

## THE CONFORMATION AND VIBRATIONAL SPECTRA OF 2-ETHYNYL-1,3-BUTADIENE (3-METHYLENE-4-PENTENE-YNE)

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### ABSTRACT

A sample of 2-ethynyl-1,3-butadiene was synthesized by a thermal rearrangement of 1,2-hexadiene-5-yne at ca. 770 K. Infrared spectra were recorded of the vapour, the liquid and of the amorphous and crystalline solids at 90 K in the region  $4000-50\text{ cm}^{-1}$ . Raman spectra were obtained of the cooled liquid, including semiquantitative polarization measurements, and of the crystalline solid at 90 K. The spectral data indicate that 2-ethynyl-1,3-butadiene exists as the *s-trans* conformer in the various states of aggregation but the possibility of small amounts of a second conformer cannot be excluded.

### INTRODUCTION

2-Ethynyl-1,3-butadiene (acronym: EBUT) is one of the 15 possible non-cyclic isomers of benzene. Five of these, 1,2,4,5-hexatetraene (biallenyl) [1, 2], 1,5-hexadiyne (bi-propargyl) [3-6], 2,4-hexadiyne (dimethylacetylene) [7], 1,2-hexadiene-5-yne (propargylallene) [8, 9], and 1,5-hexadiene-3-yne (divinylacetylene) [10, 11], have previously been studied by vibrational spectroscopy and by electron diffraction. Other related hydrocarbons which have also been investigated include 3-butene-yne (vinylacetylene) [12], 1,2,4-pentatriene (vinylallene) [13], and 1,3,4,6-heptatetraene (divinylallene) [14].

These highly unsaturated molecules are not only of interest as model compounds for spectroscopic studies but have also been employed extensively as substrates in organic synthesis in recent years [15-22]. The title compound, for example, constitutes a new diene system of considerable preparative potential in Diels-Alder additions [23]. It has been known for many years [24] that the *cis*-conformation (whether this is the preferred conformation in the ground state or only achieved during the addition pro-

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cess) of the diene is a prerequisite for a successful (2 + 4) cycloaddition.

Against this background a thorough investigation of the preferred geometry of EBUT seemed desirable. In this paper we present our results from vibrational spectroscopy studies while the results from a gaseous electron diffraction investigation will be published later [25].

## EXPERIMENTAL

### *Preparation*

EBUT was prepared as described previously by the pyrolysis of 1,2-hexadiene-5-yne in a flow reactor at 770 K [26]. An analytically pure sample was obtained from the pyrolysate by preparative gas chromatography (Carbowax, 60°C).

### *Spectral studies*

IR spectra were recorded on a Perkin-Elmer model 225 spectrometer (5000–200  $\text{cm}^{-1}$ ) and on a Bruker IFS 114C interferometer (600–20  $\text{cm}^{-1}$ ). Vapour spectra of EBUT at saturation pressure (ca. 60 Torr) and lower were recorded at ambient temperature in cells equipped with either CsI or polyethylene windows. Spectra of the pure liquid were recorded in sealed cells and the solid state spectra were obtained before and after annealing using cryostats cooled with liquid nitrogen (CsI or polyethylene windows).

Raman spectra were recorded on a Dilor RTI 30 triple monochromator interfaced to the data system of the Bruker interferometer. The 488 and 514.8 nm lines of a CRL 52G argon ion laser were used for excitation. EBUT was studied as a neat liquid in a sealed ampoule cooled to ca. 250 K, and semiquantitative polarization data were obtained. Spectra of the solid compound at liquid nitrogen temperature were recorded before and after annealing.

## RESULTS AND DISCUSSION

### *Conformation*

An IR vapour spectrum of EBUT is shown in Fig. 1, while Fig. 2 displays the spectrum of the annealed, crystalline solid at ca. 90 K. A Raman spectrum of the neat liquid is given in Fig. 3. The wavenumbers of the observed IR and Raman bands are collected in Table 1.

