

The Molecular Structure of 3-Methylene-1,4-pentadiene Studied by Gas-Phase Electron Diffraction and by Vibrational, NMR and Ultraviolet Spectroscopy

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3-Methylene-1,4-pentadiene, which can be considered as the parent of all cross-conjugated systems, was synthesized and was studied by gas-phase electron diffraction (ED) at ambient temperature with two nozzle-to-plate distances. The spectroscopic techniques: ultraviolet, infrared, Raman and NMR (¹H and ¹³C) spectroscopy were applied, and spectra were recorded at various temperatures and states of aggregation, including matrix isolation at 14 K and high-pressure (infrared spectroscopy) at 60 kbar.

Starting from molecular mechanics calculations, the ED data were refined to reveal an *anti*, *skew* conformation consisting of a bent *anti* butadiene fragment with the third vinyl group making a dihedral angle of 40° from the butadiene plane, rotated from the *cis* configuration. The cross-conjugated C=C bond was observed to be 0.0075 Å larger than the other C=C bonds, in agreement with theoretical predictions. The two types of C=C bonds cannot, however, be claimed to be significantly different. The existence of a second conformer, possibly with a 10 kJ mol⁻¹ higher ΔH° value, was suggested from the vibrational spectral data.

The electronic spectra seem compatible with the proposed *anti*, *skew* conformation. Raman polarization data, the NMR results and the force constant calculation seem to favour a conformer with a low molecular symmetry (C₂ or C_s without being a planar molecule). The apparent discrepancy may be due to strong local symmetry in the molecule (IR, Raman) and rapid internal motion on the NMR time scale. The vibrational spectra have been interpreted.

Dedicated to Professor Otto Bastiansen on his 70th birthday

Cross-conjugation is a phenomenon that occurs widely in organic chemistry, as illustrated by numerous classes of compounds, among them quinones, fulvenes, many dyestuffs, fused-ring aromatics, and cross-conjugated polymers. If only

hydrocarbon frameworks are considered, the simplest cross-conjugated molecule is 3-methylene-1,4-pentadiene (MPD, 2-vinyl-1,3-butadiene), which hence may be regarded as the parent of all cross-conjugated systems. In view of the importance of the cross-conjugation phenomenon it seemed desirable to carry out a detailed structural analysis of MPD. Since MPD and its vinyllogues have recently become interesting starting materials in preparative organic chemistry,¹ there was additional impetus to study the

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triene. Finally, MPD is an unusual 1,3-butadiene derivative, a member of a class of compounds we have been interested in for a long time.

Theoretical calculations²⁻⁶ of bond orders in cross-conjugated hydrocarbon systems indicate that the π -electron distributions in cross-conjugated polyenes differ systematically from those in linear polyenes. The most conspicuous characteristic of a cross-conjugated polyene is a reduced π -bond order of the cross-conjugated double bond. If the C=C bonds of a potentially cross-conjugated molecule are not coplanar, the effect described above is expected to be reduced and eventually to disappear when non-overlapping π systems are involved. It is of interest to study whether it is possible to detect any differences in C=C bond lengths in MPD.

In the present paper we describe the synthesis of MPD and detailed structural and spectroscopic investigations of MPD in the vapour phase, in solution, as a neat liquid at various temperatures and as an amorphous solid at 90 K. Moreover, the sample was studied under high pressure (ca. 60 kbar) in a diamond anvil cell. Finally, IR matrix isolation spectra of MPD in argon and nitrogen matrices at 14 K were obtained by the hot-nozzle method. The purpose of all these investigations was to determine the molecular structure of MPD, to establish whether one or more conformers were present in the various states of aggregation, and possibly the energy difference (ΔH^0) between them. Additionally, it was our purpose to interpret the IR, Raman, NMR and UV spectra in terms of the structure and to compare them with those of related polyenes.

Experimental

Preparation. MPD was first prepared in 1955 by pyrolysis of an appropriate di-⁷ or triacetate⁸ precursor, and the same method was used to synthesize the material used in this study. However, since the material required for the spectroscopic and structural investigations had to be very pure, extensive purification was carried out using vacuum transfer techniques at 0.01 Torr and preparative gas chromatography (20% Squalan on Chromosorb W, 353 K). The hydrocarbon finally isolated was more than 98% pure, and contained no acidic impurities (acetic acid from the pyrolysis). Some of the preliminary IR, Raman and

NMR spectra were recorded using a sample which had not been subjected to preparative gas chromatography, and these spectra clearly revealed the presence of impurities. Therefore, all the final spectra and the electron diffraction patterns were recorded using the highly purified sample.

Electron diffraction study. Electron diffraction diagrams were recorded with the Oslo apparatus⁹ using a nozzle-tip temperature of 298 K. The electron wavelength was 0.06375 Å, as calibrated against the diffraction pattern for benzene. The estimated deviation in the determination of the wavelength is 0.1%. Electron diffraction photographs were recorded on Kodak Electron Image plates at nozzle-to-plate distances of 484.94 mm (6 plates) and 204.94 mm (3 plates). Ranges of data were 1.50–20.75 and 6.50–43.75 Å⁻¹, with Δs increments of 0.25 Å⁻¹. The experimental data were treated in the usual way,¹⁰ and the modification function used was $s \times f_c^{-2}$. The scattering amplitudes and phases were calculated¹¹ using the partial-wave method, based upon the analytical HF potentials for the C atoms¹² and the best electron density of bonded hydrogen for the H atoms.¹³ The inelastic scattering factors used were those of Tavard *et al.*¹⁴

Spectral studies. The IR spectra were recorded on a Perkin-Elmer model 225 spectrometer and on a Bruker model 114 C Fourier transform spectrometer in the region 4000–50 cm⁻¹. MPD was studied as vapour in cells of path length 10 cm (4000–300 cm⁻¹) and 20 cm (600–50 cm⁻¹) with pressures of 80 and 20 Torr, respectively. The sample was shock frozen on a window of CsI (mid IR) or Si (far IR) at 85 K and spectra of the unannealed, amorphous compound were obtained. Numerous attempts were made to crystallize MPD, either by annealing the amorphous sample or by slowly cooling the liquid from room temperature down to 80 K.

A sample of MPD was compressed in a diamond anvil cell (DAC) using a hole of diameter 0.4 mm in a spacer of bronze. The DAC was coupled to a 4x beam condenser from Perkin-Elmer, and the IR spectra were recorded at ca. 60 kbar and at a negligible pressure. By visual observation in a polarization microscope it was verified that the sample did not crystallize at high pressure.

MPD mixed with argon or nitrogen in a ratio of 1:500 was deposited at different rates up to 5 mmol h⁻¹ on a CsI window in a Displex unit from Air Products. The temperature of the window was ca. 14 K during deposition and recording of the IR spectra. Before deposition, the sample passed through a quartz nozzle surrounded by a heating wire, and the depositions were performed at 313 and 500 K. The IR spectra were recorded immediately after deposition and after the sample had been annealed to 38 K. Apart from minor matrix effects, no significant changes in the spectra were observed.

Raman spectra were recorded with a Dilor triple monochromator spectrometer RT 30 interfaced to the Aspect 2000 computer of the Bruker spectrometer. An argon ion laser model 2000 from Spectra Physics was employed, using the 514.5 nm line for illumination. The vapour was filled to full pressure (ca. 80 Torr at ambient temperature) in a glass cell with Brewster windows. A multiple-pass unit from Spex giving ca. 10 reflections was used with 1.2 watt of laser power. Slits giving 3, 4 and 5 cm⁻¹ were employed, and photon counting times as long as 8 sec were in some cases used to improve the signal/noise ratio. The liquid was evaporated into a capillary of 2 mm inner diameter surrounded by a Dewar vessel cooled by a flow of cold nitrogen gas.¹⁵ The liquid was studied at various temperatures between 270 and 100 K, and polarization measurements were carried out. Additional spectra were recorded of the solid formed when the vapour was deposited on a copper finger cooled with liquid nitrogen. None of these attempts led to crystallization of MPD.

