

# Vibrational Spectra and Symmetry of 3,3,6,6-Tetramethylcyclohexa-1,4-diene

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The vibrational spectra of 3,3,6,6-tetramethylcyclohexa-1,4-diene as a vapour, a liquid, a crystalline solid and isolated in argon and nitrogen matrices at 13 K have been recorded and interpreted in terms of a planar ring structure ( $D_{2h}$ ). The fundamental modes of vibration have been assigned with the aid of a normal coordinate calculation and by comparison with the spectra of cyclohexa-1,4-diene.

## INTRODUCTION

Previous investigations of 3,3,6,6-tetramethylcyclohexa-1,4-diene (TMCHD)<sup>1-4</sup> did not include the vibrational spectra, nor has the molecular structure been determined. On the other hand, there has been much controversy over the molecular structure of the unsubstituted cyclohexa-1,4-diene (CHD). Early investigations of the IR and Raman spectra of CHD<sup>5,6</sup> were interpreted in terms of a planar ring ( $D_{2h}$  symmetry), although a non-planar form with a low barrier to inversion could not be ruled out.<sup>6</sup>

Within 2 years two electron diffraction investigations of CHD<sup>7,8</sup> were reported. In the first, the electron diffraction pattern was interpreted as indicative of a planar configuration; the second reported a boat-form structure ( $C_{2v}$ ) with a dihedral angle of 159.3°. It must be noted, however, that the shrinkage effect was neglected in both investigations. Conclusive evidence for a planar equilibrium geometry of CHD was finally provided by IR and Raman spectral studies of the lowest ring puckering mode.<sup>9,10</sup>

In view of the results for CHD, and with additional evidence provided by NMR spectra of a series of substituted cyclohexa-1,4-dienes,<sup>11</sup> a planar ring geometry has also been proposed for TMCHD.<sup>4</sup>

## EXPERIMENTAL

The IR spectra of TMCHD were recorded on a Perkin-Elmer Model 225 grating spectrometer (4000–200  $\text{cm}^{-1}$ , resolution 1  $\text{cm}^{-1}$ ) and on an evacuable Bruker 114C Fourier transform spectrometer (700–40  $\text{cm}^{-1}$ , resolution 2  $\text{cm}^{-1}$ ). A closed cycle helium cooled cryostat (Displex, Air Products) was used in the mid-IR matrix isolation work. Both Ar and  $\text{N}_2$  were used as matrix materials (typical solute to matrix ratios of 1:400 to 1:1000), and the matrices, once deposited on a CsI window, were kept at a temperature of 13 K. The matrices were annealed at ca 35 K.

The Raman spectra of the crystalline sample at 77 K and of the pure liquid including polarization measurements were recorded with a Dilor RT 30 triple monochromator, interfaced to the datasystem of the Bruker

FTIR instrument. The blue line (488.0 nm) of an argon ion laser (CRL Model 52G) was used for excitation and a 90° scattering geometry was employed. The experimental setup for polarization measurements gave a depolarization ratio,  $\rho$ , of 3/4 for depolarized bands and  $\rho < 3/4$  for polarized bands and the spectral resolution was ca 4  $\text{cm}^{-1}$ .

3,3,6,6-Tetramethylcyclohexa-1,4-diene (TMCHD) was prepared in a three-step synthesis by dimethylation of 5,5-dimethylcyclohexa-1,3-dione (dimedone) to 2,2,5,5-tetramethylcyclohexa-1,3-dione, reduction of the latter to 2,2,5,5-tetramethylcyclohexane-1,3-diol, which by elimination twice of water gave the final product 3,3,6,6-tetramethylcyclohexa-1,4-diene, according to the literature.<sup>3</sup> However, the prescribed dehydration by treatment with *p*-toluenesulphonyl chloride in pyridine under reflux yielded after distillation a complex mixture of products in 25% yield, from which pure TMCHD could be isolated by gas chromatography (Apiezon L, 125 °C) in very poor yields only. A variety of alternative methods of dehydration were tried out on 2,2,5,5-tetramethylcyclohexane-1,3-diol, which were either unsuccessful or did not improve the yield of TMCHD. The samples were purified by repeated gas chromatography (ca 98% purity), giving a colourless liquid with a freezing point of ca 6–7 °C.

## RESULTS AND DISCUSSION

The IR and Raman spectra of TMCHD as a liquid are given in Figs 1 and 2, respectively, and the corresponding wavenumbers, including those of the IR spectra of the vapour and the matrix isolated compound, are given in Table 1. Table 2 contains the assigned fundamentals of TMCHD, with the assignments of CHD included for comparison, and an approximate description of the normal modes.

