The Vibrational Spectra and Molecular Structure of *trans*- and *cis*-1,2-Diethynylcyclobutane

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The infrared spectra of *trans*- and *cis*-1,2-dieth-ynylcyclobutane were recorded for the vapour, liquid and crystalline states. Raman spectra of the liquid and crystalline compounds were obtained.

The trans compound was shown to exist in only one conformer in all phases. The evidence strongly favours this conformer being that with both acetylenic groups equatorial. The fundamental frequencies were assigned for both compounds, supported by normal coordinate calculations.

The two title compounds offer an interesting pair. If a non-planar ring is present in the *trans* isomer, two different conformers may result, while a planar ring implies only one conformer. On the other hand, the *cis* compound exists only in one conformer whether the ring is planar or not (Fig. 1).

For many years we have been studying the spectra of compounds which may exist in more than one conformation. In a loose sense this work is an extension of our earlier work on bipropargyl, 1,2 which can be seen clearly if one mentally substracts the two carbon atoms which are not attached to acetylenic groups along with their associated hydrogen atoms. Two conformers were expected for the trans isomer in accordance with gas phase electron diffraction results on trans-1,3-bromochlorocyclobutane ³ and vibrational spectroscopic results on 1,1,2trichloro-2,3,3-trifluorocyclobutane,4 for which two conformers were found. However, only one conformer was found for cis-1.3-dibromocyclobutane and for cis-1,3-bromochlorocyclobutane by electron diffraction.3

EXPERIMENTAL

The samples used for the spectral measurements were prepared by photodimerization of

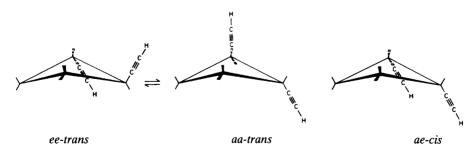


Fig. 1. The ee and aa conformers of trans-1,2-diethynylcyclobutane and the ae conformer of cis-1,2-diethynylcyclobutane.

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Table 1. Symmetry species and possible conformers for cis- and trans-diethynylcyclobutane.

	cis			trans		
	Symmetry	Symmetry species	Possible conformers	Symmetry	Symmetry species	Possible conformers
Planar ring Non-planar ring	C_s C_1	21A'+21A" 42A	1 1 (ae)	$C_2 \\ C_2$	22A+20B 22A+20B	1 2 (aa, ee)

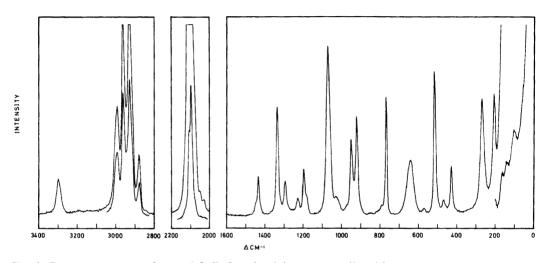


Fig. 2. Raman spectrum of trans-1,2-diethynylcyclobutane as a liqquid.

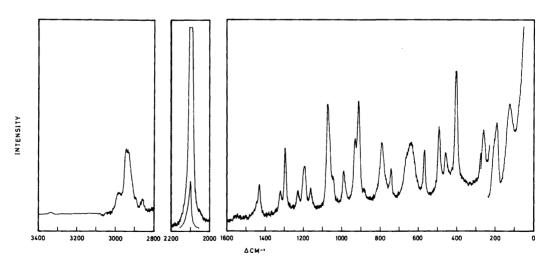


Fig. 3. Raman spectrum of cis-1,2-diethynylcyclobutane as a liquid.

vinylacetylene.⁵ The pure isomers were obtained by preparative gas chromatographic separation.

The infrared spectra were recorded with a Perkin-Elmer model 225 spectrometer (4000–200 cm⁻¹) and a Bruker IFS-114C evacuable fast scan Fourier spectrometer (700–50 cm⁻¹). Spectra were taken of both compounds as vapours (4000–400 cm⁻¹) and as unannealed and annealed solids (4000–250 cm⁻¹). The *trans* isomer was studied as a pure liquid and as a solute in CCl₄ solution (4000–400 cm⁻¹), and in cyclohexane solution (400–50 cm⁻¹). The *cis* isomer was studied in CCl₄ solution (4000–400 cm⁻¹) and in benzene solution (400–50 cm⁻¹).

The Raman spectra were recorded with a Cary model 81 Raman spectrometer equipped with a Spectra Physics 125A helium-neon laser and a CRL model 52G argon ion laser. The spectrum of the liquid phase of the *trans* isomer, including semi-quantitative polarization measurements, was obtained with the argon ion laser. Because of problems with decomposition in the argon ion laser beam, the spectrum of the liquid phase of the *cis* isomer, including semiquantitative polarization measurements, was obtained with the helium-neon laser. Unannealed and annealed solids of both compounds were studied at 90K with the argon ion laser.

