	ring (CH_2 sym.str.)	939	0.00	997	—
ν_{16}	C=C str.	865	0.00	923	—
ν_{17}	ring str. + ring (δCH_2 sciss.)	804	0.00	723	—
ν_{18}	δ(=CH_2 sciss.) (1,2) + ring str.	475	0.00	531	—
ν_{19}	ring str. + ring (δCH_2 sciss.)	115	0.00	208	—
B_1					
ν_{20}	ring (δCH_2 sciss.) + ring str.	3079	34.62	3142	—
ν_{21}	ring def. + ring (δCH_2 sciss.)	3067	27.94	3120	—
ν_{22}	δ(=CH_2 rock.) (1,2) + ring def.	2906	50.28	3031	2890
ν_{23}	δ(=CH_2 rock.) (1,2) + ring def.	1617	0.37	1851	—
ν_{24}	ring (δCH_2 sciss.) + ring str.	1406	8.20	1362	—
ν_{25}	ring (δCH_2 sciss.) + δ(=CH_2 sciss.) (1,2)	1382	0.02	1350	—
ν_{26}	ring str. + ring (δCH_2 sciss.)	1233	11.60	1273	—
ν_{27}	ring (δ CH_2 sciss.) + ring def.	1138	2.84	1138	—
ν_{28}	δ(=CH_2 rock.) (1,2) + ring def.	876	0.00	926	—
ν_{29}	ring def. + CC=C def.	554	0.41	618	—
ν_{30}	ring def. + δ(=CH_2 rock.) (1,2)	403	0.81	512	—
B_2					
ν_{31}	ring (CH_2 asym.str. rock.)	2909	109.30	3037	2930
ν_{32}	ring (δCH_2 rock.) + ring puck.	970	1.97	1022	950
ν_{33}	γ(=CH_2 wag.) (1,2)	870	4.07	929	880
ν_{34}	ring (δCH_2 rock.) + ring puck.	717	2.75	803	725
ν_{35}	γ(=CH_2 twist.) (1,2) + ring(δCH_2 rock.)	679	0.11	619	—
ν_{36}	γ(C=C) + ring puck.	291	0.03	415	—

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.)], 1.20 (=CH_2 twist.), 1.06 (=CH_2 sciss. + ring str.), 1.05 [ring (CH_2 sciss.) + ring str.], and 1.00 for others. δ: in-plane. γ: out of-plane.

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

Figure 3 shows the graphical representation of some vibration modes of 1,2-dimethylene cyclobutane, C_{2v}, as drawn through the DRAW.MOL routine.

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

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

where the A_g, B_{1g}, B_{2g} and B_{3g} modes are Raman ac-

Table 5. MINDO/3-FORCES calculated geometric values of 1,3-dimethylene cyclobutane; length (Å), angle (deg.).

This work Bond lengths, bond angles and dihedral angles	MINDO/3-FORCES	Other work calcd. [18]
(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
$\measuredangle(C_1C_3C_6)$, $\measuredangle(C_1C_8C_{10})$	135.3	—
$\measuredangle(C_3C_5C_8)$, $\measuredangle(C_3C_1C_8)$	90.7	—
$\measuredangle(C_1C_3C_5)$, $\measuredangle(C_1C_8C_5)$	89.3	89.3
$\measuredangle(HC_1H)$, $\measuredangle(HC_5H)$	104.1	104.0
$\measuredangle$(HC=C)	124.7	—
$\measuredangle(HC_6H)$, $\measuredangle(HC_{10}H)$	110.5	110.6
$\measuredangle$(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	—

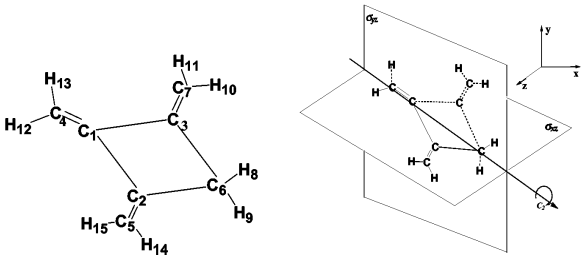


Fig. 6. Equilibrium structure for 1,2,3-trimethylene cyclobutane (TMCB) with C_{2v} symmetry as calculated by both MINDO/3-FORCES and PM3 methods.

tive and IR inactive, the B_{1u}, B_{2u} and B_{3u} modes are IR active only, and the A_u mode is Raman and IR inactive, for D_{2h} point group contains a center of symmetry and the rule of mutual exclusion is holds. The corresponding scaled frequencies and IR intensities are listed in Table 6.