The UV spectra were recorded with a Shimadzu model 260 ultraviolet-visible spectrometer in the range 350–190 nm. MPD was dissolved in n-hexane solution and the solution filled into a 1 cm cell, whereas the vapour mixed with air was recorded in a cylindrical cell of 2.5 cm path length.

Proton and ¹³C NMR spectra of MPD were recorded on a Varian XL-300 FT spectrometer using a 5 mm ¹H/broadband switchable probe. Spectra were run at both 263 and 203 K using CD₂Cl₂ as the solvent and TMS as the reference. ¹³C resonance assignments were made with the help of DEPT spectra.

Determination of molecular structure and conformation

Electron diffraction. The molecular structure and conformation of MPD were studied by interactive least-squares intensity refinements. The non-bonded interatomic distances of the molecular models were calculated on the basis of r_{α} parameters, which include corrections for shrinkage effects.¹⁶

Molecular mechanics (MM) calculations often give useful starting parameters for an electron diffraction (ED) study. When conformational problems are involved it may furthermore be of advantage to know the calculated conformational energies of the various conformers.

In the present case, MM calculations were carried out for 7×7 conformers of MPD with the MMP2 program.¹⁷ These 49 models correspond to combinations of the two dihedral angles at the CC single bonds, when each of them was varied between 0° and 180°, in steps of 30°. In each case all parameters were relaxed except the two dihedral angles. The calculations gave two minima, corresponding to *anti,cis* and *cis,cis* conformers. The two energy minima were practically equal, favoring the *cis,cis* conformer by 0.28 kJ mol⁻¹. The *anti,cis* conformer is, however, favoured statistically, and the MM calculations therefore indicate that MPD might exist in an *anti,cis/cis,cis* conformational mixture with an estimated 2:1 relative abundance of the two conformers.

Normal coordinate calculations were carried out for *anti,cis* and *cis,cis* conformers of MPD. These calculations yielded vibrational amplitudes (u_{ij}) for all interatomic distances, as well as the perpendicular correction coefficients (K_{ij}), necessary for carrying out an ED study including shrinkage corrections. The normal coordinate analyses were based on the quantum mechanical force field for 1,3-butadiene.¹⁸ The torsional frequencies were calculated to be 108 and 86 cm⁻¹.

The choice of molecular parameters for MPD in the beginning of the study was partly based on the MM results for the *anti,cis* and *cis,cis* conformers. The following independent parameters were used for the first ED models: $r(C^1=C^2)$, $r(C^3=C^4) = r(C^5=C^6)$, $r(C^2-C^3) = r(C^2-C^5)$, $r(C-H)$, $\angle C^1=C^2-C^3_{cis} = \angle C^1=C^2-C^5_{cis}$, $\angle C^1=C^2-C^5_{anti}$, $\angle C^2-C^5=C^6_{anti} = \angle C^2-C^3=C^4_{cis}$ = $\angle X^2-C^5=C^6_{cis}$, $\angle C=C-H$ (Fig. 1). In the two low-energy MM models the C=C-H angles var-

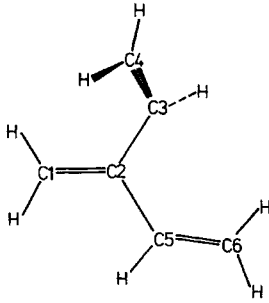


Fig. 1. The molecular structure of 3-Methylene-1,4-pentadiene (MPD) in the *anti,skew* conformation.

ied between 115.0 and 123.8°. An average C=C–H angle was used as a parameter, while the C=C–H angle differences from the *anti,cis* and *cis,cis* MM models were built into the ED models. In addition to the geometrical parameters described above, the C¹=C²–C³=C⁴ (φ_1) and C¹=C²–C⁵=C⁶ (φ_2) dihedral angles were introduced as independent parameters. The vibrational amplitudes were set equal to the calculated u_{ij} values.

In the beginning of the study both conformers were kept planar. The R_1 factor (for the long camera data) was 7.53% for an *anti,cis* conformer and 9.73% for a *cis,cis* conformer, while

a 2:1 conformational mixture of the two gave R_1 equal to 8.07%. Inspections of theoretical and experimental RD curves indicated that a change from local planar *cis* to non-planar *skew* arrangements might improve the fit between the theoretical and experimental RD curves. When non-planarity of the carbon skeleton was allowed for, the conformational composition refined to 75.0 (6.6)% *anti,skew* + 25.0% *skew,skew*, and the *skew* angle was determined to 34.6(1.6)°, while R_1 was reduced to 6.70% (the numbers in brackets are standard deviations from the least-squares refinements).

The non-bonded interactions in a *cis* and in a *skew* C=C–C=C fragment are different. The C=C–H angle differences that were introduced in the beginning of the study were therefore removed, and two types of C=C–H angles [\angle C=C(C)–H and \angle C=C(H)–H] were used as independent parameters. This clearly improved the models, and R_1 was reduced to 6.40%.

Since the vibrational amplitudes and perpendicular amplitude corrections that had been used so far were calculated for planar *anti,cis* and *cis,cis* conformers, the normal coordinate calculations were repeated for the non-planar ED models. When the new sets of u_{ij} and K_{ij} values were introduced, the R factors for the long and short camera distances were reduced, as ex-

Table 1. Structural parameters determined for *anti,skew* 3-methylene-1,4-pentadiene (MPD). Distances in Å, angles in degrees, 3 × standard deviations in brackets.

Parameter	r_a , \angle_a	r_a	u_a
$r(\text{C}^1=\text{C}^2)$	1.349(27)	1.343	0.0436(27)
$r(\text{C}^3=\text{C}^4)$	1.342(15)	1.315	0.0437(27)
$r(\text{C}^5=\text{C}^6)$		1.315	0.0437(27)
$r(\text{C}-\text{C})$	1.479(3)	1.476	0.0518(26)
$r(\text{C}-\text{H})$	1.091(4)		0.0801(33)
$\angle\text{C}^1=\text{C}^2-\text{C}^3$	121.7(2.2)	$u(\text{C}^1\dots\text{C}^5)$	0.0616(78) ^a
$\angle\text{C}^1=\text{C}^2-\text{C}^5$	118.7(2.7)	$u(\text{C}^1\dots\text{C}^4)$	0.1214(150)
$\angle\text{C}^2-\text{C}^3=\text{C}^4$	125.2(3.8)	$u(\text{C}^3\dots\text{C}^6)$	0.1085(150)
$\angle\text{C}^2-\text{C}^5=\text{C}^6$	126.6(3.1)	$u(\text{C}^1\dots\text{C}^6)$	0.0676(99)
$\angle\text{C}=\text{C}(\text{H})-\text{H}$	121.3(1.9)	$u(\text{C}^4\dots\text{C}^5)$	0.0931(99)
$\angle\text{C}=\text{C}(\text{C})-\text{H}$	116.2(8.1)	$u(\text{C}^4\dots\text{C}^6)$	0.1615(456)
$\varphi(\text{C}=\text{C}-\text{C}=\text{C})_{\text{skew}}$	39.3(8.3)	$u(\text{C}^1\dots\text{H}^8)$	0.0801(33) ^b
$R_1(\text{long C.D.})/\%$ ^c	4.17		
$R_2(\text{short C.D.})/\%$	9.50		

^aAll C...C distances over one valence angle refined in a group. ^bAll C...H distances over one valence angle refined in a group. ^c $R = [\sum_i w_i (l_i(\text{calc}) - l_i(\text{obs}))^2 / \sum_i w_i l_i(\text{obs})^2]^{1/2}$.