RESULTS AND DISCUSSION

The spectral alternatives for planar and nonplanar rings for both compounds are shown in Table 1. For the *cis* compound, only one conformer can exist. This has, in principle, both polarized and depolarized bands in Raman if the ring is planar, but only polarized bands if the ring is non-planar. For the *trans* compound, all reasonable structures have the same symmetry (Fig. 1).

The experimental results obtained are shown in Table 2 (trans) and Table 3 (cis). Liquid phase Raman spectra for the two compounds are shown in Figs. 2 and 3, far infrared spectra for both compounds in the liquid phase in Figs. 4 and 5, and mid infrared spectra for the trans isomer in both unannealed and the crystalline solid phases in Fig. 6.

Conformation of the ring. Our assumption is that both rings are non-planar. Any of three different events could have occurred which would have provided information on planarity. First, observation of a series of puckering transitions either in the far infrared or in the Raman spectra or a series of combination bands involving puckering frequencies can give aid for deciding on planarity. Second, reliable polarization measurements on the cis compound would have helped to distinguish between planar C_s (21 polarized fundamentals and 21 depolarized fundamentals) and non-planar C_1 (all 42 fundamentals polarized). Finally, evidence for two conformers in the trans compound would clearly have demonstrated the existence of a non-planar ring.

A careful inspection of our spectra reveals no series of bands which we can interpret as a puckering series. The two compounds were not

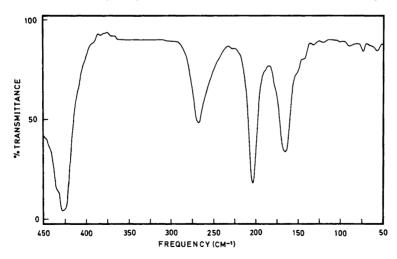


Fig. 4. Far infrared spectrum of trans-1,2-diethynylcyclobutane dissolved in cyclohexane, path 1 mm. Acta Chem. Scand. A 37 (1983) No. 6

Table 2. Infrared and Raman spectral data for trans-1,2-diethynylcyclobutane (cm⁻¹).

Infrared ^a		Raman		Interpretation	
Vapour	Liquid	Solid, 90 K	Liquid	Solid 90 K	
3335 vs)					
3330 vs }	3300 vs ^b	3284 vs	3296 m, P	3284 w	v_1, v_{23}
3324 vs J		3272 vs		3276 w	
3310 m,sh		3257 w			
3304 m,sh		5 2 57		2204	
3010 s,sh	2004	2000	2002 L.D.	3304	
2002 C	2994 s	2999 s	2993 m,sh,D	2000	v_{24}
3002 vs C J 2994 s				2998 m	
2994 8	2986 s,sh	2987 s	2983 s,P	2985 m	v_2
2987 s	2700 3,311	2707 3	2705 3,1	2703 III	v ₂
2970 s		2955 s		2955 m,sh)	
2966 s,A	2954 s	}	2953 vs,P	}	v_3
2959 s	2,0.0	2951 s,sh	_,,,,	2953 m	• 5
2945 m	2934 m,sh	2940 w,sh		2940 m	
2919 w,sh	2910 w,sh	2923 w	2920 vs,P	2924 s	v_{25}
2893 w		2894 w		2898 w	v_{26}
2889 m		2867 w		2868 w)
}	2874 m	}	2872 m P	}	v_4
2884 m		2858 w		2861 w	
				2145 w	
		2131 vw			
2128 m,bd	2119 m	2120	2116 vs,sh,P?	2120 vs	v_5, v_{27}
		2120 w	2107 D	2100	ED.
			2106 vs,P	2109 vs 2090 m	FR
1469 w	1460 w	1453 w	1458 w,sh,P	1455 w	M
1459 w,sh)	1400 W	1434 m)	1436 W,SII,F	1433 w 1440 w)	v_6
1452 m A	1446 m	1434 III	1445 s D	1440 W	v_{28}
1446 w	1110 III	1431 w,sh	111000	1437 w	* 28
1,		1378 m		- · · · · · · · · · · · · · · · · · · ·	
1352 m		1359 w		1355 w	
}	1345 m	}	1344 vs P	}	v_7
1344 m		1350 w		1349 s	
1311 m		1307 w			
1307 m A }	1302 m	}	1301 m D	1306 m	v_{29}
1301 m		1301 m			
1275 w,sh	1270 m,bd	1281 m,bd			v_8
1261 s		10/7			
1255 s 1251 s		1267 w			
1231 5		1240 w		1244 w)	
1231 w,sh	1234 w	1240 W	1233 w,D	1211 "	<i>v</i> ₃₀
1201 17,011	1201 11	1233 m	1200 11,12	1235 w	- 50
		1217 m		1215 vw	
1203 w	1200 w	}	1203 s P	}	<i>V</i> 9
		1203 w		1203 m	•
1185 w,sh	1182 w,bd	1192 w	1188 m P	1190 w	v_{10}
1110 w		1093 w	1095 vw,D	1097 w	v_{32}
				1087 s	
			1075 vs P	1000	v_{11}
				1080 m	

