

THE CONFORMATION AND VIBRATIONAL SPECTRA OF 1,5-HEXADIENE-3-YNE (DIVINYLLACETYLENE) AND PERCHLORO-1,5-HEXADIENE-3-YNE (PERCHLORODIVINYLLACETYLENE)

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ABSTRACT

Infrared spectra of 1,5-hexadiene-3-yne (divinylacetylene) have been recorded in the vapour phase, in solution and in the amorphous and crystalline solid states at 90 K in the region $4000-20\text{ cm}^{-1}$. Correspondingly, IR spectra of perchloro-1,5-hexadiene-3-yne (perchlorodivinylacetylene) as a melt, as a solute in various solvents and as a solid at 90 K have been obtained. Raman spectra of the two compounds were recorded in the liquid (molten) state including polarization measurements, and as crystalline solids at 90 K.

The spectral data indicate that each compound exists as one conformer only in the various states of aggregation. In divinylacetylene the molecular symmetry appears to be *anti* (C_{2h}) while for perchlorodivinylacetylene the symmetry is either C_{2v} (*syn*) or C_2 (*gauche*). Vibrational assignments for the spectra of both molecules are presented and the values are compared with the results of normal coordinate analyses.

INTRODUCTION

1,5-Hexadiene-3-yne or divinylacetylene (DVA) is an interesting compound with possibilities for extended conjugation within the carbon skeleton. However, since the electron density of the acetylene group has cylindrical symmetry, the amount of conjugation should be largely independent of the dihedral angle between the vinyl groups. Thus, the position of the potential minima, the barrier to internal rotation and the torsional force constant should depend only on the attractive and repulsive terms between the vinyl groups. Therefore the molecular symmetry of DVA cannot be easily predicted, while for example in 1,3-butadiene the planar conformation is a result of the conjugation in this compound. The DVA molecule can have essentially free rotation (D_{2h}^*) or preferred conformations such as *anti* (C_{2h}), *gauche* (C_2) or *syn* (C_{2v}).

With the formula C_6H_6 , DVA is one of the 12 possible structural isomers of benzene. Three of these, 1,2,4,5-hexatetraene (biallenyl) [1, 2], 1,6-hexadiyne (bipropargyl) [3, 4] and 1,2-hexadiene-5-yne (propargylallene)

[5], have previously been studied by vibrational spectroscopy and by electron diffraction. Other related molecules which have already been investigated include vinylallene [6]. Incomplete IR spectra of DVA vapour [7, 8] and a Raman spectrum of the liquid [9] have been recorded.

Perchloro-1,5-hexadiene-3-yne or perchlorodivinylacetylene (CDVA) obviously has the same possible conformers as DVA, although there will be differences arising from the larger size and higher electronegativity of chlorine compared with hydrogen. Extensive work dealing with the syntheses and chemical properties of CDVA and related molecules has been published by Roedig and co-workers. Roedig and Kiepert [10] have published IR and UV spectra of CDVA. The vibrational fine structure and position of the maxima (296 and 311 nm) suggest a nearly planar structure with considerable conjugation within the π -system [10].

EXPERIMENTAL

Preparations

A catalyst solution is prepared by adding water (150 ml), concentrated hydrochloric acid (8 g), copper powder (25 g), ammonium chloride (98 g) and copper(I) chloride (250 g) to a three-necked flask equipped with a mechanical stirrer, a reflux condenser and a nitrogen inlet. The mixture is refluxed overnight and stirred until the green colour of the copper salts disappears. A rapid stream of acetylene purified by passing through wash bottles of sodium hydrogensulphate and concentrated sulphuric acid is passed into the catalyst mixture at room temperature for 4 h. The reaction mixture is then kept for one week at room temperature under a nitrogen atmosphere. The acetylene oligomers are distilled off under nitrogen until only water distils over (bath temperature about 140°C) [11]. The organic layer is separated, sodium sulphate and a trace of hydroquinone are added, and the DVA distilled carefully under inert gas protection. A yield of 10–12 ml of colourless liquid, b.p. 82°C (760 torr) is obtained. DVA may be kept for extended periods at -30°C without apparent decomposition or polymerization.

The CDVA was prepared as reported previously [10]. Gas chromatographic analysis showed the sample to be very pure.

Instrumental

IR spectra were recorded on a Perkin-Elmer model 225 spectrometer (5000–200 cm^{-1}) and on a Bruker IFS-114C evacuable fast scan Fourier spectrometer (4000–10 cm^{-1}). Vapour spectra of DVA at saturation pressure (ca. 50 torr) and lower were recorded at ambient temperature in a 1-m folded cell (KRS-5 windows), a 10-cm cell (CsI windows) and a 20-cm cell (polyethylene windows). Spectra of the pure liquid (DVA) and dilute

solutions of DVA and CDVA in CS_2 , CCl_4 and C_6H_{12} were recorded in sealed cells. CDVA was melted between KBr and polyethylene plates. Spectra of the solid samples deposited on a CsI or polyethylene window cooled with liquid nitrogen were recorded before and after annealing.

Raman spectra were recorded on a Cary 81 spectrometer modified for 90° irradiation [12], excited by a CRL model 52 G argon ion laser, using the 5145- and 4880-Å lines. DVA was studied as a neat liquid in a sealed ampoule; CDVA was heated to ca. 60°C and recorded as a melt. Both compounds were studied at liquid nitrogen temperature when deposited on a copper plate, and the spectra of DVA were recorded before and after annealing.

RESULTS AND DISCUSSION

DVA

Conformation

The IR spectra of DVA in the vapour phase and in the crystalline state at 90 K are shown in Figs. 1 and 2, respectively, while the Raman spectra are given in Fig. 3 (liquid) and Fig. 4 (solid, 90 K). The wavenumbers of the observed IR and Raman bands are listed in Tables 1 and 2, respectively. Our IR spectra are in reasonably good agreement with the survey spectra reported [7, 8]. However, the Raman spectra have practically no resemblance to the frequencies listed by Batuev et al. [9]. Of the 39 Raman bands listed [9], 22 were not detected by us, whereas only very intense bands in our spectra were observed by Batuev et al. Probably their sample consisted predominantly of other material than DVA. Therefore, their conclusion, which involved the existence of conformational equilibria in the liquid state [9], cannot be accepted from their Raman spectra.

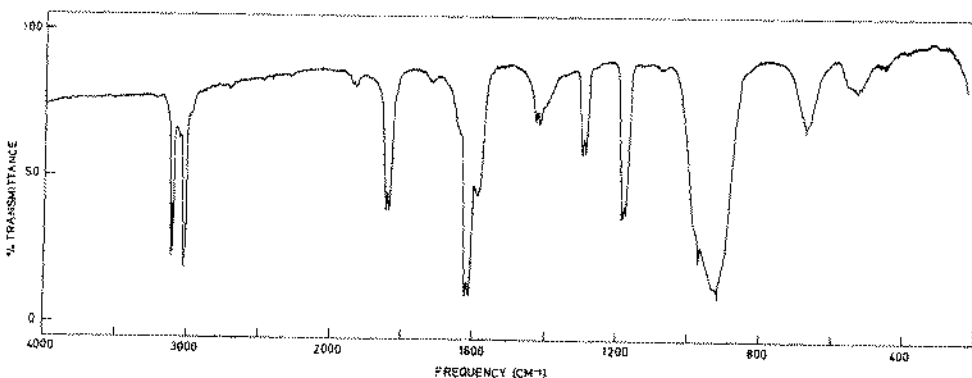


Fig. 1. The IR vapour spectrum of DVA at ca. 50 torr; path length 10 cm above 400 cm^{-1} and 18 cm below 400 cm^{-1} .