Figure 7 shows the graphical representation of some vibration modes of the 1,3-di-methylene cyclobutane molecule as drawn through the DRAW.MOL routine.

Finally MINDO/3-FORCES treatment was done for trimethylene cyclobutane with C_{2v} symmetry (Fig. 6). The calculated geometric values are listed in Table 7. The number of fundamental vibrations ($3N-6$) is 39. These are classified into the following irreducible representations:

$$14A_1 + 5A_2 + 12B_1 + 8B_2.$$

The corresponding scaled frequencies and IR absorption intensities as calculated by the MINDO/3-FORCES method are listed in Table 8.

Table 6. Calculated vibration frequencies and IR absorption intensities for 1,3-dimethylene cyclobutane (DMCB), compared with available experimental frequencies.

	Symmetry and description	MINDO/3-FORCES Scaled frequency [cm^{-1}]	Intensity A [km/mol]	PM3 Frequency [cm^{-1}]	expt. [13] Frequency [cm^{-1}]
A_g					
ν_1	=CH_2 sym.str.	3068	0.00	3131	—
ν_2	ring (CH_2 sym.str.)	2899	0.00	3019	—
ν_3	C=C str.	1693	0.00	1933	—
ν_4	δ(=CH_2 sciss.) + ring str.	1436	0.00	1397	—
ν_5	δ(=CH_2 sciss.) + ring (δCH_2 sciss.)	1392	0.00	1368	—
ν_6	ring breathing + ring (δCH_2 sciss.)	1105	0.00	1104	—
ν_7	ring breathing	531	0.00	622	—
A_u					
ν_8	ring (γCH_2 twist.)	954	0.00	1016	—
ν_9	γ(=CH_2 twist.)	711	0.00	687	—
B_{1g}					
ν_{10}	ring (CH_2 asym.str.)	2891	0.00	3011	—
ν_{11}	ring (γCH_2 twist.) + γ=CH_2 twist.	962	0.00	867	—
ν_{12}	γ(=CH_2 twist.) + ring (δCH_2 rock.)	664	0.00	679	—
B_{1u}					
ν_{13}	=CH_2 sym.str.	3068	49.74	3130	3060
ν_{14}	C=C str.	1650	1.60	1897	1650
ν_{15}	δ(=CH_2 sciss.) + ring def.	1416	2.55	1390	—
ν_{16}	ring (γCH_2 wag. + δ=CH_2 sciss.)	1226	48.86	1277	1220
ν_{17}	ring (γCH_2 wag.)	927	6.48	1009	—
B_{2g}					
ν_{18}	ring (γCH_2 twist.) + ring puck.	1028	0.00	1106	—
ν_{19}	γ(=CH_2 wag.)	871	0.00	953	—
ν_{20}	ring puck. + γ(=CH_2 wag.)	379	0.00	454	—
B_{2u}					
ν_{21}	=CH_2 asym.str.	3080	82.82	3139	3070
ν_{22}	ring (CH_2 sym.str.)	2895	134.72	3028	2890
ν_{23}	ring str. + ring (δCH_2 sciss.)	1337	18.17	1392	1330
ν_{24}	ring str. + ring (δCH_2 sciss.)	1246	1.12	1293	1235
ν_{25}	(=CH_2 rock.) + ring def.	864	2.68	921	860
ν_{26}	ring def. + δ(=CH_2 rock.)	267	0.22	363	—
B_{3g}					
ν_{27}	=CH_2 asym.str.	3080	0.00	3140	—
ν_{28}	ring str. + ring (γCH_2 wag.)	1225	0.00	1276	—
ν_{29}	ring (γCH_2 wag.) + ring def.	1118	0.00	1193	—
ν_{30}	δ(=CH_2 rock.) + ring (γCH_2 wag.)	876	0.00	933	—
ν_{31}	ring def. + δ(=CH_2 rock.)	396	0.00	467	—
B_{3u}					
ν_{32}	ring (CH_2 asym.str.)	2891	70.88	3006	2885
ν_{33}	ring puck. + ring (δCH_2 rock.)	940	940	942	1008
ν_{34}	γ(=CH_2 wag.)	868	868	868	923
ν_{35}	ring puck. + ring (δCH_2 rock.)	410	410	412	493
ν_{36}	ring puck. + γ(=CH_2 wag.)	95	95	97	215

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.)], 1.20 (=CH_2 twist.), 1.06 (=CH_2 sciss. + ring str.), 1.05 [ring (CH_2 sciss.) + ring str.], and 1.00 for others.