1070 w 1063 w 1066 m 1066 m 1062 w 1023 w 1023 w 1021 w 1020 w 1024 w D 1022 w 982 vw 981 vw 986 vw 978 w,sh D 982 vv 995 v 995 w			1071 w)		1070 w	
1033 w	1070 w	1063 w	1062 w }	1064 s,sh	1062	v_{33}
1023 w 1021 w 1020 w 1024 w D 1022 w 982 vw 981 vw 986 vw 978 w,sh D 960 s v34 955 w 961 w 955 s D 960 s v34 955 w 961 w 955 s D 960 s v34 915 w 915 w 922 s 912 w 926 vw 920 m 911 m 917 m 917 vw? 916 w,sh 858 w P 859 vw 814 vw P 815 vw 675 w,sh 668 m 672 w,sh 668 m 672 w,sh 668 m 675 w,sh 666 s 663 vs 636 vs 632 vs 632 vs 517 m,sh 519 s 519 vs P 523 m v18 718 72	1033 w			1036 w P	1062 W	
982 vw 981 vw 986 vw 978 w,sh D 982 vw 955 w 961 w 955 s D 960 s v34 956 vw 955 w 961 w 955 s D 960 s v34 956 vw 955 w 961 w 953 w 948 w,sh P? 950 w,sh v12 912 w 912 w 922 s 912 w 926 vw 920 m 911 m 917 m 917 vw? 916 w,sh v14 858 vw P 859 vw 823 vw 821 vw 821 vw 814 vw P 8814 vw P 8815 vw? 7750 w 664 vs 680 vw 666 s 666 s 663 vs 646 vs 666 s 666 s 666 s 663 vs 643 w P? 635 m V16, V17, V36, V37 532 w,sh 517 m,sh 519 s 519 vs P 523 m V18 511 m 507 s 508 s 509 w,sh D 513 w V39 517 m,sh 519 s 519 vs P 523 m V18 511 m 507 s 508 s 509 w,sh D 513 w V39 514 w,sh 680 vw 465 w 468 vw 465 w 465 w 468 vw 465 w 468 vw 465 w 468 vw 465 w 465 w 468 vw 465 w 465 w 468 vw 468 w 46		1021 w			1022 w	
963 vw 955 w 961 w 953 w 948 w,sh P? 950 w,sh V12 912 w 926 vw 920 m 911 m 917 m 917 w 916 w,sh V14 823 vw 821 vw 821 vw 821 vw 774 w 774 w 7750 w 694 vs 668 m 672 w,sh 668 m 675 w,sh 668 m 666 s 632 vs 634 vs 632 vs 644 ws 634 vs 644 w,sh 644 w,sh 650 w 6						
956 vw 915 w 922 s 912 w 926 vw 922 s 912 w 926 vw 920 m 911 m 917 m 917 rw? 916 w,sh						Va
912 w 926 vw 926 vw 920 m 921 m 927 m 926 vs P 926 vs V ₁₃ 911 m 917 m 917 vw? 916 w,sh 858 vw P 859 vw 814 vw P 823 vw 821 vw 814 vw P 801 w 797 w, C 796 w 798 s 795 w D 800 w V ₃₅ 7797 w, C 771 vw 774 w 772 vs P 774 m V ₁₅ 736 vw? 750 w 694 vs 692 w Interactions in the crystal 675 w,sh 668 m 672 w,sh 668 m 672 w,sh 668 m 666 s 663 vs 646 vs 630 vs 646 vs 630 vs 646 vs 633 s 643 m P? 635 m V ₁₆ , V ₁₇ , V ₃₆ , V ₃₇ 582 w,sh 569 w,Q 572 w 569 s 573 w D 572 vw V ₃₈ 522 vw,sh 517 m,sh 519 s 519 vs P 523 m V ₁₈ 511 m 507 s 508 s 509 w,sh D 513 w V ₃₉ 504 m,sh 481 w,sh 472 m,C 464 w,sh 472 m,C 464 w,sh 482 w 465 w 465 w 430 w 429 m 433 s 430 m P 436 w V ₁₉ 269 w 274 w 271 vs P? 278 s V ₂₀ 269 w 274 w 271 vs P? 278 s V ₂₀ 269 w 274 w 271 vs P? 278 s V ₂₀ 269 w 274 w 271 vs P? 278 s V ₂₀ 269 w 274 w 271 vs P? 278 s V ₂₀ 279 w V ₄₁ 165 m 169 w D 164 w V ₄₂ 143 w P 120 m V ₄₁ 165 m 169 w D 164 w V ₂₁ 147 vw 143 w P 120 m V ₂₁ 147 vw 143 w P 120 m V ₂₁ 147 vw 