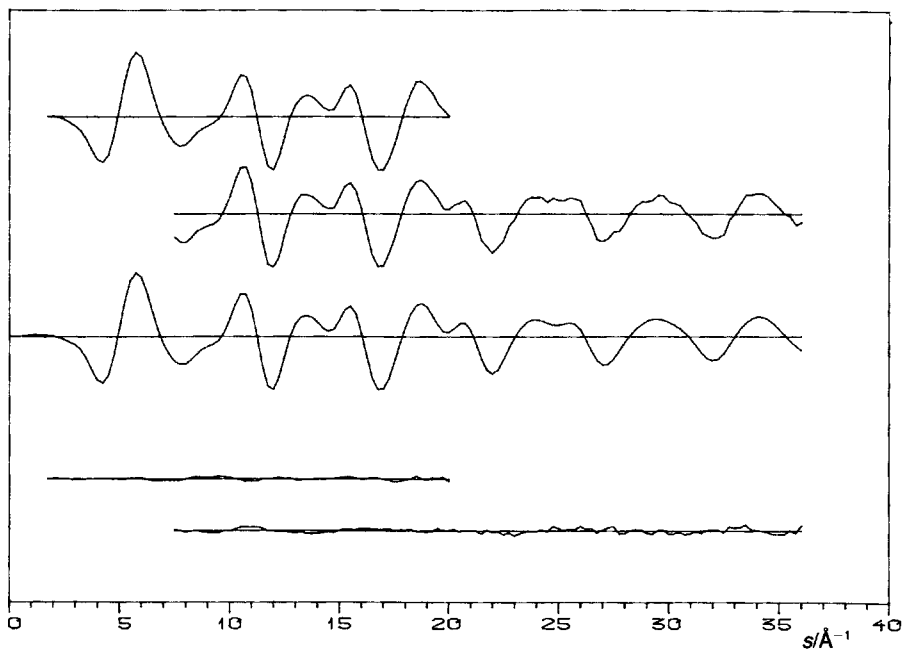


Fig. 2. The theoretical intensity curve (3rd curve) calculated from the model in column 2, Table 1, together with the experimental intensities of the short (1st curve) and long (2nd curve) plate distances with their differences (4th and 5th curves).

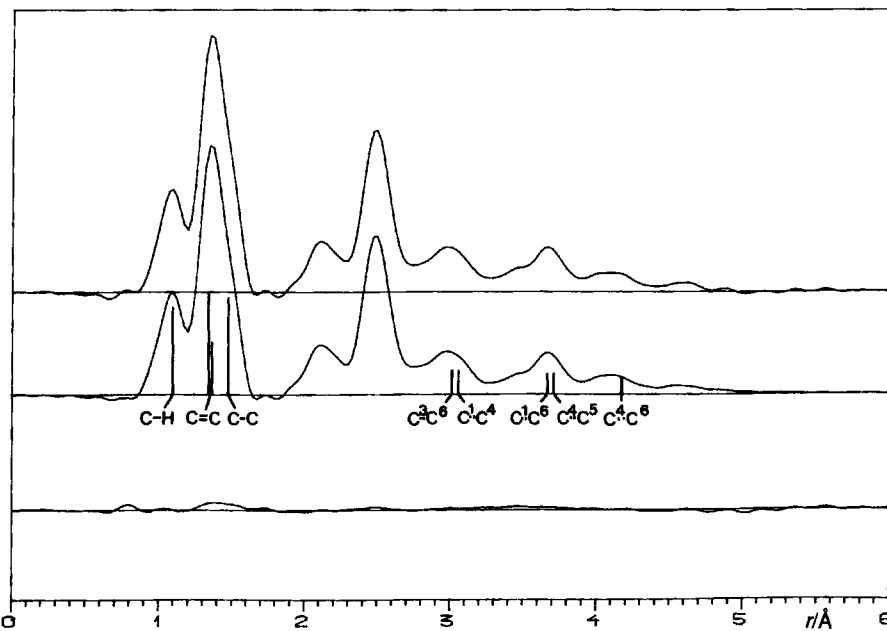


Fig. 3. The theoretical (top) and experimental (bottom) radial distribution (RD) curves for MPD and their differences. The vertical bars indicate contributions from some of the important distances.

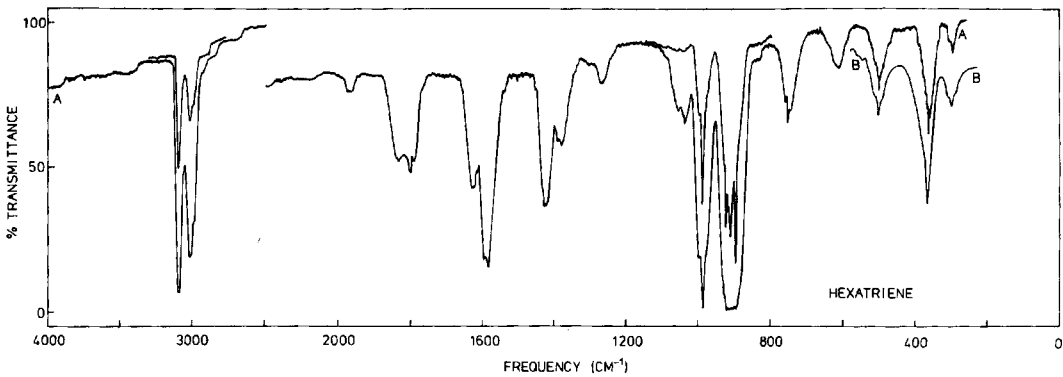


Fig. 4. Vapour infrared (IR) spectrum of MPD in 10 cm (4000–300 cm^{-1}) and 20 cm cells (600–200 cm^{-1}); curves A and B: 80 Torr; curve C: 20 Torr.

pected, but in addition two important parameters were altered. The conformational composition was now determined to be 93.2% *anti,skew*/6.8% *skew,skew*, and the *skew* dihedral angle increased from ca. 35° to ca. 40°. The error limit of the conformer fractions is 18.8%, and it might therefore be concluded that the electron diffraction data are in accordance with conformationally homogeneous MPD molecules. In the further study a conformationally homogeneous *anti,skew* model was therefore used.

Table 1 shows the final structural results obtained for 3-methylene-1,4-pentadiene. In this model all C=C–C valence angles were determined independently, and most of the vibrational amplitudes have been refined. The theoretical intensity curve calculated from the parameters given in Table 1 is shown in Fig. 2, while the corresponding theoretical and experimental RD curves are presented in Fig. 3.

Vibrational spectra. Among the many IR spectra recorded of MPD, a vapour spectrum is given in Fig. 4, a spectrum of the amorphous solid at 90 K in Fig. 5, and a spectrum of the compound isolated in a nitrogen matrix (1:500) at 14 K and nozzle temperature equal to 313 K in Fig. 6. A Raman spectrum of the vapour is shown in Fig. 7, whereas a spectrum of the liquid cooled to 240 K is shown in Fig. 8. A fairly comprehensive set of the spectral data are listed in Table 3. In two older studies the authors claim to have isolated MPD, and certain IR frequencies⁸ and an incomplete IR spectrum⁷ are presented. However, these data have very little resemblance to our present results.