Figure 8 shows the 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 Tables 2, 4, 6 and 8 indicates that all four molecules are common in the following relations:

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

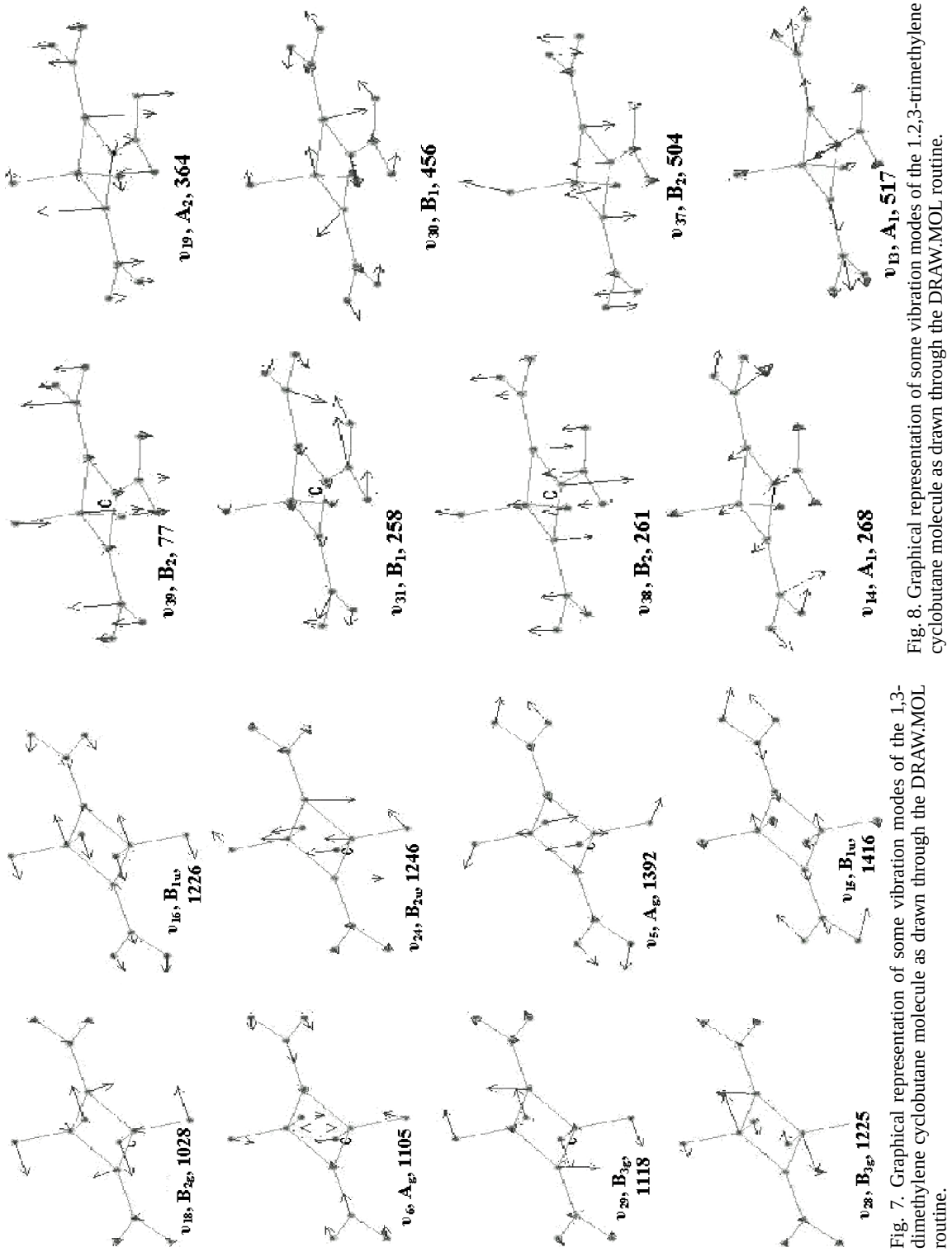


Fig. 7. Graphical representation of some vibration modes of the 1,3-dimethylene cyclobutane molecule as drawn through the DRAW.MOL routine.

Fig. 8. Graphical representation of some vibration modes of the 1.2,3-trimethylene cyclobutane molecule as drawn through the DRAW.MOL routine.

Table 7. MINDO/3-FORCES calculated geometric values of 1,2,3-trimethylene cyclobutane; length (Å), angle (deg.).