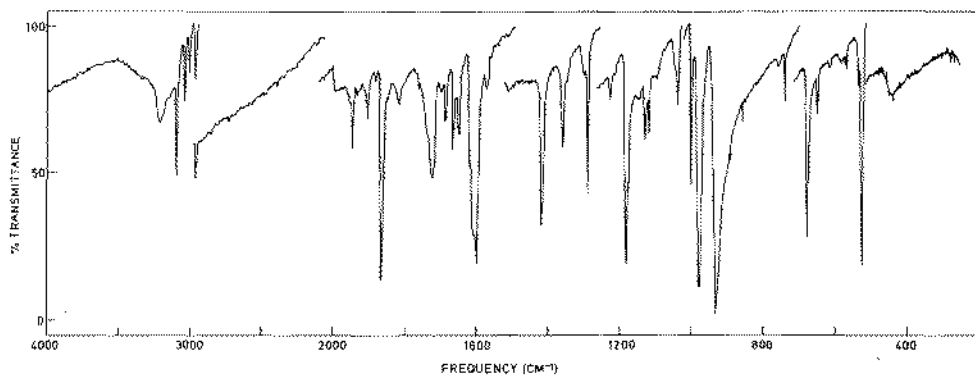


Fig. 2. The IR spectrum of DVA as a crystalline solid at ca. 90 K.

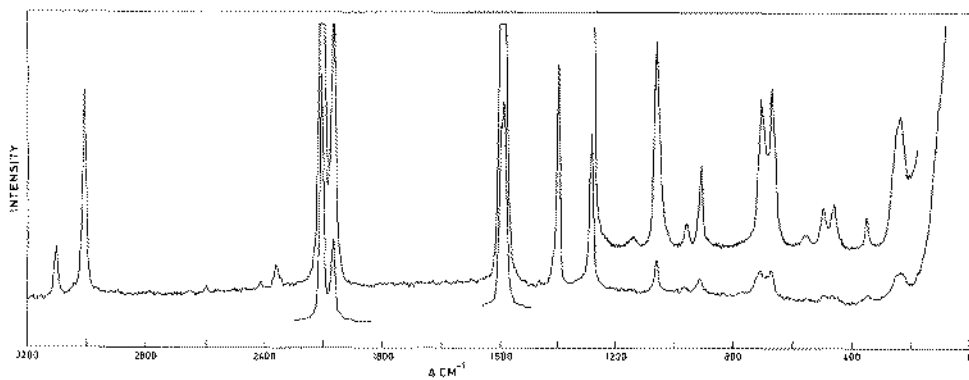


Fig. 3. Raman spectrum of DVA in the liquid state.

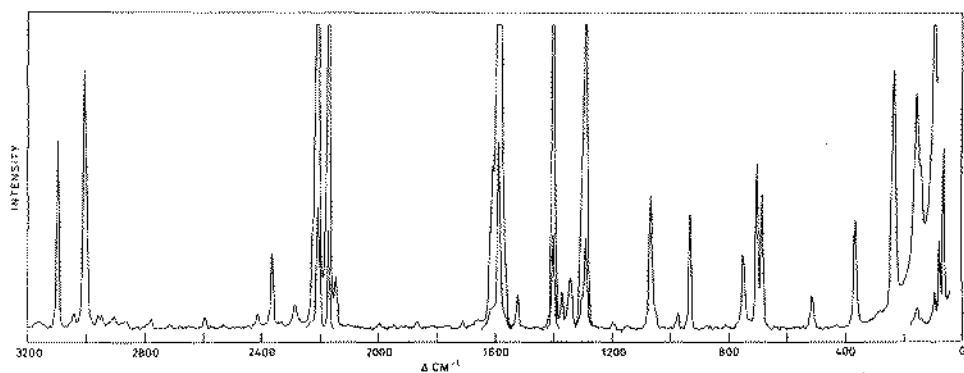


Fig. 4. Raman spectrum of DVA as a crystalline solid at ca. 90 K.

solutions of DVA and CDVA in CS_2 , CCl_4 and C_6H_{12} were recorded in sealed cells. CDVA was melted between KBr and polyethylene plates. Spectra of the solid samples deposited on a CsI or polyethylene window cooled with liquid nitrogen were recorded before and after annealing.

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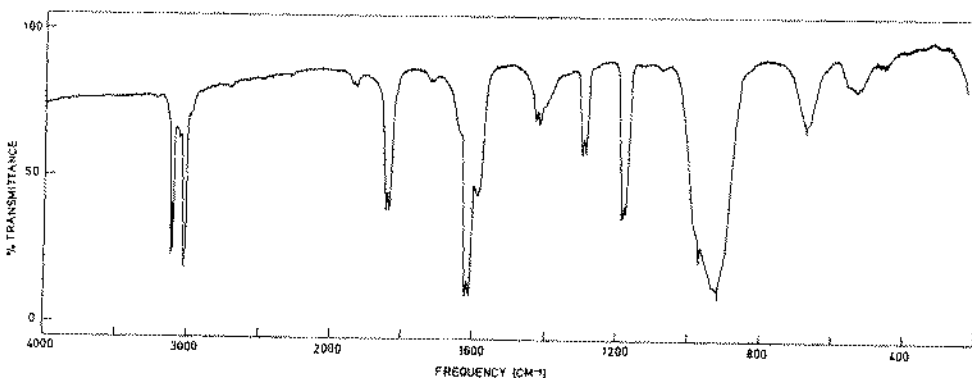


Fig. 1. The IR vapour spectrum of DVA at ca. 50 torr; path length 10 cm above 400 cm^{-1} and 18 cm below 400 cm^{-1} .

TABLE 1

IR spectral data^a for DVA

Vapour		Solution (CCl ₄)	Cryst. -180°C	Interpretation
3116 m ^b	} A/B	3094 m	3100 m	$\nu_{21} b_u$
3112 m			3088 w	$\nu_3 + \nu_{30} = 3133 B_u$
3107 m				
3060 vw	} B?	3039 m	3043 m	$\nu_{22} b_u$
3047 vw				
3027 m	} B	3013 m	3012 m	$\nu_{23} b_u$
3021 m				
2992 vw	} A/B	2963 w ^c	2968 m	$\nu_5 + \nu_{25} = 3006 B_u$
2988 vw			1950 w	$\nu_{17} + \nu_{28} = 1969 A_u$
2980 vw				
1940 w	} B	1930 w	1947 m	$\nu_{20} + \nu_{24} = 1958 A_u$
1930 w			1907 w	$\nu_{18} + \nu_{28} = 1920 A_u$
			1903 w	$\nu_{10} + \nu_{25} = 1920 B_u$
			1885 vw	1882 w
1945 m	} B	1840 s	1867 vs, br	$\nu_{19} + \nu_{27} = 1851 A_u$
1836 m			1848 w	$\nu_{12} + \nu_{24} = 1853 B_u$
1761 w	} A/B?		1725 m	$\nu_{20} + \nu_{25} = 1764 A_u$
1747 w			1687 m	$\nu_9 + \nu_{12} = 1687 A_u$
1733 w			1685 m	
	} B	1638 m	1666 m	$\nu_{10} + \nu_{27} = 1682 B_u$
			1657 w	$\nu_{19} + \nu_{25} = 1670 A_u$
1648 w, sh			1649 m	$\nu_{11} + \nu_{25} = 1659 B_u$
			1621 s	$\nu_9 + \nu_{13} = 1638 A_u$
			1613 s	
1622 vs	} B	1612 vs	1609 s	$\nu_{24} b_u$
1613 vs			1600 vs	
1590 m	C?	1587 m		$\nu_{20} + \nu_{26} = 1639 B_u$
1428 m	} A/B	1418 m	1419 m	
1423 m			1417 s	$\nu_{25} b_u$
1418 m			1414 m	
1400 w			1402 m	$\nu_7 + \nu_{30} = 1413 B_u$
		1340 w	$\nu_7 + \nu_{16} = 1350 A_u$	
1298 m	} A/B	1288 m	1299 w	
1293 m			1289 s	$\nu_{26} b_u$
1288 m			1282 w	
			1226 w	$\nu_9 + \nu_{29} = 1241 B_u$
1187 s	} B	1180 s	1182 vs	
1178 s			1178 m	$\nu_{27} b_u$
			1176 m	
			1130 m	
1125 vvw, C?	C?	1105 vw, sh ^c	1119 m	$\nu_{15} + \nu_{17} = 1141 B_u$