### Symmetry

A quick perusal of the spectral data reveals that TMCHD, like CHD, is centrosymmetric. The few coincidences between the IR and Raman spectra are with only one exception caused by the isopropylidene ( $\text{CMe}_2$ ) group vibrations. Distinction of  $C_{2h}$  from  $D_{2h}$  rests on

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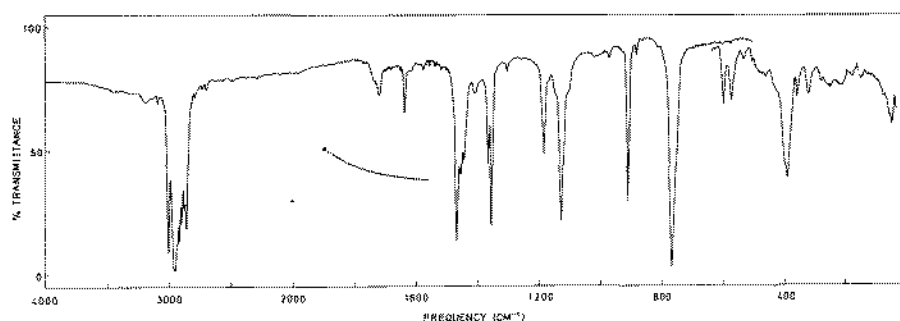


Figure 1. Infrared spectrum of liquid 3,3,6,6-tetramethylcyclohexa-1,4-diene.

the polarization measurements alone. In principle the IR vapour contours should also provide structural information but only a few bands have a distinct PQR structure. With the same definition of the molecular axes as Stidham,<sup>6</sup> the vibrations divide into:  $\Gamma_v = 12A_g + 6B_{1g} + 9B_{2g} + 9B_{3g} + 7A_u + 11B_{1u} + 9B_{2u} + 9B_{3u}$  or  $\Gamma_v = 21A_g + 15B_g + 16A_u + 20B_u$  for  $D_{2h}$  or  $C_{2h}$  symmetry, respectively. Below  $1300\text{ cm}^{-1}$  eleven polarized bands are expected if the symmetry is  $C_{2h}$  and only six if it is  $D_{2h}$ , whereas eight are in fact observed. Of these eight polarized bands, one ( $790\text{ cm}^{-1}$ ) is found in a region where no *gerade* fundamental is expected. Hence, the mere number of polarized bands suggests  $D_{2h}$  symmetry, and a closer inspection of the spectral data definitely rules out the  $C_{2h}$  alternative.

#### Normal coordinate calculation

As an aid during the assignment of the vibrational spectra we have performed a normal coordinate calculation. A valence force field, transferred from cyclohexene<sup>12</sup> and from the saturated hydrocarbons,<sup>13</sup> was employed in the calculation of fundamental frequencies. Both force fields have proved their merit in numerous cases. The force constants for the ring puckering coordinates were obtained from a least-squares procedure using the vibrational frequencies of CHD and the fully deuteriated CHD.<sup>6,9</sup> Our calculation confirms the original assignment of CHD by Stidham<sup>6</sup> except for the ring stretching of  $B_{3u}$  symmetry at  $1405\text{ cm}^{-1}$ . The calculated fundamentals of CHD, and in particular the CH in plane bendings, depart from previous calculations based on the consistent force field approach.<sup>14</sup> Details

of the calculations are available from the authors on request.