The first question which arises is: are our spectral results in agreement with the presence of one or more conformers of MPD in the different states of aggregation? With the formula C_6H_8 , MPD has 36 fundamentals of which 28 should be

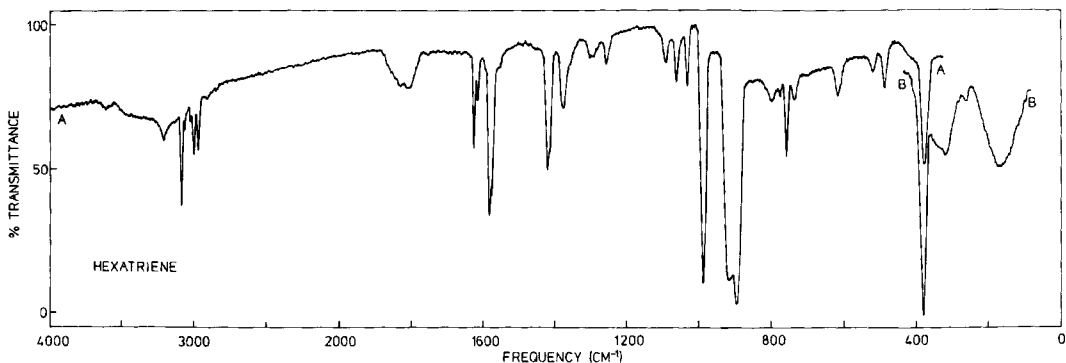


Fig. 5. IR spectrum of MPD as an amorphous solid at 90 K.

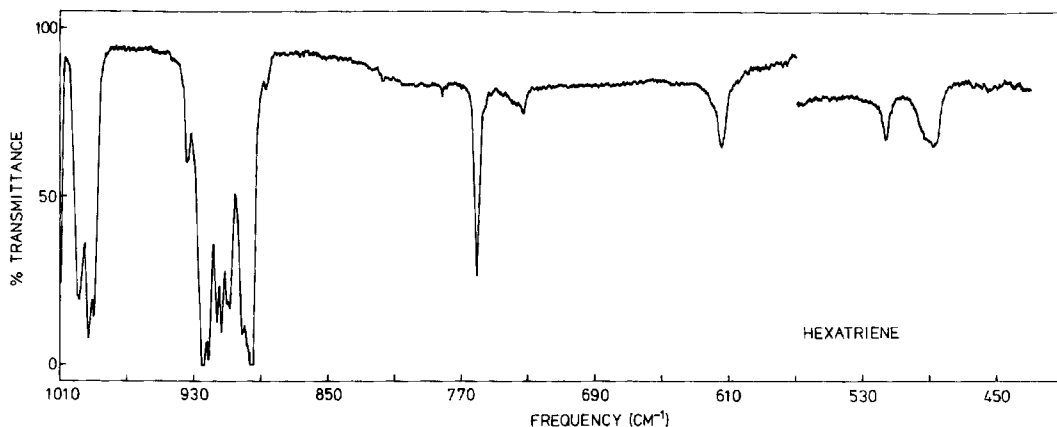


Fig. 6. IR spectrum of MPD isolated in nitrogen matrix (1:500) at 14 K; nozzle temperature 313 K.

situated below 1700 cm^{-1} . A quick count of the prominent IR and Raman bands from Figs. 4–8 or the data of Table 3 reveal approximately the same number. Therefore, these superficial arguments suggest one predominant conformer. Most compounds with possibilities for conformational equilibria exist as only one conformer (generally the most stable in the liquid) in the crystalline state. From a comparison between the vapour, liquid and matrix spectra on the one hand, and the crystal spectra on the other, a definite conclusion regarding the existence of conformers can be reached. Unfortunately, for reasons not known to us, all attempts to crystallize MPD by cooling or by applying pressure failed (see above). It is

our experience that organic molecules which are difficult to crystallize by cooling crystallize readily under pressure, as recently shown for 1,1,2-trichloro-1,2,2-trifluoroethane.¹⁹ The IR spectra of MPD under increasing pressure changed irreversibly, probably as a result of polymerization.

The hot-nozzle method of matrix isolation, pioneered by Günthard and co-workers,²⁰ assumes that the high-temperature equilibrium conformers in the vapour are trapped on the cold window and maintained in the matrix. Unless the barrier to conversion is quite low (ca. 5 kJ mol^{-1} for 14–16 K at the window), as was recently discussed for monohalocyclobutanes,²¹ the hot-nozzle method is very sensitive for detecting less

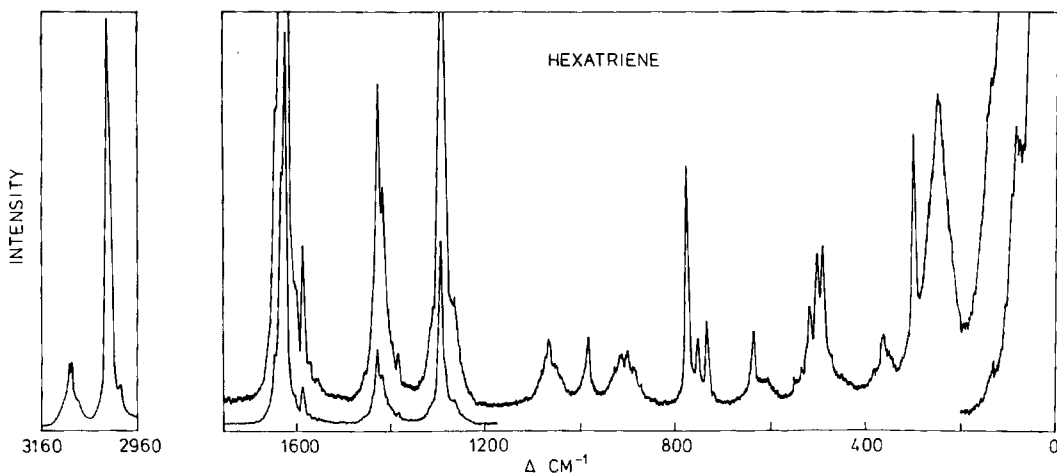


Fig. 7. Vapour Raman spectrum of MPD at ambient temperature; resolution 4 cm^{-1} .

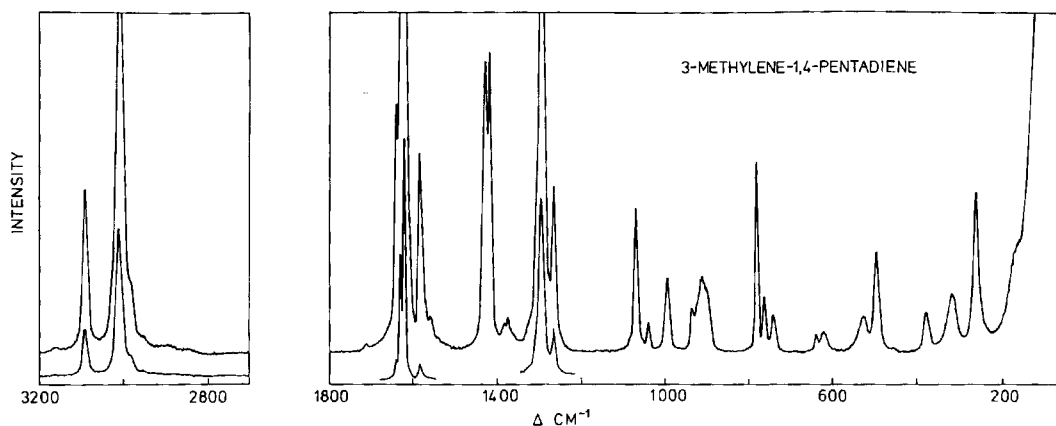


Fig. 8. Raman spectrum of MPD as a liquid, cooled to 240 K.

stable conformers which may have a ΔH° as high as 10 kJ mol^{-1} above that of the most abundant conformer. In the present IR matrix isolation spectra with argon and nitrogen, only very small intensity changes between the 313 and 500 K spectra were observed. The only exception was the weak IR band at 1575 cm^{-1} which was considerably enhanced compared to the neighbour band at 1590 cm^{-1} . This band is also present in the Raman spectra of the vapour and liquid and was also enhanced with temperature. Tentatively, this band is attributed to a C=C stretching mode of a second conformer of MPD.