TABLE 1 (continued)

Vapour		Solution (CCl ₄)	Cryst. -180°C	Interpretation
1080 vw } 1070 vw }	B	1065 w ^c		$\nu_{17} + \nu_{30} = 1093 A_u$
		~1020 w, sh ~995 m, sh	1036 m 999 s	$\nu_{18} + \nu_{30} = 1044 A_u$ $\nu_{28} b_u$
972 vs,	C	970 vs	980 vs } 977 vs }	$\nu_{12} a_u$
920 vs,	C	921 vs	931 vs } 923 s }	$\nu_{13} a_u$
			754 vw 737 w	$\nu_{11} + \nu_{29} = 769 B_u$ $\nu_{16} + \nu_{19} = 738 B_u$
674 m,	C	671 m	686 w, sh } 680 w, sh }	$\nu_{14} a_u$
			676 s 671 m 668 w, sh	
662 w 570 vw } 560 vw }	B?	555 w ^c	533 w	$\nu_{10} + \nu_{15} = 673 A_u$ $\nu_{10} + \nu_{16} = 562 A_u$
530 w } 524 w }			A/B	528 w
520 w }		381 vw ^d		
		171 m ^d	226 m } 207 w }	$\nu_{15} a_u$
		123 w, sh ^d	145 m } 127 w }	$\nu_{30} b_u$
			107 vw	Lattice mode

^aWeak bands in the regions 5000–3200 and 2950–2300 cm⁻¹ are omitted. ^bAbbreviations: s, strong; w, weak; v, very; br, broad; sh, shoulder. A, B and C denote band contours. ^cCarbon disulphide solution. ^dCyclohexane solution.

By comparing the IR and Raman spectra of the vapour phase, the liquid or solution with those of the solid state, it is immediately apparent that all the major bands remain in the various states of aggregation. Also, the frequent cases of correlation splitting observed in the low-temperature IR (Table 1) and Raman (Table 2) spectra reveal that the sample was indeed crystalline. The data strongly suggest that only one conformer is present. An eventual additional conformer in the vapour or liquid states must be present in very low concentration (below 5%). The appearance of two intense Raman bands in the C≡C and C=C stretching regions (see below) can be explained as binary combination bands in Fermi resonance with the fundamentals, rather than the existence of two conformers [8, 9]. The number of IR and Raman bands observed in the appropriate regions independently support the existence of only one stable conformer in DVA.

TABLE 2

Raman spectral data for DVA

Liquid	Cryst. -180°C	Interpretation	Liquid	Cryst. -180°C	Interpretation
3102 m, P ^a	3099 m	$\nu_1 a_g$	1570 m, sh	1569 m, sh	$\nu_3 + \nu_{14} = 1592 A_g$ FR
3051 w, D?	3044 vw	$\nu_2 a_g$		1526 w	$\nu_7 + \nu_{11} = 1531 A_g$
3010 vs, P	3011 vs 3007 s	$\nu_3 a_g$	1418 w, sh	1419 m	$\nu_{20} + \nu_{28} = 1421 A_g$
2968 vw, P?	2968 vw 2953 vw		1401 vs, P	1400 vs	$\nu_6 a_g$
2930 vw, P?	2920 vw 2901 vw	$\nu_5 + \nu_6 = 2989 A_g$		1370 w	$\nu_9 + \nu_{19} = 1388 B_g$
2888 vw, D?	2888 vw 2867 vw			1341 w	$2\nu_{14} = 1348 A_g$
	2815 vw	$\nu_4 + \nu_9 = 2925 A_g$	1290 vs, P	1300 m, sh	$\nu_{17} + \nu_{20} = 1316 A_g$
2787 w, P	2792 vw 2721 vw			1180 vw, D	1288 s
2414 w, P	2416 w 2288 vw	$\nu_{24} + \nu_{26} = 2900 A_g$	1069 m, P	1190 vw	$\nu_{14} + \nu_{29} = 1199 B_g$
	2275 vw, sh	$\nu_5 + \nu_7 = 2878 A_g$		1070 m	$\nu_8 a_g$
2208 vs, P	2225 m, sh 2207 vs	$2\nu_{25} = 2836 A_g$		1046 w	
2166 vs, P	2181 vs 2167 vs	$2\nu_6 = 2802 A_g$	970 vw, D	976 w	$\nu_{17} b_g$
2146 m, P	2144 w	$\nu_4 + \nu_{10} = 2710 A_g$	921 m, D	932 m	$\nu_{18} b_g$
1997 vw	2000 vw 1948 vw	$\nu_4 + \nu_{11} = 2449 A_g$		751 w	$\nu_{10} + \nu_{11} = 743 A_g$
	1872 vw 1860 vw	$\nu_5 + \nu_{14} = 2305 A_g$	717 m, P	697 m	
1600 vs, P	1607 m	$\nu_{14} + \nu_{24} = 2291 B_g$	678 m, D	682 m	$\nu_9 a_g$
1588 vs, P	1592 vs	$\nu_4 a_g$ FR	~560 vw, br	513 w	$\nu_{19} b_g$
		$\nu_{27} + \nu_{28} = 2179 A_g$ FR	502 w, P	470 w, P	$\nu_{16} + \nu_{29} = 584 B_g$
			470 w, P	346 w, D?	363 m
		$3\nu_8 = 2151 A_g$ FR	241 m, P	233 s	$2\nu_{11} = 482 A_g$
		$\nu_7 + \nu_9 = 2007 A_g$		228 m	$\nu_{20} b_g$
		$\nu_7 + \nu_{19} = 1961 B_g$		150 m	$\nu_{11} a_g$
		$\nu_{12} + \nu_{15} = 1891 A_g$		136 w	
		$\nu_{17} + \nu_{18} = 1891 A_g$	115 w, P?	118 w	$2\nu_{16} = 120 A_g$
		$\nu_{27} + \nu_{29} = 1708 A_g$		93 m	Lattice modes
		$\nu_{14} + \nu_{28} = 1670 B_g$		74 m	
		$\nu_{18} + \nu_{19} = 1592 A_g$ FR		60 m	Lattice modes
		$\nu_5 a_g$ FR			

^a Abbreviations: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder; P, polarized; D, depolarized; FR, Fermi resonance.

With more or less linear acetylene and planar vinyl groups, DVA can exist in an *anti* conformation with C_{2h} symmetry, as *syn* with C_{2v} symmetry, as *gauche* with C_2 symmetry and finally with essentially free internal rotation. In the last case the wavefunctions must be classified according to the double group D_{2h}^* [13], which is isomorphous with D_{2h} . In D_{2h}^* the normal vibrations divide into $\Gamma(Q) = 11a_{1g} + 4a_{2u} + 10b_{1u} + 4b_{2g}$. The selection rules for D_{2h}^* symmetry are: the gerade modes are active in the Raman only (a_{1g} modes being polarized, b_{2g} modes being depolarized); the ungerade modes are active in the IR only (b_{1u} modes having A/B hybrid vapour contours, a_{2u} modes having C-type vapour contours).

A photoelectron spectroscopic investigation of DVA has been reported [14]. The vertical ionization energies are supposedly in agreement with a planar *anti* conformation. However, a very low barrier to internal rotation, i.e. almost free rotations, cannot be excluded from these data. There are certain analogies with 1,4-dichlorobutylene [15] and 1,4-dibromobutylene [16] ($XCH_2-C\equiv C-CH_2X$) which have been studied in some detail. These compounds apparently have *anti*, *syn* and *gauche* conformers in the liquid state

at room temperature [15, 16]. In the solid state 1,4-dichlorobutyne can exist in separate crystalline forms with *anti* and presumably with *syn* conformations according to the cooling technique [15] whereas 1,4-dibromobutyne crystallizes in the *anti* conformation [16].