EBUT can a priori exist in several conformations, the most probable, however, being the planar *s-trans* (*anti*-periplanar) form. By comparing the spectra of the vapour phase and the liquid with those of the solid state, it is immediately apparent that all the major bands remain in the various states of

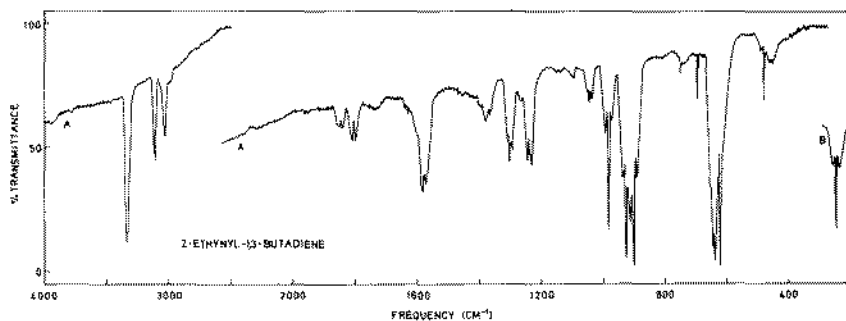


Fig. 1. The mid IR spectrum of 2-ethynyl-1,3-butadiene (EBUT) in the vapour phase,  $p \approx 60$  Torr. A, 10 cm pathlength; B, 25 cm pathlength.

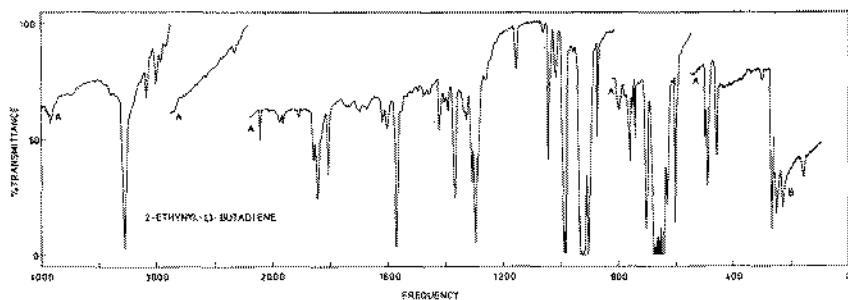


Fig. 2. The mid IR spectrum of 2-ethynyl-1,3-butadiene (EBUT) as a crystalline solid at 90 K.

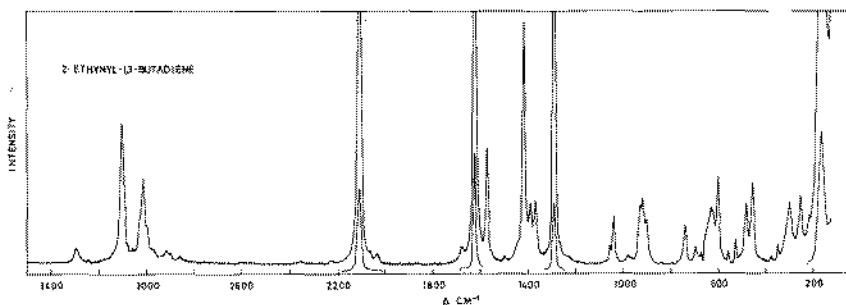


Fig. 3. The Raman spectrum of 2-ethynyl-1,3-butadiene (EBUT) as a liquid at ca. 250 K.

aggregation. Also, the frequent cases of correlation splitting observed in the low-temperature spectra reveal that the sample was indeed crystalline. The data strongly suggest that only one conformer (or a very dominant conformer) is present. Any additional conformer in the vapour or liquid states must be present in very low concentration.