#### Raman spectra

Ten of the twelve  $A_g$  fundamentals are readily assigned to either strong or very strong polarized bands. The bands at  $3012$ ,  $1683$  and  $1225\text{ cm}^{-1}$  are characteristic of the olefinic part of TMCHD and the bands at  $2940$ ,  $2904$ ,  $1379$  (weak but definitely polarized),  $1164$  and  $938\text{ cm}^{-1}$  are caused by the saturated part. The antisymmetric methyl group deformation is assigned to the shoulder around  $1448\text{ cm}^{-1}$ , for which we have no polarization data (both of the neighbouring bands at  $1459$  and  $1445\text{ cm}^{-1}$  are depolarized). As expected, the ring breathing and ring deformation observed at  $712$  and  $490\text{ cm}^{-1}$ , respectively, are shifted to lower wavenumbers compared with CHD. Finally, the band at  $284\text{ cm}^{-1}$  is interpreted as the  $CMe_2$  deformation mode. For comparison, the corresponding mode in 2,2-dimethylpropane (neopentane) is observed at  $335\text{ cm}^{-1}$ .<sup>15</sup> Six fundamentals of  $B_{1g}$  symmetry are expected, four of which are methyl group vibrations. The medium to strong bands at  $2967$ ,  $1145$  and  $977\text{ cm}^{-1}$  are ascribed to the antisymmetric methyl stretching, deformation and rocking modes, respectively, whereas the methyl torsion is assigned to the weak band at  $238\text{ cm}^{-1}$ , observed only in the spectrum of the crystalline solid. The C-H out of plane bending, observed as a weak band at  $706\text{ cm}^{-1}$  in CHD,<sup>6</sup> is assigned to the weak band at  $758\text{ cm}^{-1}$ , close to the corresponding  $B_{2u}$  mode which gives rise to the very intense IR band at  $766\text{ cm}^{-1}$ . Alternatively, one can assume the C-H out-of-

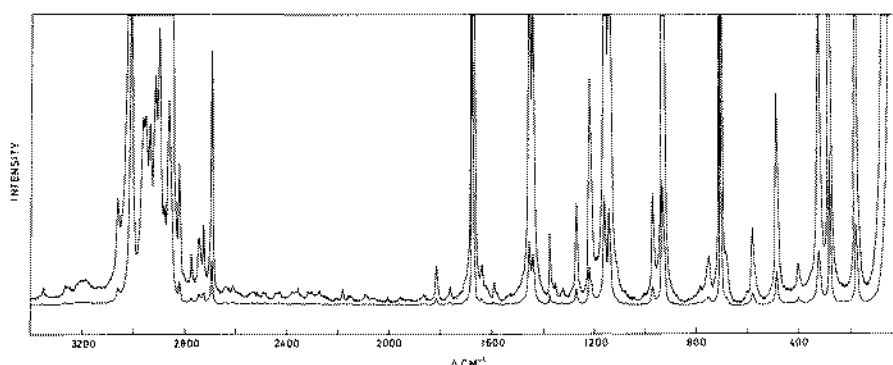


Figure 2. Raman spectrum of liquid 3,3,6,6-tetramethylcyclohexa-1,4-diene.

Table 1. Infrared and Raman spectral data for 3,3,6,6-tetramethylcyclohexa-1,4-diene<sup>a</sup>