A comparison between the IR and Raman frequencies of Tables 1 and 2 reveals that ca. half of the IR bands have no Raman counterpart and vice versa, although the Raman bands at 3102, 3010, 1588, 1290, 1069, 970, 921 and 678 cm^{-1} (liquid) had IR bands (solution) situated within 10 cm^{-1} . Therefore, based on the IR and Raman activity alone, C_2 symmetry (*gauche*, all fundamentals IR and Raman active) and C_{2v} (*syn*, all fundamentals Raman active, five fundamentals, a_2 , IR inactive) can be excluded. In contrast, the IR and Raman activities as well as the IR vapour contours and Raman polarization measurements suggest C_{2h} symmetry (*anti*) or D_{2h}^* symmetry (free rotation). Except for the torsional mode, the selection rules are (at least under low or medium resolution) "the same" for C_{2h} and D_{2h}^* symmetries. Hence, a distinction between these symmetries from the vibrational spectra alone depends on the observation of the torsional vibration. Since the UV vapour spectra of DVA revealed vibrational fine structure [17] a planar conformation is suggested, and since *syn* can be excluded, this conformation should be *anti*. On the other hand, preliminary MO ab initio calculations on the *syn* and *anti* forms and the conformer with 90° dihedral angle (*gauche*) suggest [18] approximately the same energy for the *syn* and *anti* forms and a very low (ca. 0.6 kJ mol^{-1}) potential barrier, which means practically free rotation. A Raman band observed at ca. 120 cm^{-1} (see below) can be interpreted as an overtone of the torsional fundamental at ca. 60 cm^{-1} (not detected in IR), indicating a considerable potential barrier (ca. 5 kJ mol^{-1}). In the following the spectra of DVA have been interpreted in terms of C_{2h} but free rotation cannot be excluded. A forthcoming study of DVA by gaseous electron diffraction might solve this problem.

The eight observed IR and Raman coincidences are not a serious objection to the assumed C_{2h} symmetry (*anti*). Firstly, the listed coincidences are typical group frequencies and (see below) they are generally observed at nearly the same wavenumber in 1-butene-3-yne (vinylacetylene) also [19]. Secondly, apart from the $\text{C}\equiv\text{C}$ stretch and the $\text{C}-\text{C}$ torsional fundamentals, all the vibrational modes of DVA exist as in-phase (Raman active) and out-of-phase (IR active) modes. They may often coincide in DVA just as they did in six cases for the *anti* conformer of 1,4-dibromobutyne [16]. No indication of the $\text{C}\equiv\text{C}$ stretch, appearing as an intense Raman band at 2208 cm^{-1} , was observed in the IR, again a strong sign of C_{2h} symmetry. The IR vapour contours and Raman polarization data are in good agreement with C_{2h} symmetry in all the states of aggregation. Finally, the fact that no rotational spectrum of DVA was detected in a microwave spectrometer is an argument (although a negative one) that DVA, at least in the vapour phase, is not present as a *syn* or *gauche* conformer.

Spectral interpretation

The fundamentals $11a_g$, $5a_u$, $4b_g$ and $10b_u$ are expected for DVA (C_{2h}). The a_g modes are polarized and the b_g modes depolarized in the Raman. Assuming reasonable interatomic distances and angles, DVA is found to be a nearly prolate symmetric top with rotational constants 0.850, 0.046 and 0.043 cm^{-1} . As a planar molecule the b_u modes will have A/B hybrid contours and the a_u modes C -type contours in the IR vapour spectrum. The PR separation was calculated [20] to be ca. 9.8 and 14 cm^{-1} for the A -, B - and C -type bands, respectively.

The assigned fundamentals are listed in Table 6, together with the results of the force constant calculations. Both the force field and the assignments were supported by our results for vinylacetylene [19]. For the sake of brevity we shall discuss only the uncertain assignments of the DVA spectra.

The $11a_g$ modes can with confidence be assigned to polarized Raman bands, mostly of high intensities, in the expected regions. Two equally intense bands were observed at 2208 and 2166 cm^{-1} , as frequently observed for acetylenes substituted with two alkyl groups [21, 22]. While the 2208-cm^{-1} band was considered as the fundamental ν_4 , the 2166-cm^{-1} band should be a combination band or overtone of species A_g in Fermi resonance with ν_4 . The only good alternative is the combination $\nu_{27} + \nu_{28} = 2179 \text{ cm}^{-1}$ (A_g), giving independent support for ν_{28} at 999 cm^{-1} (see below). Another case of Fermi resonance is provided by the intense Raman band at 1600 cm^{-1} , attributed as $\nu_{18} + \nu_{19}$ (A_g) close to ν_5 at 1588 cm^{-1} .

The b_g modes ν_{17} , ν_{18} and ν_{19} were observed as weak or medium intense, depolarized Raman bands and are characteristic group frequencies for the vinyl out-of-plane bending modes. A final b_g mode ν_{20} (skeletal bend) was assigned to the depolarized Raman band at 346 cm^{-1} .

A weak Raman band at 115 cm^{-1} (liquid) has a much lower wavenumber than expected for any of the a_g or b_g modes. Tentatively, this band is interpreted as an overtone of the torsional fundamental ν_{16} , although the latter could not be detected in the far-IR spectra. It is well known that the higher harmonics of the torsional modes often have quite high intensities in Raman [23].

The a_u modes are clearly distinguished in the IR vapour spectra from the distinct C -contours. Also, ν_{12} , ν_{13} and ν_{14} are the out-of-phase $C-H$ vinyl frequencies corresponding to the in-phase modes ν_{17} , ν_{18} and ν_{19} . No reliable IR vapour bands were observed below 500 cm^{-1} at 50-torr pressure in a 20-cm cell. Thus, the lowest IR-active fundamentals must be assigned on the basis of solution and low-temperature spectra, combined with help from the normal coordinate analysis. A medium intense band at 171 cm^{-1} corresponding to the crystal spectra doublet at 226 and 207 cm^{-1} is assigned as ν_{15} , in good agreement with the results of the calculations (Table 6). No IR bands in the region $100-30 \text{ cm}^{-1}$ were detected in any of the spectra, and the lowest a_u mode ν_{16} connected with $C-C$ torsion therefore remained unobserved.

The fact that no torsional mode was observed might be interpreted as an argument for free rotation (D_{2h}^* symmetry). However, the Raman bands at 115 cm^{-1} (liquid) and 118 cm^{-1} (solid at 90 K) could be interpreted neither as a_g or b_g fundamentals nor as a difference band. The only reasonable explanation would be as $2\nu_{16}$, which leaves ν_{16} around 60 cm^{-1} .

Most of the b_u modes had resolved A/B hybrid contours with PR separations around $8\text{--}9\text{ cm}^{-1}$ in the IR vapour spectra, but the bands are not as distinct as the a_u fundamentals. The three C—H stretches ($\nu_{21}\text{--}\nu_{23}$), the C=C stretch (ν_{24}), CH_2 scissor (ν_{25}) and C—H bend (ν_{26}) can be assigned to IR bands with the expected contours. These fundamentals were all situated quite close to the corresponding a' modes in vinylacetylene [19]. An intense band with B -contour at 1183 cm^{-1} was considered to be ν_{27} , connected with C—C stretching. A b_u fundamental connected with CH_2 deformation (ν_{28}) was expected close to the corresponding a_g mode (ν_8) at 1069 cm^{-1} , leaving 1075 , 1036 or 999 cm^{-1} as possibilities. When the force constants derived for vinylacetylene and vinylacetylene-4d, [19] were employed with smaller modifications (see below), the calculations strongly suggested ν_{28} to be situated around 1000 cm^{-1} . Therefore, the sharp, distinct crystal band at 999 cm^{-1} was assigned as ν_{28} , only visible as a shoulder on the intense ν_{12} in CS_2 solution. An independent support for this assignment was provided by the intense Raman combination band at 2166 cm^{-1} in Fermi resonance with ν_4 . The remaining b_u modes are assigned to the bands at 524 cm^{-1} (ν_{29}) and 123 cm^{-1} (ν_{30}), in good agreement with the results of the force constant calculations.