Bonds lengths, bond 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
$\measuredangle(H_{14}C_5H_{15})$, $\measuredangle(H_{11}C_7H_{10})$	110.5
$\measuredangle(H_{14}C_5C_2)$, $\measuredangle(H_{15}C_5C_2)$, $\measuredangle(H_{10}C_7C_3)$, $\measuredangle(H_{11}C_7C_3)$	125.1
$\measuredangle(C_5C_2C_1)$, $\measuredangle(C_7C_3C_1)$, $\measuredangle(C_5C_2C_6)$, $\measuredangle(C_7C_3C_6)$	134.8
$\measuredangle(H_8C_6\ H_9)$	103.9
$\measuredangle(H_8C_6C_2)$, $\measuredangle(H_9C_6C_3)$	115.8
$\measuredangle(C_1C_2C_6)$, $\measuredangle(C_1C_3C_6)$	89.7
$\measuredangle(C_2C_1C_3)$, $\measuredangle(C_2C_6C_3)$	90.2
$\varphi(H_8C_6C_2C_5)$	60.7
$\varphi(H_8C_6C_3C_7)$	−60.7
φ(CCCC ring)	0.00
$\varphi(C_1C_2C_6H_9)$	118.8

It was further found:

1. The =CH_2 stretching vibrations are unaffected by the number of methylene groups.

2. The ring symmetrical CH_2 vibrations depend on the number of methylene groups in the following sense:

a)

$$\begin{array}{ccc} \text{ring}(CH_2\text{sym.str.}) & > & \text{ring}(CH_2\text{sym.str.}) \\ \text{1,2-DMCB} & & \text{MCB} \\ 2913\ \text{cm}^{-1} & & 2905\ \text{cm}^{-1} \end{array}$$

$$> \text{ring}(CH_2\text{sym.str.})$$
$$\text{TMCB}$$
$$2900\ \text{cm}^{-1}$$

and

$$\begin{array}{ccc} \text{ring}(CH_2\text{sym.str.}) & > & \text{ring}(CH_2\text{sym.str.}) \\ \text{1,2-DMCB} & & \text{1,3-MCB} \\ 2913\ \text{cm}^{-1} & & 2895\ \text{cm}^{-1} \end{array}$$

b)

$$\begin{array}{ccc} \text{ring}(CH_2\text{asym.str.}) & > & \text{ring}(CH_2\text{asym.str.}) \\ \text{MCB} & & \text{1,2-DMCB} \\ 2918\ \text{cm}^{-1} & & 2910\ \text{cm}^{-1} \end{array}$$

$$> \text{ring}(CH_2\text{asym.str.})$$
$$\text{TMCB}$$
$$2893\ \text{cm}^{-1}$$

and

$$\begin{array}{ccc} \text{ring}(CH_2\text{asym.str.}) & > & \text{ring}(CH_2\text{asym.str.}) \\ \text{1,2-DMCB} & & \text{1,3-MCB} \\ 2910\ \text{cm}^{-1} & & 2891\ \text{cm}^{-1} \end{array}$$

Table 8. Calculated vibration frequencies and IR absorption intensities for 1,2,3-trimetlene cylobutane, compared with available experimental frequencies.