The Raman polarization measurements indicate a planar conformation,

TABLE 1

IR and Raman spectral data<sup>a</sup> for 2-ethynyl-1,3-butadiene (EBUT)

IR			Raman		Interpretation		
Vapour	Liquid	Crystal (90 K)	Liquid (250 K)	Crystal (90 K)			
3333	} vs,A/B <sup>b</sup>	3300 vs	3280 vs	3295 vw,P	3280 vw	$\nu_1 a'$	
3327 Q					3243 vw,P		
3320					3138 vw,P		
~3120	} m,A	3104 w,sh	3098 w	3104 w	3112 vw	$\nu_2 a'$	
3114 Q					3099 w		
3106 Q	} m,A	3097 m	3093 w	3097 w,P	3088 vw,sh	$\nu_3 a'$	
3099							
~3065 vw		3057 vw	3054 vw			$\nu_4 a'$	
3035	} w	~3025 m,sh	3020 w	~3025 vw,sh		$\nu_5 a'$	
3032 Q							3011 w
3028 Q	} m,A	3015 m	3007 w	3012 w,P	3011 w	$\nu_6 a'$	
3021							
2988 vw				2997 vw,sh	2997 w		
2976 vw		2973 vw	2966 w				
		~2100 vw	2108 vw	2104 s,P	2115 m	$\nu_7 a'$	
			2105 w		2105 s		
				2063 vw,P	2084 vw		
				2032 vw,P	2063 vw		
			2033 vw	2032 vw,P	2034 vw		
				1676 vw	1678 vw		
		1626 w	1624 vw	1624 vs,P	1621 vs	$\nu_8 a'$	
			1621 w				
1598 w		1602 w	~1605 w				
		1577 m,sh	1576 w,sh				
1582	} m,B	1573 s	1573 s	1572 m,P	1571 m	$\nu_9 a'$	
1571			1570 s,sh				1570 vs
		~1565 m,sh	1565 w				
1558 w		1559 w	1552 vw				
			1500 vw	1498 vw			
			1478 vw				
			1460 vw				
			1456 vw				
			1424 w				
		1419 w	1418 vw	1419 m,P	1425 m	$\nu_{10} a'$	
			1404 vw				
					1407 vw		
1395	} w,B	1391 w	1393 vw	1391 w	1395 vw	$\nu_{11} a'$	
1385							
1378	} w,B	1370 m	1371 s	1369 w,P	1370 vw	$\nu_{12} a'$	
1365							

TABLE 1 (continued)

IR			Raman		Interpretation
Vapour	Liquid	Crystal (90 K)	Liquid (250 K)	Crystal (90 K)	
		1336 w			
		1328 w			
		1311 m			
1307		1299 s			
1302 Q	m,A	1295 vs			
1295		1289 m			
1292 Q	m	1287 m	1289 s,P	1288 m	$\nu_{13} a'$
1285					
1265 vw	$\approx 1250$ w,br	1267 vw,br	$\sim 1250$ vw,br		
1244					
1232	m,B				
1152		1157 vw			
1140	vw,B	1141 vw			
1097 vw					
	1065 vw	1065 vw			
1050		1046 s	1055 vw,D?		
1044	w,A/B	1041 m,sh	1039 w,P	1043 w	$\nu_{14} a'$
1035		1036 w			
	1026 w	1025 w,sh			
		1020 w			
993		991 s			
982 Q	s,C	985 s	982 vw	987 vw	$\nu_{12} a''$
971					
		961 vw			
		946 vw			
		937 vs,sh	930 vw	931 w,sh	$\nu_{15} a'$
934		930 vs			
923 Q	vs,C	925 s,sh	920 vw,D?	923 w	$\nu_{13} a''$
911		922 vs			
900 Q	vs,C	915 vs,sh	904 vw	901 vw	$\nu_{24} a''$
891		909 s,sh			
		903 vs			
		896 w,sh			
	874 w	875 w			
	800 vw	802 w			
	792 vw	798 w			
	776 vw	778 vw			
	762 vw	763 m			
752 vw,C?	749 vw	755 vw	$\sim 750$ vw,sh	755 vw	$\nu_{25} a''$
740 vw	742 vw	744 m	740 w,P	742 w	$\nu_{16} a'$
706		707 vs			
695 Q	w,C	705 vs	697 vw,D	703 vw	$\nu_{26} a''$
682		702 vs			
650		676 vs			
645 Q	vs,A/B	671 vs	$\sim 650$ w,sh	672 vw	$\nu_{17} a'$
638		665 vs			
		658 vs			