CDVA

Conformation

The IR spectrum of melted CDVA is shown in Fig. 5, the Raman spectra are given in Figs. 6 (melt) and 7 (solid), while the experimental data are collected in Table 3. No simplification of the IR or Raman spectra was

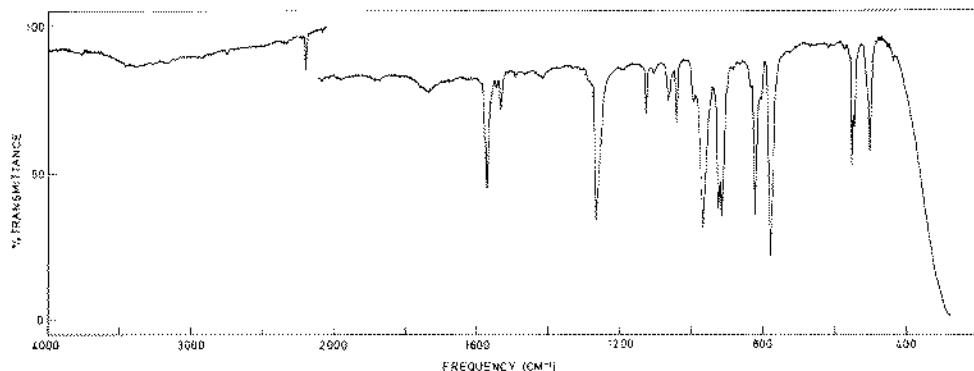


Fig. 5. The IR spectrum of CDVA as capillary melt.

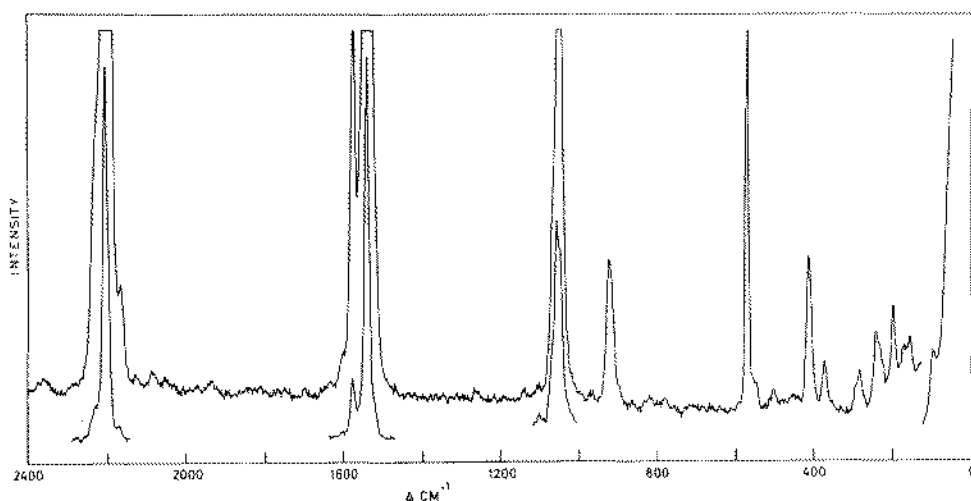


Fig. 6. Raman spectrum of CDVA as a melt at ca. 335 K.

observed when the melt was solidified or when it was cooled to 90 K, although the correlation splitting suggests that the solid phase was really crystalline. Thus, it seems probable that CDVA like DVA has only one preferred conformer in the melt, in solution as well as in the solid state.

Unlike the results for DVA, it is immediately apparent from the spectral data that most of the IR and Raman bands of CDVA coincide. Therefore, the *anti* conformation (C_{2h}) or "free rotation" (D_{2h}^*) can be ruled out and the molecule should have either *syn* (C_{2v}) or *gauche* (C_2) conformations. Apparently, when the hydrogen atoms in DVA are interchanged with the

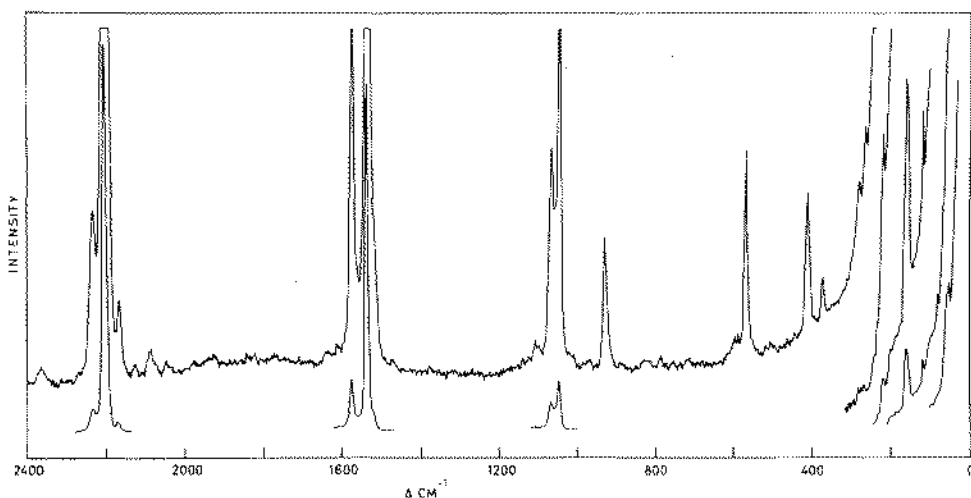


Fig. 7. Raman spectrum of CDVA as crystalline solid.

TABLE 3

IR and Raman spectral data for CVDA

IR			Raman		Interpretation
Melt	Solution (CCl ₄)	Cryst. -180°C	Melt	Solid	
			2288 vw, P?		$\nu_1 + \nu_{15} A_2$
			2230 s, sh, P	2230 s	$\nu_{22} + \nu_{23} A_1$
2201 w ^a	2201 w	2200 m	2200 vs, P	2203 vs	$\nu_1 a_1$
			2162 w, sh, P?	2164 m	$\nu_3 + \nu_{22} B_2$
			2124 vw, P	2124 vw	$\nu_{23} + \nu_{25} A_1$
2086 vw			2081 w, P	2086 w	$2\nu_3 A_1$
2036 vw			2045 w, P	2044 w	$\nu_{22} + \nu_{24} A_1$
1978 vw			1968 vw	1971 vw	$\nu_6 + \nu_{21} B_2$
			1940 vw, P?	1937 vw	$\nu_3 + \nu_4 A_1$
			1931 w, P	1925 vw	$\nu_2 + \nu_6 A_1$
1883 vw	1880 vw				$\nu_2 + \nu_{27} B_2$
1869 vw					$\nu_2 + \nu_7 A_1$
			1835 vw, P	1835 vw	$2\nu_4 A_1$
			1809 vw, P	1818 vw	$\nu_{22} + \nu_{25} A_1$
1757 vw	1768 vw		1764 vw, P	1765 vw	$\nu_{21} + \nu_{29} A_1$
1733 w	1735 vw				$\nu_4 + \nu_8 A_1$
			1698 vw, P		$\nu_{22} + \nu_{26} A_1$
			1632 w, P	1636 vw	$2\nu_5 A_1$
			1599 w, P	1605 vw	
1588 vw		1585 w			$\nu_3 + \nu_{17} B_1$
1577 w, sh					$\nu_{13} + \nu_{22} B_1$
1572 s	1574 m	1574 s	1573 s, D?	1572 s	$\nu_{21} b_2$
1543 vw				1557 w	$2\nu_{23} A_1$
1533 m	1522 m	1536 m 1534 w, sh	1536 vs, P	1535 vs	$\nu_2 a_1$
1492 vw			1516 m, sh, P?	1517 m, sh	$\nu_{23} + \nu_{25} A_1$
1465 vw			1469 vw	1472 vw	$\nu_4 + \nu_{17} B_1$
1417 vw		1420 vw			$\nu_{16} + \nu_{22} B_2$
1367 vw			1371 vw, P	1374 vw	$\nu_3 + \nu_7 A_1$
1307 vw			1303 vw, P		$\nu_3 + \nu_8 A_1$
1288 vw					$\nu_4 + \nu_{27} B_2$
1265 vs	1261 s	1275 vs 1263 vw 1261 vw 1218 vw	1261 w, D?	1269 w	$\nu_{22} b_2$
					$\nu_3 + \nu_9 A_1$
					$\nu_5 + \nu_8 A_1$
1193 vw	1190 vw ^b	1195 vw	1189 w, P	1191 vw	$\nu_4 + \nu_8 A_1$
	1143 vw		1139 w, D	1139 w	$\nu_3 + \nu_{20} B_2$
1126 m	1133 vw	1131 w			$2\nu_{25} A_1$
1104 vw	1103 vw ^b	1107 vw	1100 w, P	1106 w	$\nu_5 + \nu_8 A_1$
1065 w	1065 w	1068 w	1067 s, sh, P	1066 s	$\nu_{24} + \nu_{28} A_1$
			1052 vs, P	1055 m	$\nu_5 + \nu_9 A_1$
1042 m	1043 w	1048 w 1046 w	1043 vs, P	1044 s	$\nu_3 a_1$
995 w		997 w	1008 w, P?	1010 vw	$\nu_{25} + \nu_{26} A_1$