Symmetry and description	MINDO/3-FORCES Scaled frequency [cm^{-1}]	Intensity A [km/mol]	PM3 Frequency [cm^{-1}]	expt. [13] Frequency [cm^{-1}]
A_1				
ν_1 =CH_2 asym.str. (2,3)	3080	76.051	3145	3075
ν_2 =CH_2 sym.str. (1,2,3)	3070	4.47	3137	—
ν_3 =CH_2 sym.str. (1,2,3)	3067	14.93	3133	—
ν_4 ring (CH_2 sym.str.)	2900	67.375	3088	2890
ν_5 C=C str. (1,2,3)	1703	0.04	1920	—
ν_6 C=C str. (1)	1603	0.14	1805	—
ν_7 ring (δCH_2 sciss.)	1420	3.68	1386	—
ν_8 δ(=CH_2 sciss.) (1)	1413	10.65	1322	—
ν_9 δ(=CH_2 sciss.) (1,2,3) + ring (δCH_2 sciss.)	1390	0.02	1305	—
ν_{10} ring str. + ring (δCH_2 sciss.)	1208	1.04	1231	—
ν_{11} ring def. + δ(=CH_2 rock.) (2,3)	940	0.22	953	—
ν_{12} δ(=CH_2 rock.) (2,3) + ring def.	826	1.42	850	—
ν_{13} ring breathing	517	0.21	633	—
ν_{14} δ(=CH_2 rock.) (2,3) + ring def.	268	0.33	264	—
A_2				—
ν_{15} ring (γCH_2 twist.)	992	0.00	1032	—
ν_{16} γ(=CH_2 wag.) (2,3)	867	0.00	984	—
ν_{17} γ(=CH_2 twist.) (1) + ring puck.	786	0.00	670	—
ν_{18} γ(=CH_2 twist.) (1,2,3)	681	0.00	592	—
ν_{19} ring puck. + γ(=CH_2 twist.)	364	0.00	384	—
B_1				—
ν_{20} =CH_2 asym.str. (1,2,3)	3081	25.41	3145	—
ν_{21} =CH_2 asym.str. (1, 2,3)	3079	10.99	3144	—
ν_{22} =CH_2 sym.str. (2,3)	3068	46.68	3136	—
ν_{23} C=C str. (2,3)	1633	0.89	1720	1644
ν_{24} δ(=CH_2 sciss.) (2,3)	1413	7.41	1324	—
ν_{25} γ(=CH_2 twist.)	1224	11.28	1229	—
ν_{26} ring str. + ring (γCH_2 wag.)	1181	9.79	1211	—
ν_{27} ring def. + ring (γCH_2 wag. + δ=CH_2 rock.) (1,2,3)	1034	1.14	1080	—
ν_{28} δ(=CH_2 rock.) (2,3) + ring (γCH_2 wag.)	886	0.73	878	—
ν_{29} δ(=CH_2 rock.) (1)	829	0.20	851	—
ν_{30} ring def. + δ(=CH_2 rock.) (1,2,3)	456	0.74	485	—
ν_{31} δ(=CH_2 rock.) (1,2,3)	258	0.15	237	—
B_2				—
ν_{32} ring (CH_2 asym.str.)	2893	64.12	3031	—
ν_{33} ring (δCH_2 rock.) + ring puck.	903	5.43	1035	—
ν_{34} γ(=CH_2 wag.) (1)	868	5.92	1007	—
ν_{35} γ(=CH_2 wag.) (1,2,3) + ring (δCH_2 rock.)	855	0.35	954	865
ν_{36} ring puck. + γ(=CH_2 twist.) (2,3)	694	0.06	727	—
ν_{37} ring (δCH_2 rock.) + γ(=CH_2 twist.) (2,3)	504	0.06	559	—
ν_{38} ring puck. + γ(=CH_2 wag.) (1,2,3)	261	0.05	272	—
ν_{39} ring puck. + ring (δCH_2 sciss. + γ=CH_2 wag.) (1,2,3)	77	0.00	106	—

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.)], 1.20 (=CH_2 twist.), 1.06 (=CH_2 sciss. + ring str.), 1.05 [ring (CH_2 sciss.) + ring str.].

3. The asymmetrical CH_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 exo-methylene groups increases:

$$\begin{array}{ccccc} \text{C=C str.} & > & \text{C=C str.} & > & \text{C=C str.} \\ \text{MCB} & & \text{1,3-DMCB} & & \text{TMCB} \\ 1669\ \text{cm}^{-1} & & 1650\ \text{cm}^{-1} & & 1633\ \text{cm}^{-1} \end{array}$$

such that the C=C stretching vibration frequencies of 1,2-DMCB show the lowest value 1617 cm^{-1}.

5. The values of the ring stretching frequencies decrease 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}

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

The $=CH_2$ bending frequencies decrease as the number of methylene groups increases:

a)

$\delta(=CH_2$ sciss.)	>	$\delta(=CH_2$ sciss.)
MCB		1,3-DMCB
1422 cm^{-1}		1417 cm^{-1}
$> \delta(CH_2$ sciss.)	>	$\delta(=CH_2$ sciss.)
1,2-DMCB		TMCB
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}

6. The CH_2 bending frequencies increase as the number of methylene groups increases:

ring(δCH_2 sciss.)	>	ring(δCH_2 sciss.)
TMCB		1,2-DMCB
1421 cm^{-1}		1406 cm^{-1}
> ring(δCH_2 sciss.)		
MCB		
1338 cm^{-1}		

and

ring(δCH_2 rock.)	>	ring(δCH_2 rock.)
TMCB		1,2-DMCB
903 cm^{-1}		717 cm^{-1}
> ring(δCH_2 rock.)		
MCB		
692 cm^{-1}		

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

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