The Raman spectra of liquid MPD recorded at various temperatures between 140 and 270 K

were plotted together and manipulated with the data system to detect small relative band intensity differences. It was observed that the three Raman bands at 1641 , 1572 and 1088 cm^{-1} were all enhanced relative to the neighbour bands with increase in temperature. These bands are tentatively assigned to a second conformer, and rough calculations suggest a ΔH° difference between the conformers of ca. 10 kJ mol^{-1} , indicating less than 2% abundance at ambient temperature. Moreover, the C=C stretching modes around 1600 cm^{-1} are among the strongest bands both in the IR and in the Raman, and it is therefore no surprise that these bands (1641 and 1575 cm^{-1}) may be detected at a conformer abundance of ca. 2%.

Some additional Raman bands of high or medium intensities at 1418 , 1265 , 899 and 372 cm^{-1} , all assigned as fundamentals of the stable conformer, changed slightly in peak intensity with temperatures relative to their neighbour bands. These variations were possibly counteracted by bandwidth variations keeping their areas constant with temperature. Finally, a drastic enhancement of the weak Raman line at 639 cm^{-1} relative to the neighbour bands with increasing temperature cannot easily be explained.

The Raman spectral data reveal a considerable number of depolarized bands. Below 1800 cm^{-1} we observed 16 clearly polarized and 13 apparently depolarized bands in addition to some very uncertain cases. The vapour Raman band contours generally support the polarization measurements, giving narrow bands with sharp Q -

Table 2. Comparison between the presently obtained results for 3-methylene-1,4-pentadiene with those from theoretical calculations.

	ED $r_d/\text{\AA}$ or $\angle_d/^\circ$	<i>ab initio</i> ^a (6-31G)	MM ^a
$r(\text{C}^1=\text{C}^2)$	1.3495	1.3325	1.3569
$r(\text{C}^3=\text{C}^4)$	1.3420	1.3237	1.3471
$r(\text{C}^5=\text{C}^6)$	1.3420	1.3255	1.3471
$r(\text{C}^2-\text{C}^3)$	1.4788	1.4826	1.4733
$r(\text{C}^2-\text{C}^5)$	1.4788	1.4788	1.4740
$\angle(\text{C}^1=\text{C}^2-\text{C}^3)$	121.7	121.45	121.31
$\angle(\text{C}^1=\text{C}^2-\text{C}^5)$	118.7	119.93	117.70
$\angle(\text{C}^2-\text{C}^3=\text{C}^4)$	125.2	125.28	125.17
$\angle(\text{C}^2-\text{C}^5=\text{C}^6)$	126.6	126.88	124.91
$\psi(\text{C}=\text{C}=\text{C})_{\text{skew}}$	39.3	41.38	23.30

^aRef. 6.

Table 3. Infrared and Raman spectral data for 3-methylene-1,4-pentadiene (MPD).

Infrared				Raman			Assign.
Vapour	Ar-matrix 14 K	N ₂ -matrix 14 K	Solid amorph. 90 K	Vapour	Liquid 150 K	Solid amorph. 90 K	
3106		3108 vw ^a	3102 w				
3101	-s,A	3103 m	3097 m	3101 m			v ₁
3099				3086 m	3091 m,D?	3090 m	v ₂
3096	-s	3095 w	3090 w	3096 m			
3092		3092 vw					
3087							
3082	-w	3074 vw	3072 w	3064 w	3081 w	3065 vvw	v ₃
3078							
3072	vw						
3063	vw		3050 vw				
3047		3036 w	3034 w				
3041	w	3031 w	3028 mw	3027 w	3039 vw		v ₄
3035							
					3028 w,sh	3025 w,sh	
3030							
3026	-m	3022 vw	3018 w	3024 vw	3023 vvs		v ₅
3022							
3016							
3013	-m	3011 vw	3006 vw	3009 vw	3014 s		v ₆
					3010 vs,P	3007 s	
3008	-m	3000 vw	2993 vw	3003 mw	3008 m		v ₇
3002		2989 vw	2990 vw				
2992	-w	2903 vw	2983 vw	2973 mw	2994 mw	2985 w	v ₈
2984							
2978	vw					2980 w,sh	2978 w,sh
2974	vww	2976 vw	2974 vw		2975 vvw		2974 w,sh
2966	vww			2960 vw		2954 vvw	
1852	w,sh	1856 vw	1855 vw			1865 vvw	
1845	w	1844 mw	1844 vw				
1835	m	1835 vw	1837 vw	1837 vvw		1852 vvw	
1829	m,sh		1831 vw				
1818	w	1820 mw	1825 vw				
1802	m	1798 w	1799 vvw	1808 vw		1817 vvw	
1792	m	1789 m	1794 w				
1786	w,sh						
1651	vw	1644 vw	1644 vw	1640 vw	1649 m,sh	1641 m,P	1642 m,sh
1641							*
1637	-m	1636 mw	1634 m	1630 m	1636 vs	1630 s,D?	1631 vs
1632							
1627	-w	1629 vw	1627 w	1621 w	1628 vvs	1621 vs,P	1621 vs
1623			1622 vw	1617 vw,sh			v ₁₀
1616	w						
1610	w	1615 vvw	1612 vw	1608 vvw	1608 w,sh	1609 w,sh	1610 w,sh
1606	vw						
1597				1586 s			1587 m
	-s,B	1590 s	1590 s		1591 mw	1584 m,P	
1584		1581 w,sh	1580 w,sh	1580 s			1582 m
1576	m	1575 w	1575 w	1575 w,sh	1576 vw	1572 w,P	*
1569	w	1571 vvw	1570 vw				
1560	vw			1560 vvw	1560 vvw	1561 w	1562 vw
1436							
1430	-m,A	1429 s	1429 s	1425 m	1432 s	1429 s,P	1433 s
1424		1426 w,sh	1427 w,sh				v ₁₂
1419	-m	1418 mw	1419 mw	1418 m,sh	1422 s,sh	1418 s,D	1419 s
1413		1415 w,sh	1414 w,sh				v ₁₃

contd

Table 3. (contd)

Infrared				Raman			Assign.	
Vapour	Ar-matrix 14 K	N ₂ -matrix 14 K	Solid amorph. 90 K	Vapour	Liquid 150 K	Solid amorph. 90 K		
1394	} -w,B w,sh vw vww	1387 m	1385 m	1384 w,sh 1379 mw	1388 vw	1385 vw,D? 1384 w	V ₁₄	
1381		1381 w,sh						
1374		1374 vw	1373 w	1365 vw		1376 vw,P 1365 vvw?	1376 vw,sh V ₁₅	
1362								
1350								
1298	vww?	1308 vw	1309 w	1310 vw 1298 vw	1314 w,sh 1298 vs	1312 w,sh 1295 s,P 1297 s 1275 vw	V ₁₆	
1278	} -vw	1264 vw	1265 vvw	1263 vw?	1269 w	1265 m,D	1265 m V ₁₇	
1269								
1260								
					1085 vw,sh	1088 w	*	
1076	} -mw	1069 mw	1070 m	1078 mw	1071 w 1058 vw,sh	1069 m,P	1070 m	V ₁₈
1069								
1060								
1046								
1040	} -m,A	1039 m	1030 m	1037 mw	1042 vvw?	1039 w,D?	1038 w	V ₁₉
1032								
		1026 w 1001	1026 w					
1000	s,sh	} s 997	998 s	1000 m,sh	995 vw,sh	993 w,P 995 w	V ₂₀	
991	} -vs,C	990 vs 987 m,sh	993 w,sh	991 s	988 w		V ₂₁	
988			992 vs					
985			989 s,sh					
976			m					
934	w,sh	934 vw 929 vvw	934 vw	934 w,sh	932 vw,sh	935 w,D 936 w,sh	V ₂₂	
927	} m -vs,C	921 s 916 m	926 vs	922 vs	918 vvw?	920 w,D	920 w,sh	V ₂₃
922			921 s					
918				916 m				
912				914 m	915 w?			
910	} -vs,C	908 s	910 m	906 vvw?	910 w,D	912 w	V ₂₄	
907			908 m					
901			901 s					
897	} -vs,C	897 s 893 vs	898 s	899 vs	893 vvw?	899 w,D	900 w,sh	V ₂₅
891			896 vs					
887	w,sh	889 w,sh	887 w,sh					
782	vw	782 vvw	782 vvw	781 vw	781 m	781 m,P	783 m	V ₂₆
762	} -m,A	761 vw 759 m	760 m	763 m	756 w	762 w,P	764 w	V ₂₇
756								
748								
738	w,sh	733 w	733 w	741 w	737 w	739 w,P	741 w	V ₂₈
636	vw	638 vw	638 vw		637 w	639 w,P	640 vw,sh	
618	} -w,B	619 w 612 w	615 mw	623 w		619 vw,D	621 vw	V ₂₉
614								
606								
564	vw			613 vw,sh	607 vvw			
551	} -vww	565 vvw	569 vvw	560 vvw	552 vvw	553 vvw		
538								

contd

Table 3. (contd)