Infrared				Raman		Interpretation
Ar-matrix	N <sub>2</sub> -matrix	Liquid	Vapour	Liquid	Depolarization ratio (ρ)	
		3097 vw				1459 + 1644 ( $b_{2g} \times b_{3u}$ )
3032 w	3029 w	3050 vw sh		3064 vw	0.76	2904 + 181 ( $a_g \times b_{3g}$ )
	3020 w					1683 + 1357 ( $a_g \times b_{1u}$ )
3025 m	3018 m					Site effect
3017 m	3013 m	3010 s	3017 s			$b_{1u}$ fundamental
				3012 vs	0.09	$b_{3u}$ fundamental
2996 w	2995 w	2980 sh				$a_g/b_{2g}$ fundamental
2991 w	2992 w					1644 + 1379 ( $b_{3u} \times a_g$ )
	2990 w					2967 + 50 ( $b_{1g} \times b_{2u}$ )
						Site effect
2975 vs	2975 vs	2964 vs	2977 s } 2974 vs } 2969 vs }			$b_{1u}$ fundamental
2973 vs	2973 vs					2957 + 50 ( $b_{3g} \times b_{2u}$ )
2969 vs	2970 vs					$b_{3u}$ fundamental
				2967 s	0.78	$b_{1g}/b_{2g}$ fundamental
2966 vs	2965 vs	2954 vs	2964 s sh			$b_{2u}$ fundamental
2963 s	2964 vs					1683 + 1310 ( $a_g \times b_{3u}$ )
2959 s	2959 sh					2940 + 50 ( $a_g \times b_{2u}$ )
				2957 s	0.73	$b_{3g}$ fundamental
2945 s	2944 s	2938 s	2940 sh			2904 + 50 ( $a_g \times b_{2u}$ )
2943 m sh						Site effect
				2940 s	Pol. <sup>b</sup>	$a_g$ fundamental
2932 m	2932 mw	2922 s	2931 sh			2904 + 50 ( $b_{3g} \times b_{2u}$ )
2929 m	2930 m					1459 + 1472 ( $b_{2g} \times b_{3u}$ )
	2927 w					Site effect
2923 w	2922 vw					1448 + 1472 ( $a_g \times b_{3u}$ )
				2920 s	0.05	$2 \times 1472$ ( $b_{3u} \times b_{3u}$ )
2917 w	2918 vw		2918 w			1274 + 1644 ( $b_{2g} \times b_{3u}$ )
	2915 vw					Site effect
2908 m	2909 w	2901 s	2911 w			$b_{1u}$ fundamental
				2904 vs	0.02	$a_g/b_{3g}$ fundamental
2902 m	2905 w					$b_{2u}$ fundamental
2887 mw	2888 m	2882 s	2887 w			1448 + 1455 ( $a_g \times b_{1u}$ )
				2884 m	0.06	$2 \times 1448$ ( $a_g \times a_g$ )
2878 m	2878 ms	2870 s sh	2874 s			1448 + 1446 ( $a_g \times b_{2u}$ )
	2876 m sh					Site effect
2870 m	2869 m	2864 s				1445 + 1446 ( $b_{1g}/b_{3g} \times b_{2u}$ )
				2867 s	0.02	$2 \times 1446$ ( $b_{2u} \times b_{2u}$ )
2862 mw	2862 w	2858 s sh				1225 + 1644 ( $a_g \times b_{3u}$ )
	2852 vw					Site effect
	2840 vw	2836 w sh				1379 + 1472 ( $a_g \times b_{3u}$ )
	2828 vw					1379 + 1455 ( $a_g \times b_{1u}$ )
				2826 w	0.05	$2 \times 1445$ ( $b_{1g} \times b_{1g}$ )
				1683 vs	0.07	$a_g$ fundamental
				1646 w	0.09	1164 + 490 ( $a_g \times a_g$ )
						Site effect
1644 w	1644 vw	1638 w	~ 1630 vw			$b_{3u}$ fundamental
1643 w	1641 w					Site effect
				~ 1632 sh	Pol. <sup>b</sup>	938 + 712 ( $a_g \times a_g$ )
				1597 vw	0.07	1011 + 611 ( $b_{3g} \times b_{3g}$ )
				1586 vw	0.21	1188 + 399 ( $b_{2u} \times b_{2u}$ )
				1545 vw	~ 0.01	1370 + 181 ( $b_{3g} \times b_{3g}$ )
1472 s	1472 s	1469 s	1472 s			$b_{3u}$ fundamental
1468 m	1466 m					284 + 1188 ( $a_g \times b_{2u}$ )
1462 mw	1461 w					490 + 973 ( $a_g \times b_{1u}$ )
				1459 s	0.75	$b_{2g}$ fundamental
1455 m	1454 m	1455 m	~ 1465 m			$b_{1u}$ fundamental
				1448 sh <sup>b</sup>		$a_g$ fundamental
1446 m	1445 ms	1445 m	~ 1457 sh			$b_{2u}$ fundamental
				1445 s	0.75	$b_{1g}/b_{3g}$ fundamental
1416 vw	1416 vw	1412 vw				284 + 1135 ( $a_g \times b_{1u}$ )
	1405 vw					Site effect
				1379 w	0.14	$a_g$ fundamental

Table 1 (continued)