TABLE 1 (continued)

IR			Raman		Interpretation
Vapour	Liquid	Crystal (90 K)	Liquid (250 K)	Crystal (90 K)	
631	} vs,C	649 vs	630 m,br,D	645 vw	$\nu_{27} a''$
621 Q		646 vs		634 vw	
610		634 s		634 vw	
	604 ms	604 vs	602 m,P	603 w	$\nu_{18} a'$
		600 m			
494	} w,C	500 m	484 m,D	488 vw	$\nu_{28} a''$
481 Q		484 m		492 s	
465		489 s		489 s	
457 Q	} w,A/B	463 m	458 m,P	459 w	$\nu_{19} a'$
~ 450		460 m			
		307 vw	302 m,br	305 vw	
259	} w,C	267 s,sh		266 vw	$\nu_{29} a''$
248 Q		254 s	254 m,D	252 vw	
236		230 m			
		165 w	165 vs,D?	168 m	
				106 m	
				94 m	

<sup>a</sup>Weak bands in the regions (4000–3400  $\text{cm}^{-1}$ ), (2900–2200  $\text{cm}^{-1}$ ) and (2000–1700  $\text{cm}^{-1}$ ) have been omitted. <sup>b</sup>Abbreviations: s, strong; m, medium; w, weak, v, very; sh, shoulder; br, broad; P and D, polarized and depolarized in the Raman effect. A, B, C and Q denote IR vapour phase band contours and Q-branch, respectively.

and it is possible to distinguish between the *s-cis* (*syn*-periplanar) and *s-trans* conformations using the IR vapour phase band contours. The theoretical band contours [27] for the *s-cis* and *s-trans* conformations are depicted in Fig. 4. The separation between the band maxima for the *s-trans* form are approximately 15, 11 and 23  $\text{cm}^{-1}$  for the A, B, and C-type bands, respectively, while the corresponding values for the *s-cis* form are 13, 12 and 18  $\text{cm}^{-1}$ . Though the calculated A and B-type bands appear almost indistinguishable for the two conformers, the C-type bands are sufficiently different to allow an unambiguous determination of the molecular conformation as *s-trans* (c.f. Table 1). However, a small amount, up to ca. 5%, of another conformer cannot be excluded by our spectral data.

### Spectral interpretations

Assuming  $C_s$  symmetry the normal modes of vibration divide into:  $\Gamma_v = 21a' + 9a''$ . The  $a'$  modes should be polarized in the Raman effect and show A/B hybrid IR vapour phase contours while the  $a''$  modes should display typical C-type vapour phase contours in the infrared.

We have been able to assign with confidence all of the fundamental modes of vibration except the =C–C= torsional mode, which may be

TABLE 2

Observed and calculated fundamental vibrational frequencies ( $\text{cm}^{-1}$ )