Infrared				Raman			Assign.
Vapour	Ar-matrix	N ₂ -matrix	Solid amorph.	Vapour	Liquid	Solid amorph.	
	14 K	14 K	90 K		150 K	90 K	
525							
517	-w 516 w	516 w	525 w	520 w	525 vw,D	525 w	V ₃₀
509							
505	-m,A 496 vw	496 vw	503 vvw?	504 m			
497							
492	-w,A 489 w	488 w	493 w	492 m	494 w,P	495 mw	V ₃₁
486							
456	-vvw?458 vvw?	458 vvw?			455 vw,D		
372	375 w						
367	-m 371 m	371 m	377 m	364 w	372 w,D?	381 w	V ₃₂
362				351 vw,sh			
311							
302	-w 314 vw	314 vw	315 w	300 m	314 w,P	316 w	V ₃₃
290							
245	vw? 260 vvw?	258 vvw?	261 vw	247 m	257 m,D?	260 m	V ₃₄
133	vw?		166 w	135 w	158 w,P?	165 w	V ₃₅
			130 w		~100 vw	125 w	V ₃₆
				85 mw		89 w,sh	

^aAbbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; P, polarized; D, depolarized; A, B, and C denote vapour contours; asterisks (*) signify bands believed to be due to an unstable conformer.

branches for the polarized bands and broad, diffuse contours with *O*-, *P*-, *R*- and *S*-branches for the depolarized bands.

The vapour IR contours were in most cases not very well resolved, but some *A*-type contours (1430, 1040, 756, 505 and 492 cm⁻¹) and *C*-type contours (988, 922, 910 and 897 cm⁻¹) were observed. We have frequently calculated not only the *PR* separation but the complete *A*, *B* and *C* band contours²² for various possible geometries, most recently for the related molecule 3-methylene-4-pentene-1-yne (2-ethynyl-1,3-butadiene). The present IR and Raman contours would not justify such calculations.

The number of polarized and apparently depolarized Raman bands suggests a symmetry element in MPD like a two-fold axis (*C*₂) or a symmetry plane (*C*_s). The planar *anti,anti* or *cis,cis* structures with *C*_{2v} symmetry can both be ruled out (13 polarized and 18 depolarized Raman bands, 5 IR inactive bands). Also, the planar *anti,cis* conformer with *C*_s symmetry (25 polarized and 11 depolarized Raman bands) seem in-

compatible with the present results. The *skew, skew* conformers with the vinyl groups C3,C4 and C5,C6 rotated in the same sense or in the opposite sense from *cis,cis* or from *anti,anti* would have *C*₂ or *C*_s symmetry, respectively. These molecular symmetries would lead to nearly the same number (18*a* + 18*b* for *C*₂; 19*a*' + 17*a*' for *C*_s) of polarized and depolarized Raman bands.

Thus, if no structural results from ED were available, we would definitely have interpreted the vibrational spectra in terms of either *C*₂ or *C*_s symmetry. The *anti, skew* model strongly favoured from ED (see above) as well as from *ab initio* calculations⁶ has no symmetry (*C*₁), and all the vibrations belong to the same symmetry species. Accordingly, all the Raman bands should be polarized, and all the vapour IR and Raman contours should be hybrids, contrary to our results. It seems unlikely that MPD can lack symmetry in the vapour phase (ED) and have *C*_s or *C*_s symmetry in the liquid as indicated by the Raman polarization measurements, since there are no significant changes in the IR or Raman spectrum

Table 4. Observed and calculated fundamental frequencies for 3-methylene-1,4-pentadiene.

v	Obs. ^c	<i>anti,skew</i> ^a		<i>skew,skew</i> ^b	
		Calc.	PED ^d	Calc.	PED ^d
1	3101	3121	CH ₂ as(97)	3121	CH ₂ as(97)
2	3096	3112	CH ₂ as(97)	3112	CH ₂ as(96)
3	3082	3112	CH ₂ as(97)	3111	CH ₂ as(97)
4	3041	3047	CH s(75)	3048	CH s(77)
5	3026	3044	CH s(70)	3044	CH s(70)
6	3013	3032	CH ₂ ss(85)	3032	CH ₂ ss(89)
7	3008	3030	CH ₂ ss(71)	3030	CH ₂ ss(71)
8	2992	3027	CH ₂ ss(87)	3027	CH ₂ ss(85)
9	1637	1716	C=C s(71)	1684	C=C s(76)
10	1627	1647	C=C s(65)	1633	C=C s(68)
11	1591	1611	C=C s(70)	1603	C=C s(70)
12	1430	1473	CH ₂ δ(67), C-C s(22)	1476	CH ₂ δ(47), C-C s(35)
13	1419	1455	CH ₂ δ(87)	1452	CH ₂ δ(85)
14	1388	1416	CH ₂ δ(66)	1406	CH ₂ δ(62)
15	1374	1332	C-C s(20), CH ro (19)	1382	C-C s(11), CH ₂ δ(29)
16	1298	1306	CH ro(55)	1309	CH ro(53)
17	1269	1297	CH ro(43), C=C s(20)	1299	CH ro(48), C=C s(16)
18	1069	1071	CH ₂ ro(59)	1064	CH ₂ ro(61)
19	1040	1052	CH ₂ ro(70)	1046	CH ₂ ro(72)
20	1000	1010	CH ₂ tw(51), CH wa(37)	1005	CH ₂ tw(51), CH wa(37)
21	988	991	CH ₂ tw(56), CH wa(40)	994	CH ₂ tw(55), CH wa(40)
22	834	940	CH ₂ ro(73), C-C s(20)	935	CH ₂ ro(70), C-C s(20)
23	922	922	CH ₂ wa(90)	923	CH ₂ wa(92)
24	910	916	CH ₂ wa(98)	916	CH ₂ wa(95)
25	897	913	CH ₂ wa(98)	914	CH ₂ wa(98)
26	782	769	C-C s(53)	767	C-C s(38), CH ₂ tw(18)
27	756	755	CH ₂ tw(15), CH wa(20)	751	CH ₂ tw(14), CH wa(7)
28	738	716	CH ₂ tw(46)	700	CH ₂ tw(52)
29	616	605	CH ₂ tw(16), CH wa(26)	620	CH ₂ tw(31), CH wa(30)
30	520	526	C=C-C δ(26), C-C-C δ(11)	498	C-C-C δ(39), C=C-C δ(42)
31	492	441	C=C-C δ(44), CC ₂ ro(20)	456	C=C-C δ(34), CC ₂ wa(23)
32	367	385	CC ₂ wa(33), CC ₂ ro(34)	370	CC ₂ ro(79)
33	302	288	C=C-C δ(43), CC ₂ ro(25)	301	C=C-C δ(49), CC ₂ wa(40)
34	247	223	C=C-C δ(45), C-C-C δ(38)	228	C=C-C δ(40), C-C-C δ(32)
35	135	160	C-C τ(89)	177	C-C τ(92)
36	85	119	C-C τ(88)	104	C-C τ(89)