		Infrared		Raman			
Ar-matrix	N <sub>2</sub> -matrix	Liquid	Vapour	Liquid	Depolarization ratio ( $\rho$ )	Interpretation	
1373 vw	1376 vw			1370 sh	Dep.	977 + 399 ( $b_{1g} \times b_{2u}$ ) $b_{3g}$ fundamental	
1369 w sh	1370 w					490 + 882 ( $a_g \times b_{3u}$ )	
1368 m	1369 m	1368 m	1377 sh			$b_{1u}$ fundamental	
1359 m	1359 sh			1358 vw	0.75	$b_{2u}$ fundamental 758 + 611 ( $b_{1g} \times b_{3g}$ )	
1357 s	1358 s	1358 s	1365 s			$b_{1u}$ fundamental	
	1356 m					Site effect	
1315 vw	1314 vw			1328 vw	0.2	973 + 359 ( $b_{1u} \times b_{1u}$ ) 1135 + 181 ( $b_{1u} \times b_{3g}$ )	
1310 vw	1308 vw	1306 vw				$b_{3u}$ fundamental	
				1274 m	0.75	$b_{2g}$ fundamental	
				1225 s	0.44	$a_g$ fundamental	
				1218 s	Dep. <sup>b</sup>	911 + 322 ( $b_{1u} \times b_{3u}$ )	
1197 vw						Site effect	
1193 vw	1192 w					284 + 911 ( $a_g \times b_{1u}$ )	
1189 m						Site effect	
1188 ms	1188 m	1189 m	1191 m			$b_{2u}$ fundamental	
				1164 s	0.42	$a_g$ fundamental	
1157 vw						Site effect	
1155 vw	1153 w	1150 vw				882 + 284 ( $b_{3u} \times a_g$ )	
	1152 vw					Site effect	
				1147 s	0.74	$b_{2g}$ fundamental	
1138 m sh						Site effect	
1135 s	1136 vs	1130 s	1133 s			$b_{1u}$ fundamental	
	1131 w					Site effect	
1130 m	1130 mw					$b_{3u}$ fundamental	
	1121 vw					Site effect	
1124 vw	1120 vw					238 + 906 ( $b_{1g} \times b_{2u}$ )	
1122 vw						Site effect	
				~ 1120 sh	Dep. <sup>b</sup>	359 + 761 ( $b_{1u} \times b_{2u}$ )	
1115 vw	1113 vw					238 + 882 ( $b_{1g}/b_{2g} \times b_{3u}$ )	
1106 vw		1106 vw	1096 w			712 + 399 ( $a_g \times b_{2u}$ )	
				~ 1085 sh	Dep. <sup>b</sup>	769 + 322 ( $b_{1u} \times b_{3u}$ )	
1034 vw						284 + 761 ( $a_g \times b_{2u}$ )	
				1011 vw	Dep.	$b_{3g}$ fundamental	
973 vw	973 vw	971 vw		977 m	0.76	$b_{1g}/b_{2g}$ fundamental	
						$b_{1u}$ fundamental	
				938 s	0.26	$a_g$ fundamental	
				932 m	Dep. <sup>b</sup>	$b_{3g}$ fundamental	
911 s	910 s	911 s	917 m } 912 s } 908 m }			$b_{1u}$ fundamental	
906 vw	905 vw					$b_{2u}$ fundamental	
				890 sh	Dep. <sup>b</sup>	712 + 181 ( $a_g \times b_{3g}$ )	
882 vw	884 vw					Site effect	
	882 vw	883 vw				$b_{3u}$ fundamental	
				790 vw	0.29	2 × 399 ( $b_{2u} \times b_{2u}$ )	
785 vw	785 vw					586 + CM <sub>e2</sub> twist ( $b_{2g} \times a_u$ )	
775 w sh						Site effect	
769 vs	770 vs	766 vs	766 vs			$b_{1u}$ fundamental	
	769 w					Site effect	
761 ms	756 w	758 s,sh				$b_{2u}$ fundamental	
				758 w	0.77	$b_{1g}$ fundamental	
				712 vs	0.02	$a_g$ fundamental	
				690 w	0.04	2 × 359 ( $b_{1u} \times b_{1u}$ )	
629 vw		599 vw	~ 610 w			238 + 399 ( $b_{1g} \times b_{2u}$ )	
				611 vw	0.75	$b_{3g}$ fundamental	
				586 m	0.76	$b_{2g}$ fundamental	
		572 vw				181 + 399 ( $b_{3g} \times b_{2u}$ )	
				490 vs	0.06	$a_g$ fundamental	
				407 vw	0.77	$b_{2g}$ fundamental	
399 w	397 w	391 w	~ 390 w			$b_{2u}$ fundamental	
396 w						Site effect	

Table 1 (continued)

Infrared				Raman		
Ar-matrix	N <sub>2</sub> -matrix	Liquid	Vapour	Liquid	Depolarization ratio ( $\rho$ )	Interpretation
		359 vw		326 s	0.76	$b_{1u}$ fundamental
		322 vw		284 vs	0.32	$b_{1g}$ fundamental
		~250 vw		238 vw <sup>c</sup>		$b_{3u}$ fundamental
				181 s	0.76	$a_g$ fundamental
		~50 vw				$b_{3u}$ fundamental
						$b_{1g}/b_{2g}$ fundamental
						$b_{3g}$ fundamental
						$b_{2u}$ fundamental

<sup>a</sup> Frequencies in  $\text{cm}^{-1}$ ; bands outside the fundamental regions, 3100–2800 and 1700–40  $\text{cm}^{-1}$ , omitted. Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder.

<sup>b</sup> Uncertainty in  $\rho$  due to overlapping bands.