	No.	Observed	Calculated	Characterization
$a'$	$\nu_1$	3329	3344	$\text{=C-H}$ stretch
	$\nu_2$	3114	3112	$\text{CH}_2$ asym. stretch
	$\nu_3$	3106	3110	$\text{CH}_2$ asym. stretch
	$\nu_4$	3065	3044	$\text{CH}$ stretch
	$\nu_5$	3032	3033	$\text{CH}_2$ sym. stretch
	$\nu_6$	3028	3030	$\text{CH}_2$ sym. stretch
	$\nu_7$	2104 <sup>a</sup>	2136	$\text{C}\equiv\text{C}$ stretch
	$\nu_8$	1624 <sup>a</sup>	1670	$\text{C}=\text{C}$ sym. stretch
	$\nu_9$	1576	1603	$\text{C}=\text{C}$ asym. stretch
	$\nu_{10}$	1419 <sup>a</sup>	1453	$\text{CH}_2$ sym. bend
	$\nu_{11}$	1390	1406	$\text{CH}_2$ asym. bend
	$\nu_{12}$	1371	1337	$\text{C}-\text{C}$ asym. stretch
	$\nu_{13}$	1292	1294	$\text{C}-\text{H}$ bend
	$\nu_{14}$	1044	1052	$\text{CH}_2$ asym. rock
	$\nu_{15}$	930 <sup>a</sup>	933	$\text{CH}_2$ sym. rock
	$\nu_{16}$	740	743	$\text{C}-\text{C}$ sym. stretch
	$\nu_{17}$	645	635	$\text{C}\equiv\text{C}-\text{H}$ bend
	$\nu_{18}$	602 <sup>a</sup>	608	$\text{C}=\text{C}-\text{C}(=\text{C})$ bend
	$\nu_{19}$	460	432	sym. $\text{C}=\text{C}-\text{C}(=\text{C})$ bend
	$\nu_{20}$	302 <sup>a</sup>	265	asym. $\text{C}=\text{C}-\text{C}(=\text{C})$ bend
	$\nu_{21}$	165 <sup>a</sup>	139	$\text{C}-\text{C}\equiv\text{C}$ bend
$a''$	$\nu_{22}$	982	993	$\text{CH}$ bop/ $\text{CH}_2$ twist
	$\nu_{23}$	923	916	$\text{CH}_2$ wag
	$\nu_{24}$	900	913	$\text{CH}_2$ wag
	$\nu_{25}$	752	762	$\text{CH}_2$ twist
	$\nu_{26}$	695	669	$\text{CH}$ bop/ $\text{CH}_2$ twist
	$\nu_{27}$	621	620	$\text{C}=\text{C}-\text{H}$ bend
	$\nu_{28}$	481	449	$\text{C}-\text{C}(=\text{C})$ bop
	$\nu_{29}$	248	238	$\text{C}-\text{C}\equiv\text{C}$ bend
	$\nu_{30}$		143	$(=\text{C})\text{C}-\text{C}(=\text{C})$ torsion

<sup>a</sup>Frequencies from liquid phase.

overlapping the lowest skeletal bending mode,  $\nu_{21}$  ( $a'$ ), at  $165 \text{ cm}^{-1}$ . In general, the vibrational spectra of EBUT show so many similarities with the published spectra of other 2-substituted 1,3-butadienes such as 2-chloro- [28], 2-azido- [29] and 2-methyl-1,3-butadiene [30] and obviously also with 3-butene-yne [12] that the proposed assignment hardly needs comment. Bands not assigned as fundamentals can all be explained easily as combination bands or overtones.

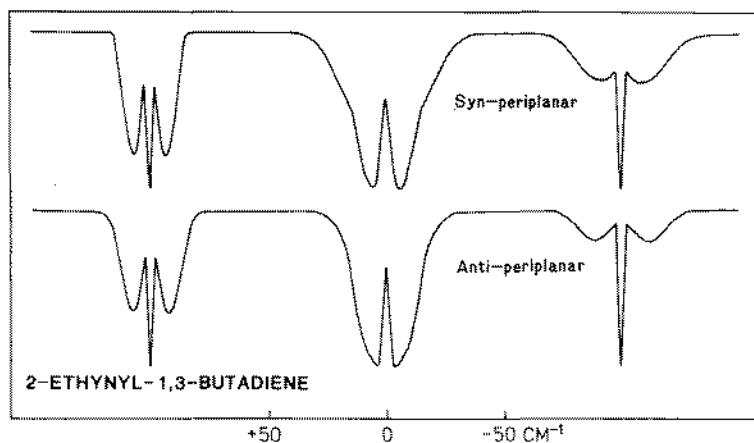


Fig. 4. Theoretical IR vapour phase contours for the two most probable conformations of 2-ethynyl-1,3-butadiene.

#### *Force constant calculation*

An approximate force field for EBUT was constructed by adopting the scaled quantum mechanical force field for 1,3-butadiene [31] and extending this with force constants from 3-butene-yne [12]. Only minor adjustments of the force constants are necessary in order to give a perfect agreement with the observations but, as seen from Table 2, little or no new information would be gained by this.

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