TABLE 3 (continued)

IR			Raman		Interpretation
Melt	Solution (CCl ₄)	Cryst. -180°C	Melt	Solid	
968 vs	967 vs	973 vs	965 vw	966 w	$\nu_{33} b_2$
952 w, sh		954 w			$\nu_4 + \nu_{20} B_1$
926 vs	923 m, sh	931 vs	923 s, P	928 m	$\nu_4 a_1$
917 vs	915 m	920 vs	915 m, sh, P	914 vw, sh	$\nu_{25} + \nu_{27} A_1$
902 vw		904 vw			$\nu_7 + \nu_{17} B_1$
885 vw		886 vw		885 w	$\nu_{13} + \nu_{25} B_1$
835 w		838 vw		832 w	$\nu_{12} + \nu_{13} A_1$
825 vs	823 vs	826 vs	821 w, br, P?	822 vw	$\nu_3 a_1$
		817 vw, sh			$2\nu_6 A_1$
806 w		810 vw			$\nu_{17} + \nu_{18} A_1$
780 vs	779 vs ^b	783 vs	779 w, D	785 w	$\nu_{24} b_1$
772 m, sh		774 m			$\nu_6 + \nu_{27} B_2$
			709 w, P	714 w	$2\nu_9 A_1$
			652 vw	662 vw	$\nu_{27} + \nu_{28} A_1$
618 vw				595 vw	$\nu_{20} + \nu_{25} A_2$
					$2\nu_{25} A_1$
573 vw				569 s	$\nu_{25} b_1$
567 vw	564 w	567 vw	565 vs, D		$\nu_6 + \nu_{10} A_1$
561 vw		563 vw			$\nu_{17} b_1$
553 s		554 s	551 w, sh, P?	554 w, sh	$\nu_8 + \nu_{18} B_1$
547 m	547 m	548 w, sh			$\nu_{26} + \nu_{30} A_1$
	534 vw		520 vw, D	521 vw	$\nu_{12} a_2$
511 w, sh		512 vw, sh			$\nu_7 + \nu_{10} A_1$
504 s	503 w ^c	504 s	501 w, P	504 w	$\nu_8 + \nu_9 A_1$
	475 w ^c				$\nu_8 + \nu_{29} B_2$
437 vw, br			447 vw, P?	445 w	$\nu_{26} b_1$
	406 w ^c	404 w ^d	411 vs, P	410 m	$\nu_6 a_1$
		370 vw	372 m, D	373 m	$\nu_{27} b_1$
	354 w ^c	355 vw ^d	356 vw, sh, P?	358 vw	$\nu_7 a_1$
			325 vw, D	320 vw	$\nu_{13} a_2$
			292 vw, sh, D?		$\nu_{28} b_1$
	282 w ^c	283 w ^d	282 m, P	282 m	$\nu_8 a_1$
	271 w ^c			267 w	$\nu_{18} b_1$
			240 m, D	247 w	$\nu_{14} a_2$
			231 m, P	228 w	$\nu_9 a_1$
	196 vw ^c	194 m ^d	196 m, D	197 m	$\nu_{29} b_1$
	187 w ^c	186 w, sh ^d		186 w	$2\nu_{15} A_1$
				175 vw	$\nu_{19} b_1$
		157 vw ^d	167 w, D	160 w	$\nu_{10} a_1$
		104 vw ^d	153 w, P		$\nu_{30} b_1$
					$\nu_{15} a_1$
		36 vvw ^d	96 m, D?	98 vw	$\nu_{20} b_1$

^aAbbreviations: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder; P, polarized; D, depolarized. ^bCarbon disulphide solution. ^cCyclohexane solution. ^dPolyethylene pellet.

electronegative and bulky chlorine atoms, the potential to internal rotation changes significantly. Recent results by molecular mechanics calculation suggest that there is a broad potential minimum at *syn* extending to a *gauche* conformer with ca. 25° dihedral angle from *syn* [23].

The vibrational fine structure of the UV spectrum supports a planar or nearly planar conformer [10]. Various chemical addition reactions of CDVA can also be understood in terms of a *syn* conformer (or a *gauche* close to *syn*) for this molecule. Thus, the catalytic hydrogenation of CDVA leads to *cis*-addition [10]. Moreover, in their extensive studies on the reactions of unsaturated polychloro compounds with thiols and thiolates, Roedig and Zaby [24] investigated the addition of *p*-chlorothiophenol to CDVA under radical conditions [25]. They found a mixture of two hexatriene derivatives revealing addition to the triple bond [25]. A large radical like *p*-chlorothiophenol is more likely to attack the *syn* (or *gauche*) conformer than the *anti* since the latter is more shielded by the bulky chlorine substituents.

No IR vapour spectrum can be obtained for CDVA owing to its low volatility. On slight heating to ca. 60°C , an intense Raman spectrum with generally well determined polarization ratios was recorded. As seen from Table 3, nearly half of the bands considered as fundamentals appear polarized (most of the combination bands and overtones were also polarized). Thus, the data indicate C_2 symmetry (16 polarized and 14 depolarized modes) since C_{2v} symmetry would require 11 polarized and 19 depolarized fundamentals. On the other hand four depolarized Raman bands (520 , 240 , 167 and 96 cm^{-1}) with no IR counterparts are possible candidates for the a_2 modes of C_{2v} symmetry. It must be concluded that the molecular symmetry cannot be decided from the vibrational spectra alone. The present data are interpreted in terms of the *syn* conformer (C_{2v}), but they can also (with minor changes) be interpreted in terms of the *gauche* conformer (C_2).

Spectral interpretation

The IR and Raman bands considered as fundamentals are listed in Table 6 together with the calculated frequencies. In the assumed C_{2v} symmetry ($11a_1 + 5a_2 + 4b_1 + 10b_2$), 11 bands should be polarized and 17 depolarized in Raman. The a_1 , b_1 and b_2 modes will all be IR and Raman active, whereas the a_2 fundamentals should be Raman active and IR inactive.

The a_1 fundamentals ($\nu_1-\nu_{10}$) can be assigned with considerable confidence to polarized Raman bands, many of which are quite intense and all but ν_9 have counterparts in the IR spectrum. Two of the Raman bands (ν_5 and ν_7) were weak and therefore had uncertain polarization ratios, but ν_5 corresponded to an intense IR band.