<sup>c</sup> Frequency taken from spectra of polycrystalline TMCHD at ca 80 K.

plane bending to be hidden by the very strong  $A_g$  mode at 712  $\text{cm}^{-1}$ , in which case the 758  $\text{cm}^{-1}$  band is explained as a combination band of  $B_{1g}$  symmetry. The remaining  $\text{CMe}_2$  twist vibration is assigned to the strong band at 326  $\text{cm}^{-1}$ , as suggested by the normal coordinate calculation.

The  $B_{2g}$  C–H stretching, ring stretching and ring deformation modes of CHD all have counterparts in the 3012, 1274 and 586  $\text{cm}^{-1}$  Raman bands of TMCHD. The methyl group stretching, rocking and torsion modes of  $B_{2g}$  symmetry are calculated at approximately the same frequency values as their  $B_{1g}$  counterparts, and the 2967, 977 and 238  $\text{cm}^{-1}$  bands are consequently assigned both to the  $B_{1g}$  and  $B_{2g}$  modes. The C–H in-plane bend is assigned to the strong band at 1147  $\text{cm}^{-1}$  and for the remaining  $B_{2g}$  mode the normal coordinate calculations indicate that the 407  $\text{cm}^{-1}$  band be interpreted as the  $\text{CMe}_2$  wag vibration. The remaining Raman active fundamentals, of  $B_{3g}$  symmetry, are assigned as follows. Although the  $B_{3g}$  antisymmetric methyl stretching is calculated at the same frequency as the corresponding  $B_{1g}$  and  $B_{2g}$  modes, the strong band at 2957  $\text{cm}^{-1}$  is interpreted as the  $B_{3g}$  fundamental. The corresponding  $B_{3g}$  symmetrical stretching and its  $A_g$  counterpart are assumed to be nearly degenerate and the Raman band at 2904  $\text{cm}^{-1}$  is duly assigned to both fundamentals. The methyl deformation modes are readily assigned to the 1445 and 1370  $\text{cm}^{-1}$  bands, whereas the methyl rocking mode is assigned to the band at 932  $\text{cm}^{-1}$ . The Raman

band at 1218  $\text{cm}^{-1}$  is ascribed to the C–Me<sub>2</sub> antisymmetric stretching, and the C–H out of plane bending, observed at 985  $\text{cm}^{-1}$  in CHD,<sup>6</sup> is found at the slightly higher frequency of 1011  $\text{cm}^{-1}$  in the Raman spectrum of TMCHD. The  $B_{3g}$  low-frequency  $\text{CMe}_2$  rocking and ring puckering modes of TMCHD are assigned to the bands at 181 and 611  $\text{cm}^{-1}$ , respectively, as suggested by the normal coordinate calculation. The remaining Raman bands, not ascribed as fundamental vibrations, can all easily be assigned to combinations as shown in Table 1.

### Infrared spectra

The IR spectra of TMCHD isolated in argon and nitrogen matrices contain a large number of bands, some of which are due to different trapping sites in the matrices. These effects can be distinguished by comparing spectra of the compound isolated in different matrices before and after annealing, as the site effects will not be the same. As mentioned earlier, the IR vapour phase band contours were of little help in the assignments. The calculated contours, depicted in Fig. 3, indicate A-type bands with prominent Q-branches for the  $B_{1u}$  fundamentals and nondescript B- and C-type bands for the  $B_{3u}$  and  $B_{2u}$  modes, respectively.

A total of eleven  $B_{1u}$  fundamentals are expected for TMCHD. Unfortunately, only the two bands at 2975

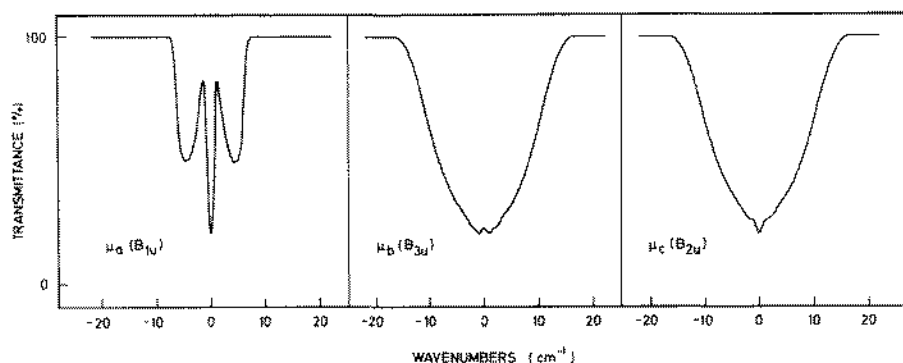


Figure 3. Calculated IR vapour phase band contours of 3,3,6,6-tetramethylcyclohexa-1,4-diene.