^aGeometry from electron diffraction with *C₁* symmetry. ^bGeometry derived by twisting the vinyl groups 30° from the *anti,anti* structure with *C₂* symmetry. ^cIR and Raman gas phase values. ^dPotential energy distribution defined as $\chi_{ik} = 100F_{ik}L_{ik}^2/\lambda_{ik}$; applied force field for butadiene,¹⁸ modified regarding the central C-C-C force constant (CC₂ ro; CC₂ wa) from Ref. 36; a, asymmetric; s, symmetric; s, stretch; δ, deformation; ro, rock.; wa, wag.; tw, twist.; τ, torsion.

between the states of aggregation. Thus, we are forced to assume that MPD maintains a high degree of local symmetry within the three fragments: the *anti* butadiene skeleton C¹, C², C⁵, C⁶ (*C_{2h}*), the *skew* butadiene C¹, C², C³, C⁴ (*C₂*), and the pentadiene C⁴, C³, C², C⁵, C⁶ (*C₂* symmetry). Reasonably localized vibrations within each of

these fragments might explain our spectral results. Somewhat reluctantly, we have therefore tried to interpret our spectra in terms of one dominant conformer (*anti,skew*) with a possible small amount (less than 2% at ambient temperature) of a second conformer of completely unknown conformation.

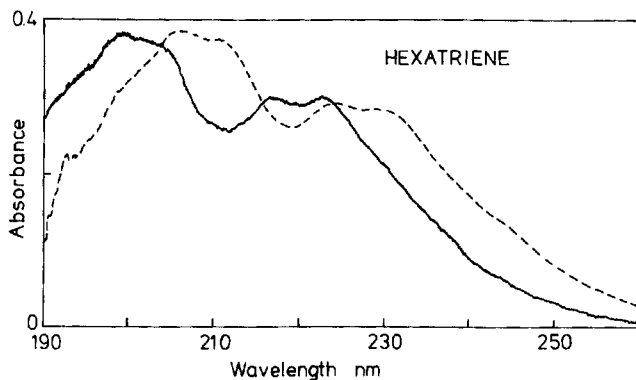


Fig. 9. Ultraviolet spectra of MPD as a vapour (solid curve) and in solution in hexane (dashed curve).

The assigned fundamentals are listed in Table 4 and compared with the results of our force constant calculations, based upon the force field for butadiene¹⁸ and modified with respect to the central C-C-C stretching and bending force constants. As is apparent from the potential energy distribution (PED), many of the vibrations appear highly mixed since there is no overall symmetry in the molecule. For the sake of brevity we shall avoid lengthy discussions regarding the assignments. It should be noted, however, that the typical group frequencies C=C stretch, =CH₂ deformation, CH=CH₂ *trans* wag, *cis* wag and CH₂ wag appear in expected regions. The deviations between the observed and calculated frequencies are in some cases quite high. This is a consequence of the transfer of the butadiene force field,¹⁸ and was also observed in the recent work²² on 2-ethynyl-1,3-butadiene for which the molecular structure was not in doubt. The fit of the calculated fundamentals to the observed bands becomes better if certain symmetric conformers are adopted. Thus, a *skew,skew* conformer with 30° dihedral angle from *anti,anti* (C₂ symmetry) gives smaller deviations regarding most of the bands compared to adopted *anti,skew* model.

The vibrational spectra of MPD may be compared with very recent results²³ reported for the isomeric compounds *E*-1,3,5-hexatriene and *Z*-1,3,5-hexatriene. Unlike MPD, these polyenes have extended conjugation in the chain rather than cross-conjugation. The spectra for these compounds have also been calculated by *ab initio*²⁴ and by semi-empirical²⁵ methods.

Ultraviolet spectra. The ultraviolet curves for MPD obtained in the vapour and in hexane so-

lution are both shown in Fig. 9. As is apparent, the following absorption maxima were found: 223, 217, 205 and 199 nm (vapour) and 231, 224, 211 and 206 nm (hexane solution). The two spectra are quite similar except for a red-shift of 6–8 nm for each peak between vapour and solution. A shift of this magnitude is expected as a result of the phase change. Hence, the UV spectra indicate the same degree of conjugation in the vapour and in solution, and support the assumption that no significant structural change occurs between the two phases. Previously, $\lambda_{\max} = 224$ nm ($\log \epsilon = 4.41$) has been reported²⁶ for MPD (presumably in solution). For comparison, butadiene in the stable *anti* conformer absorbs at 217 nm ($\log \epsilon = 4.32$)²⁶ (in solution) while in the vapour phase peaks were observed²⁷ at 216, 210 and 204 nm at 195 K. In argon matrix at 20 K, the *anti* butadiene absorbs at 212 nm, whereas the unstable *cis* conformer produced by the hot-nozzle technique has a broad UV absorption with $\lambda_{\max} = 226$ nm with an extinction coefficient less than half of that for the *anti* conformer.²⁸ An unstable *skew* form of butadiene has been suggested from spectral data²⁹ and from *ab initio* calculations at the 6–31 G level. A dihedral angle of 38° was obtained.³⁰ The most recent IR and UV spectral results,³¹ however, involving polarized matrix isolation spectroscopy³² favour a planar *cis* conformer rather than *skew* for the second conformer of butadiene.

For comparison, the UV vapour spectrum of *E*-hexatriene (*anti*) had peaks at 251, 241, 234 and 232 nm. The isomeric *Z*-hexatriene (*cis*) had absorption bands at nearly the same wavelengths,³³ but larger deviations were observed in the vacuum ultraviolet. In the cross-conjugated fulvene, the three double bonds are locked into

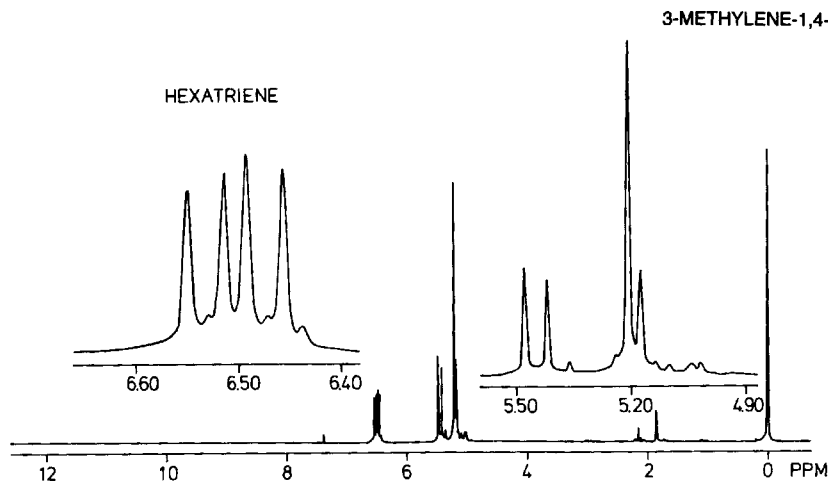


Fig. 10. ^1H NMR spectrum of MPD at 203 K; solvent CD_2Cl_2 .

the *anti,anti* positions. The UV spectral bands for this compound appear at 360 (very weak), 235 and 202 nm (both strong), $\log \epsilon = 4.1$.³⁴ Thus, the extended conjugation in *E*- and *Z*-hexatriene leads to a significant bathochromic shift relative to the spectrum of butadiene. A corresponding, but smaller, shift is also found for the cross-conjugated fulvene relative to butadiene.