As mentioned earlier, four depolarized Raman bands were observed which had no IR counterparts. These bands were all detected in the low-frequency region where the out-of-plane bending modes are situated, and were assigned as the a_2 modes $\nu_{12}-\nu_{15}$. An additional depolarized Raman band at 167 cm^{-1} with no IR counterpart did not correspond to any of the calculated a_2 modes

TABLE 4

Internal valence symmetry coordinates for DVA with reference to Fig. 8

$S_1(a_g) = T$	$S_{17}(b_g) = 2^{-1/2}(\theta_z + \theta'_z)$
$S_2(a_g) = 2^{-1/2}(D + D')$	$S_{18}(b_g) = 8^{-1/2}(\tau_{7123} + \tau_{7129} + \tau_{8123} + \tau_{8129}$ $- \tau_{45611} - \tau_{45612} - \tau_{105611} - \tau_{105612})$
$S_3(a_g) = 2^{-1/2}(S + S')$	$S_{19}(b_g) = 2^{-1/2}(\Pi_{7812} - \Pi_{131265})$
$S_4(a_g) = \frac{1}{2}(d_7 + d_8 + d_{11} + d_{12})$	$S_{20}(b_g) = 2^{-1/2}(\Pi_{1329} - \Pi_{64510})$
$S_5(a_g) = \frac{1}{2}(d_7 - d_8 + d_{11} - d_{12})$	$S_{21}(b_u) = 2^{-1/2}(D - D')$
$S_6(a_g) = 2^{-1/2}(s_9 + s_{10})$	$S_{22}(b_u) = 2^{-1/2}(S - S')$
$S_7(a_g) = 2^{-1/2}(\theta_{xy} + \theta'_{xy})$	$S_{23}(b_u) = \frac{1}{2}(d_7 + d_8 - d_{11} - d_{12})$
$S_8(a_g) = 12^{-1/2}(2\omega - \beta_9 - \gamma + 2\omega' - \beta_{10} - \gamma')$	$S_{24}(b_u) = \frac{1}{2}(d_7 - d_8 - d_{11} + d_{12})$
$S_9(a_g) = \frac{1}{2}(\beta_9 - \gamma + \beta_{10} - \gamma')$	$S_{25}(b_u) = 2^{-1/2}(s_9 - s_{10})$
$S_{10}(a_g) = 12^{-1/2}(2\alpha - \beta_7 - \beta_8 + 2\alpha' - \beta_{11} - \beta_{12})$	$S_{26}(b_u) = 2^{-1/2}(\theta_{xy} - \theta'_{xy})$
$S_{11}(a_g) = \frac{1}{2}(\beta_7 - \beta_8 + \beta_{11} - \beta_{12})$	$S_{27}(b_u) = 12^{-1/2}(2\omega - \beta_9 - \gamma - 2\omega' + \beta_{10}$ $+ \gamma')$
$S_{12}(a_u) = 2^{-1/2}(\theta_z - \theta'_z)$	$S_{28}(b_u) = \frac{1}{2}(\beta_9 - \gamma - \beta_{10} + \gamma')$
$S_{13}(a_u) = 8^{-1/2}(\tau_{7123} + \tau_{7129} + \tau_{8123} + \tau_{8129} + \tau_{45611}$ $+ \tau_{45612} + \tau_{105611} + \tau_{105612})^a$	$S_{29}(b_u) = 12^{-1/2}(2\alpha - \beta_7 - \beta_8 - 2\alpha' + \beta_{11}$ $+ \beta_{12})$
$S_{14}(a_u) = 2^{-1/2}(\Pi_{7812} + \Pi_{111265})$	$S_{30}(b_u) = \frac{1}{2}(\beta_7 - \beta_8 - \beta_{11} + \beta_{12})$
$S_{15}(a_u) = 2^{-1/2}(\Pi_{1329} + \Pi_{64510})$	
$S_{16}(a_u) = \tau_{1256}$	

^a τ_{ijkl} and Π_{ijkl} denote torsion and out-of-plane bending coordinates involving atoms i, j, k and l as defined in ref. 28.

and was instead assigned as a b_1 mode (ν_{10}). Undoubtedly, the torsional mode ν_{16} will be extremely low for CDVA (calculated to 13 cm^{-1}) and, being covered by the Rayleigh wing, it cannot be observed.

The four out-of-plane modes $\nu_{17}-\nu_{20}$ of species b_1 are, with considerable uncertainty, attributed to the bands at $553, 267, 167$ and 36 cm^{-1} . Finally, the out-of-phase in-plane modes of species b_2 ($\nu_{21}-\nu_{30}$) were assigned to IR and Raman bands in the expected regions. The Raman bands corresponding

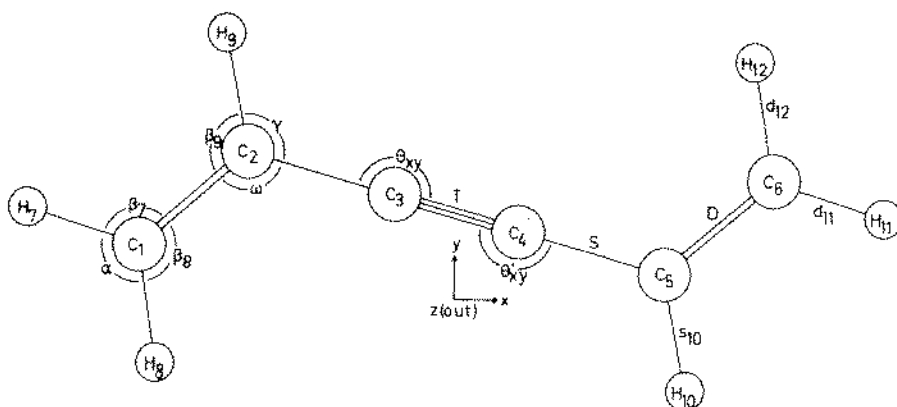


Fig. 8. Valence coordinates for DVA. In addition, π_{ijkl} and τ_{ijkl} denote out-of-plane bending and torsional coordinates, respectively, involving atoms i, j, k and l .

TABLE 5

Proposed valence force constants for DVA and CDVA

Constant	Value ^a		Constant	Value ^a	
	DVA	CDVA		DVA	CDVA
<i>Stretch</i>			<i>Stretch—stretch</i>		
$K_{C\equiv C}$	14.222	14.222	$F_{C\equiv C/C-C}$	0.5 ^b	0.5
$K_{C=C}$	8.386	8.386	$F_{C-C/C\equiv C}$	0.2 ^b	0.2
K_{C-C}	5.899	5.899	F_{C-X_2}	0.039 ^b	0.06 ^c
K_{C-X_2}	5.106	3.50 ^c	$F_{C-C/C-X}$	—	1.15 ^c
K_{C-X}	5.060	3.50 ^c	$F_{C-C/C-X}$	—	—
<i>Bend</i>			<i>Stretch—bend</i>		
H_{C-C-X}	0.581	1.094 ^c	$F_{C-C/C-C-X}$	0.22	0.22
H_{C-C-X}	0.494	1.094 ^c	$F_{C-C/C-C-X}$	—	—
H_{X-C-X}	0.342	1.325 ^c	$F_{C-C/C=C-C}$	0.30	0.30
H_{C-C-C}	0.852	0.852	$F_{C-C/C=C-C}$	—	—
$H_{C-C\equiv C}^{\text{P}}$	0.338	0.338	$F_{C-X/C=C-X}$	—	0.48 ^c
$H_{C-C\equiv C}^{\text{D}}$	0.280	0.280	<i>Bend—bend</i>		
$H_{\tau(C-C)}$	0.09744 ^b	0.14 ^c	$f_{C-C-X/C-C-X}^{\text{trans}}$	0.067 ^b	0 ^c
$H_{\Pi(CX_2)}$	0.2383 ^b	0.25	$f_{C-C-X/C-C-X}^{\text{ls}}$	-0.034 ^b	0.32 ^c
$H_{\Pi(CX)}$	0.3823 ^b	0.25	$f_{C-C\equiv C/C-C\equiv C}^{\text{D}}$	-0.147	0.147 ^d
$H_{\tau(C-C)}$	0.016	0.016	$f_{C-C\equiv C/C-C\equiv C}^{\text{D}}$	-0.090	0.090 ^d
			$f_{\Pi(CX)/\Pi(CX_2)}$	0.04 ^b	0.04
			$f_{\Pi(CX)/\tau(C-C)}$	-0.035 ^b	-0.035
			$f_{C-C-C/C-C\equiv C}$	0.04	0.04

^aUnits for stretching and stretch—stretch interaction constants are m dyn A⁻¹, for bending constants m dyn A rad⁻² and for stretch—bend interaction constants m dyn rad⁻¹.