Table 2. Assignment of fundamental frequencies of cyclohexa-1,4-diene (CHD) and 3,3,6,6-tetramethylcyclohexa-1,4-diene (TMCHD)

	CHD <sup>a</sup>	TMCHD <sup>b</sup>	Approximate description		CHD <sup>a</sup>	TMCHD <sup>b</sup>	Approximate description	
$A_g$	3032	3012	C-H stretching	$A_u$	(2950)	C-H <sub>3</sub> antisym. stretching		
		2940	C-H <sub>3</sub> antisym. stretching		(1460)	C-H <sub>3</sub> antisym. deformation		
		2904	C-H <sub>3</sub> sym. stretching		(1260)	C-H <sub>2</sub> twisting		
	2882 <sup>c</sup>		C-H <sub>2</sub> sym. stretching		(1020)	C-H bending out-of-plane		
	1680	1683	C=C stretching		(980)	C-H <sub>3</sub> rocking		
		1448	C-H <sub>3</sub> antisym. deformation		(510)	Ring puckering/C-Me <sub>2</sub> twisting		
	1426		C-H <sub>2</sub> deformation			Ring puckering		
		1379	C-H <sub>3</sub> sym. deformation		(400)	Methyl torsion		
	1197	1225	C-H bending in-plane		(240)	C-Me <sub>2</sub> twisting		
		1164	C-Me <sub>2</sub> stretching					
	938	C-H <sub>3</sub> rocking						
	854	712	Ring breathing	$B_{1u}$	3019	3025	C-H stretching	
	530	490	Ring deformation			2975	C-H <sub>3</sub> antisym. stretching	
		284	C-Me <sub>2</sub> deformation		2908	C-H <sub>3</sub> sym. stretching		
					2825	C-H <sub>2</sub> sym. stretching		
$B_{1g}$		2967	C-H <sub>3</sub> antisym. stretching			1455	C-H <sub>3</sub> antisym. deformation	
		1445	C-H <sub>3</sub> antisym. deformation		1430	C-H <sub>2</sub> deformation		
	(1250)		C-H <sub>2</sub> twisting		1368	C-H <sub>3</sub> sym. deformation		
		977	C-H <sub>3</sub> rocking		1357	C-Me <sub>2</sub> stretching		
	706	758	C-H bending out-of-plane		1159	C-H bending in-plane		
		326	C-Me <sub>2</sub> twisting		973	C-H <sub>3</sub> rocking		
		238	Methyl torsion		956	911	Ring stretching	
					887	769	Ring deformation	
						359	C-Me <sub>2</sub> deformation	
	$B_{2g}$	3032	3012	C-H stretching	$B_{2u}$		2966	C-H <sub>3</sub> antisym. stretching
		2967	C-H <sub>3</sub> antisym. stretching			2877	C-H <sub>2</sub> antisym. stretching	
		1459	C-H <sub>3</sub> antisym. deformation			2902	C-H <sub>3</sub> sym. stretching	
1377		1274	Ring stretching			1446	C-H <sub>3</sub> antisym. deformation	
(1230)			C-H <sub>2</sub> wagging			1359	C-H <sub>3</sub> sym. deformation	
1035		1147	C-H bending in-plane			1188	C-Me <sub>2</sub> antisym. stretching	
		977	C-H <sub>3</sub> rocking			906	C-H <sub>3</sub> rocking	
574		586	Ring deformation			877	C-H <sub>2</sub> rocking	
		407	C-Me <sub>2</sub> wagging			622	761	C-H bending out-of-plane
		238	Methyl torsion				399	C-Me <sub>2</sub> rocking
$B_{3g}$		2957	C-H <sub>3</sub> antisym. stretching			50	Ring puckering	
		2904	C-H <sub>3</sub> sym. stretching	$B_{3u}$	3019	3017	C-H stretching	
	2865 <sup>c</sup>		C-H <sub>2</sub> antisym. stretching			2969	C-H <sub>3</sub> antisym. stretching	
		1445	C-H <sub>3</sub> antisym. deformation			1639	C=C stretching	
		1370	C-H <sub>3</sub> sym. deformation			1472	C-H <sub>3</sub> antisym. deformation	
		1218	C-Me <sub>2</sub> antisym. stretching			1358	C-H <sub>2</sub> deformation	
	985	1011	C-H bending out-of-plane			1193	C-H bending in-plane	
		932	C-H <sub>3</sub> rocking			(960)	1130	Ring stretching
	(900)		C-H <sub>2</sub> rocking			882	C-H <sub>3</sub> rocking	
		611	C-Me <sub>2</sub> rocking/ring puckering			322	C-Me <sub>2</sub> wagging	
403		Ring puckering/C-H bending out-of-plane			250	Methyl torsion		
	181	C-Me <sub>2</sub> rocking						