The fact that the UV spectrum of MPD is so similar to that of butadiene suggested that this molecule is non-planar and therefore neither *anti,anti* nor *cis,cis*, since these structures should be accompanied by a bathochromic shift. Apparently, both the *anti-skew*, favoured by GED, and a *skew,skew* in which none of the $\text{C}=\text{C}$ bonds are coplanar, which is compatible with C_2 symmetry

favoured by the vibrational spectra, can give rise to the present UV spectrum.

NMR spectra. An ^1H NMR spectrum of MPD is shown in Fig. 10, a ^{13}C survey spectrum is given in Fig. 11, while a more detailed ^{13}C spectrum appears in Fig. 12. In all the spectra shown, the sample was dissolved in CD_2Cl_2 and the temperature was kept at 203 K. The sample of MPD employed for these spectra had not been purified by GC, and a number of weak satellite bands are due to impurities. New NMR spectra were recorded showing the presence of negligible amounts of impurities, but unfortunately these spectra vanished in the data system and could not be retrieved.

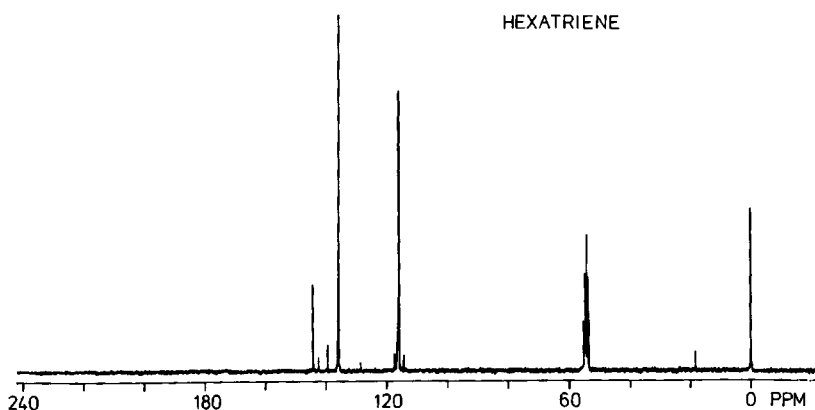


Fig. 11. ^{13}C NMR survey spectrum of MPD at 203 K; solvent CD_2Cl_2 .

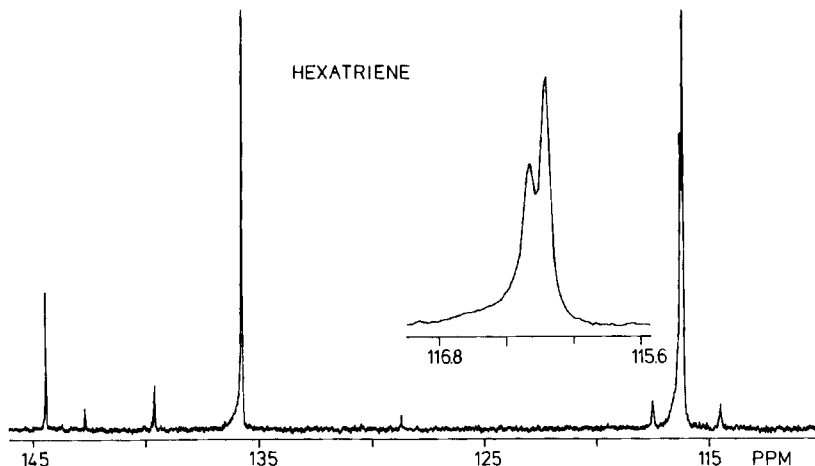


Fig. 12. Detailed ^{13}C NMR spectrum of MPD at 203 K; solvent CD_2Cl_2 .

The results can be abbreviated in the usual way: ^{13}C NMR (CD_2Cl_2 , 203 K): δ 116.17 (C4 and C6), 116.27 (C1), 136.09 (C3 and C5), 144.55 (C2). ^1H NMR (CD_2Cl_2 , 203 K): δ 5.208 (*d*, $J = 10.8$ Hz; H4 and H6), 5.21 (*s*; H1), 5.45 (*d*, $J = 16.5$ Hz; H4 and H6), 6.50 (*d* of *d*, $J = 16.5$ and 10.8 Hz; H3 and H5).

The spectra indicate a structure having a symmetry plane through C^1 and C^2 , perhaps a two-fold symmetry axis through C^1 and C^2 , or structures of lower symmetry undergoing rapid internal motion on the NMR time scale. As there is no broadening of the resonances even at 203 K it is likely that the barrier to this motion is less than 20 kJ mol^{-1} . Several different symmetrical and non-symmetrical structures can be suggested for MPD (as discussed above). If a number of these contribute to the observed spectra and are not of very similar energy we would expect that the ^{13}C shifts would be temperature-dependent. This is observed not to be the case, the largest shift alteration over the 60 degree span observed being a mere 0.4 ppm. Further details of the geometry of MPD could probably be obtained from a study of the long-range proton-proton couplings. Such couplings are observed but have not yet been assigned.

Discussion

The electron diffraction study strongly indicates that MPD exists in a non-planar, *anti-skew* conformation in the vapour phase. From the vibra-

tional and electronic spectra it can be inferred that the same conformation seems to be present in the vapour, in the liquid and in the amorphous state, while the conformer present in the crystal is completely unknown since our samples of MPD never crystallized. The vibrational and NMR spectra indicate low symmetry in the molecule (C_2 or C_s), whereas the electronic spectra suggest a structure with no increased conjugation relative to butadiene. Since the UV and NMR spectra may also be compatible with the *anti, skew* conformer, the strong evidence from electron diffraction forced us to adopt this geometry for the vibrational spectra as well.

The temperature studies in IR and Raman indicated the existence of a second conformer of much higher energy (ca. 10 kJ mol^{-1}). As is apparent from the ED results, small amounts of another conformer (presumably *skew,skew*) are in good agreement with these data.

The preferred conformation is probably primarily determined by a combination of conjugation effects and non-bonded van der Waals interactions. The conjugation effect is at a maximum for coplanar π systems (*anti,anti*, *anti,cis* and *cis,cis*). All the planar conformers do, however, exhibit increased van der Waals and/or valence angle steric strain energy. In the present case, maximum conjugation between two of the $\text{C}=\text{C}$ bonds is retained while the orientation of the second vinyl group appears to be determined by van der Waals forces. The latter conclusion is based upon the observation that the shortest con-

formation-dependent H \cdots H and C \cdots H non-bonded distances are equal to the sum of the van der Waals radii³⁵ of the atoms involved [$r(\text{H}^8\cdots\text{H}^{11}) = 2.45 \text{ \AA}$; $r(\text{C}^1\cdots\text{H}^{11}) = 2.88 \text{ \AA}$].

The MM calculations carried out in the present study, and also those by Norinder,⁶ give minimum energy for planar or nearly planar conformers, and this method does therefore appear to overestimate the importance of conjugative effects.

In Table 2 the structure parameters determined for MPD in the present ED study are compared with those from theoretical *ab initio* and molecular mechanics calculations.⁶ In both studies, the cross-conjugated C¹=C² bond was found to be slightly larger than the other C=C bonds (ED: 0.0075 \AA ; *ab initio*: 0.0089 \AA). Because of the magnitude of the estimated errors in the ED results, the two types of C=C bonds cannot be claimed to be significantly different, but it is satisfying that the observed C=C bond difference is in agreement with the theoretical prediction. In an ED study of another cross-conjugated compound, viz. 4,4-dimethyl-1-methylene-2,5-cyclohexadiene, an r_α C=C bond difference of ca. 0.005 \AA was observed.³⁵ When bond differences of this order of magnitude are discussed, the averaging of the bond lengths over the molecular vibrations is of utmost importance. This may be illustrated by the r_α values of the MPD C=C bond lengths presented in Table 1, where the observed r_α bond length differences are 2–3 times larger than those calculated.

Table 2 shows that the structural results observed for MPD are generally in excellent agreement with those calculated by Norinder.⁶

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