^bConstrained on value found for 1-butene-3-yne, ref. 19.

^cTransferred from perchloroethylene, ref. 27.

^dChange in sign of lin/lin interaction constants are caused by changed definition of the internal coordinates.

to 1572, 780, 567, 372 and 196 cm⁻¹ all appeared depolarized, for the remaining bands the polarization ratios were uncertain or not known.

Some of the stretching modes of CDVA may be considered as group frequencies, all of them belonging to the in-plane modes (a_1 and b_2). Thus the C≡C stretch (ν_1) and the two C=C stretches (ν_2 and ν_{21}) are assigned with certainty to the bands at 2201, 1533 and 1572 cm⁻¹, respectively. A very strong IR band at 1265 and a Raman band at 1043 cm⁻¹ are considered to be the ν_{22} and ν_3 modes, which probably involve predominantly C—C stretch. It is not quite clear, however, which of the very intense, polarized Raman bands at 1052 to 1043 cm⁻¹ belongs to the fundamental. We have considered the 1052-cm⁻¹ band with no IR counterpart to be a combination band in Fermi resonance with ν_3 .

TABLE 6

Observed and calculated vibrational frequencies for DVA and CDVA

DVA				CDVA				
	No.	Observed	Calculated	PED ^a	No.	Observed	Calculated	
<i>a_g</i>	ν_1	3102	3105	98S ₈	<i>a₁</i>	ν_1	2201	2205
	ν_2	3051	3052	93S ₆		ν_2	1533	1519
	ν_3	3018	3018	94S ₄		ν_3	1042	1220
	ν_4	2208	2208	79S ₁ , 23S ₃		ν_4	926	907
	ν_5	1588	1588	69S ₂ , 18S ₉ , 18S ₁₀		ν_5	825	822
	ν_6	1401	1402	32S ₇ , 59S ₁₀		ν_6	411	404
	ν_7	1290	1291	27S ₂ , 23S ₉ , 22S ₁₀		ν_7	356	381
	ν_8	1069	1069	27S ₉ , 63S ₁₁		ν_8	282	289
	ν_9	717	717	49S ₃ , 22S ₈ , 17S ₁₁		ν_9	231	221
	ν_{10}	502	502	15S ₃ , 39S ₇ , 37S ₈		ν_{10}	157	151
	ν_{11}	241	241	56S ₇ , 30S ₈		ν_{11}	—	33
<i>a_u</i>	ν_{12}	972	974	17S ₁₃ , 17S ₁₄ , 88S ₁₅	<i>a₂</i>	ν_{12}	520	544
	ν_{13}	920	927	83S ₁₄		ν_{13}	325	376
	ν_{14}	673	668	78S ₁₃		ν_{14}	240	220
	ν_{15}	171	172	95S ₁₂		ν_{15}	96	90
	ν_{16}	(60)	59	98S ₁₆		ν_{16}	—	13
<i>b_g</i>	ν_{17}	970	974	17S ₁₈ , 15S ₁₉ , 89S ₂₀	<i>b₁</i>	ν_{17}	553	507
	ν_{18}	921	927	84S ₁₉		ν_{18}	267	301
	ν_{19}	678	680	76S ₁₈		ν_{19}	167	151
	ν_{20}	346	347	90S ₁₇		ν_{20}	36	46
<i>b_u</i>	ν_{21}	3105	3105	98S ₂₄	<i>b₂</i>	ν_{21}	1572	1564
	ν_{22}	3054	3052	93S ₂₅		ν_{22}	1265	1250
	ν_{23}	3024	3019	94S ₂₃		ν_{23}	968	1109
	ν_{24}	1618	1618	64S ₂₁ , 19S ₂₂ , 18S ₂₃		ν_{24}	780	855
	ν_{25}	1423	1422	18S ₂₈ , 64S ₂₉		ν_{25}	567	588
	ν_{26}	1293	1292	25S ₂₁ , 25S ₂₆ , 21S ₂₄		ν_{26}	437	459
	ν_{27}	1183	1183	48S ₂₂ , 30S ₂₈		ν_{27}	372	359
	ν_{28}	999	1000	20S ₂₂ , 66S ₃₀		ν_{28}	292	303
	ν_{29}	524	524	81S ₂₇		ν_{29}	196	188
	ν_{30}	123	123	87S ₂₆		ν_{30}	104	88

^aPED, potential energy distribution, defined by: $\text{PED}_{ij} = 100 F_{ij} L_{ij}^2 / \lambda_j$.

The =CCl₂ out-of-phase stretching modes are expected close to 1000 cm⁻¹ [26] and are assigned to the bands at 968 (ν_{23}) and 926 cm⁻¹ (ν_4). Two additional C—Cl stretches are observed at 825 (ν_5) and 780 cm⁻¹ (ν_{24}) while the in-phase =CCl₂ stretches presumably are connected with the bands at 567 (ν_{25}) and 411 cm⁻¹ (ν_6). The out-of-phase, single C—Cl stretch and the in-phase =CCl₂ stretch are separated into three regions [26] 100–200 cm⁻¹ apart while the *a*₁ and *b*₂ modes are closely spaced. These bands are all very intense in IR or in Raman and the wavenumbers agree with the results of

the force constant calculation. Below 500 cm^{-1} various skeletal bending vibrations, the $\text{C}=\text{C}-\text{Cl}$ in-plane and out-of-plane bending and finally a torsional mode are expected. In tetrachloroethylene [27] the highest out-of-plane mode was observed around 500 cm^{-1} . In CDVA the bands at 553 and 520 cm^{-1} are assigned as ν_{17} and ν_{12} , respectively, both representing the highest out-of-plane modes in this molecule.

FORCE CONSTANT CALCULATIONS

A non-redundant set of symmetry coordinates, based on the valence coordinates indicated on Fig. 8 (DVA) are given in Table 4. For CDVA, where we have assumed the conformation to be *syn*, the symmetry coordinates are defined in an analogous way. We have used the following geometrical parameters: $r_{\text{C}-\text{C}} = 1.431$, $r_{\text{C}=\text{C}} = 1.341$, $r_{\text{C}\equiv\text{C}} = 1.209$, $r_{\text{C}-\text{H}} = 1.087$ and $r_{\text{C}-\text{Cl}} = 1.720\text{ \AA}$; $\alpha_{\text{C}-\text{C}-\text{C}} = 123.0$, $\alpha_{\text{C}=\text{C}-\text{H}} = 120.8$, $\alpha_{\text{C}=\text{C}-\text{Cl}} = 123.0$ and $\alpha_{\text{C}-\text{C}=\text{C}} = 180^\circ$.

An initial valence force field for DVA was, with a few modifications, transferred from 1-butene-3-yne (vinylacetylene) [19]. Only minor changes in the force constants were necessary to reproduce the vibrational frequencies. The resulting force constants are given in Table 5, while the observed and calculated fundamental frequencies are given in Table 6.

The force field for CDVA was in part transferred from DVA and from perchloroethylene [27]. In view of the uncertainties regarding the conformation and hence the assignments, we have not attempted to refine the force constants given in Table 5. As can be seen, the agreement in Table 6, although not perfect, is reasonable.

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