<sup>a</sup> Observed frequencies ( $\text{cm}^{-1}$ ) and assignments from Ref. 6 except where noted. Frequencies in parentheses are calculated values (this work).

<sup>b</sup> Observed frequencies ( $\text{cm}^{-1}$ ) from this work; Raman liquid; IR, argon matrix. Frequencies in parentheses are calculated values.

<sup>c</sup> Reassigned in Ref. 10.

and  $911 \text{ cm}^{-1}$  in the IR spectrum display a distinct PQR structure, the rest being either overlapped by other fundamentals or too weak to be observed in the vapour phase spectrum. Five of the  $B_{1u}$  fundamentals are characteristic methyl group frequencies and two are characteristic olefinic frequencies. Hence, the IR bands observed in the argon matrix at 2975, 2908, 1455, 1368 and  $973 \text{ cm}^{-1}$  are described as methyl group vibrations while the bands at 3025 and  $1135 \text{ cm}^{-1}$  are ascribed as the olefinic C-H stretching and bending vibrations as shown in Table 2. The ring stretching and deformation of  $B_{1u}$  symmetry are assigned to the IR bands around  $911$  and  $769 \text{ cm}^{-1}$ , respectively, both shifted towards

lower wavenumbers than observed in CHD ( $956$ ,  $887 \text{ cm}^{-1}$ ).<sup>6</sup> For the C-Me<sub>2</sub> stretching and deformation modes of  $B_{1u}$  symmetry we propose the strong band at  $1357 \text{ cm}^{-1}$  for the former and the very weak band at  $359 \text{ cm}^{-1}$  for the latter.

The CMe<sub>2</sub> vibrations of  $B_{2u}$  symmetry are readily assigned to the bands at 2966, 2902, 1446, 1359, 1188 and  $906 \text{ cm}^{-1}$  as shown in Tables 1 and 2. All six modes are fairly close to their  $B_{3g}$  counterparts. The very strong IR absorption around  $761 \text{ cm}^{-1}$  is the only candidate for the CH( $B_{2u}$ ) out-of-plane bending mode. In CHD, the corresponding fundamental (also a very strong IR band) is observed at a lower frequency,<sup>6</sup> probably owing

to the admixture of methylene rocking. For the  $CMe_2$  rocking and the ring puckering modes of  $B_{2u}$  symmetry our normal coordinate calculation suggests frequencies around 400 and 40  $cm^{-1}$ , respectively. We assign the former with confidence to the IR band at 399  $cm^{-1}$ . The latter is tentatively assigned to a very weak band at ca 50  $cm^{-1}$ , present in the IR spectra of both the liquid and crystalline solid.

The C-H and C=C stretchings of  $B_{3u}$  symmetry are ascribed to the IR bands at 3017 and 1644  $cm^{-1}$ , corresponding closely to the CHD absorptions at 3019 and 1644  $cm^{-1}$ .<sup>6</sup> The  $B_{3u}$  antisymmetric stretching and bending, pertaining to the methyl groups, are observed at 2969 and 1472  $cm^{-1}$ , respectively, whereas the methyl rocking mode is assigned to the very weak band at 882  $cm^{-1}$ . In the case of the  $B_{3u}$  C-H in-plane bending and the antisymmetric ring stretching modes, we rely strongly on the results of our normal coordinate calculation

and assign these modes to the bands at 1310 and 1130  $cm^{-1}$ , respectively. Finally, the weak band at 322  $cm^{-1}$  is ascribed to the  $CMe_2$  wagging mode while the methyl torsion is believed to be the origin of the very weak, broad feature around 250  $cm^{-1}$  in the IR spectrum of the liquid. In the solid-phase spectrum this band appears at 271  $cm^{-1}$ .

The inactive fundamentals of  $A_u$  symmetry were calculated and the results are given in Table 2. Remaining IR bands, not interpreted as fundamentals, are readily assigned to combinations as shown in Table 1.

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