143 w P 120 m V ₂₁ 147 vw 143 w P 120 m V ₂₁ 147 vw 143 w P 120 m V ₂₁ 147 vw 143 w P 120 m V ₂₁ 147 vw 143 w P 120 m V ₂₁ 147 vw 143 w P 120 m V ₂₁ 148 w S0 w 184 w P 120 m V ₂₁ 147 vw 143 w P 120 m V ₂₁ 148 w 184 w P 120 m V ₂₁ 149 w 184 w P 120 m V ₂₁ 140 w 184 w P 120 m V ₂₁ 141 w 184 w P 120 m V ₂₁ 141 w 184 w P 120 m V ₂₁ 142 w 184 w P 120 m V ₂₁ 143 w P 120 m V ₂₁ 144 w 184 w P 120 m V ₂₁ 145 w P? 95 w P? 95 w P?		755 W				
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906 w 911 m 917 m 917 w? 858 w P 859 vw 823 vw 821 vw 814 vw P 814 vw P 859 vw 814 vw P 815 vw P 859 vw 814 vw P 815 vw P 859 vw 816 vw P 815 vw P 815 vw P 859 vw 816 vw P 815 vw P 81		026 vv	722 3	025 vs P	926 vs	V
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823 vw 821 vw 821 vw 814 vw P 814 vw P 815 vw P 816 vw P 817 vw P 817 vw P 818 vw P 800 w 814 vw P 815 vw P 816 vw P 817 vw P 818 vw P 810 vw P 816 vw P 817 vw P 817 vw P 818 vv P 818 vv P 818 vv P 818 vv P 810 vw P	900 W J	011 m	,	017 vw2	016 w ch	17
823 vw 821 vw 821 vw 814 vw P 801 w 797 w, C 792 w, sh 771 vw 774 w 7750 w 694 vs 680 vw 694 vs 680 vs 666 s 663 vs 636 vs 636 vs 632 vs 822 w, sh 569 w, Q 572 w 569 s 573 w D 504 m, sh 481 w, sh 472 m, C 464 w, sh 269 w 274 w 472 s 472 s 472 s 472 s 474 s 475 s 476 s 477 s 478 s 479 w 479 w 479 w 479 w 479 w 479 w 470 m		911 III	917 III			V ₁₄
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736 vw? 750 w 694 vs 680 vw 675 w,sh 668 m 666 s 666 s 663 vs 636 vs 636 vs 636 vs 636 vs 638 vs 636 vs 638 vs 636 vs 637 vs 638 vs 638 vs 638 vs 638 vs 639 vs 630 vs 630 vs 630 vs 631 vs 632 vs 632 vs 632 vs 633 s 643 m P? 635 m 716, 717, 736, 737 736 vs 738 w D 740, 717, 736, 737 738 w D 740, 717, 736, 737 740 w 741 w 741 w 741 w 742 m,C 744 w 745 w 746 s 747 w D 748 w 748 w,sh 748 w,sh 749 w 740 w	792 w,sh			772 D	77.4	
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675 w,sh 668 m 672 w,sh 668 m 672 w,sh 668 m 673 w,sh 668 m 666 s 663 vs 646 vs 633 s 6443 m P? 635 m v ₁₆ , v ₁₇ , v ₃₆ , v ₃₇ 632 vs 582 w,sh 569 w,Q 572 w 569 s 573 w D 572 vw v ₃₈ 522 vw,sh 517 m,sh 519 s 519 vs P 523 m v ₁₈ 511 m 507 s 508 s 509 w,sh D 513 w v ₃₉ 504 m,sh 481 w,sh 472 m,C 464 w,sh 472 m,C 464 w,sh 472 m,C 468 vw 465 w 465 m 472 w D 479 w v ₄₀ 473 w 473 w 475 w 47	736 vw?					_
675 w,sh 668 m 666 s 666 s 663 vs 646 vs 633 s 644 vs 633 s 643 m P? 635 m v ₁₆ , v ₁₇ , v ₃₆ , v ₃₇ 638 vs 636 vs 646 vs 633 s 643 m P? 635 m v ₁₆ , v ₁₇ , v ₃₆ , v ₃₇ 582 w,sh 569 w,Q 572 w 569 s 573 w D 572 vw v ₃₈ 522 vw,sh 517 m,sh 519 s 519 vs P 523 m v ₁₈ 511 m 504 m,sh 481 w,sh 472 m,C 4464 w,sh 482 w 465 w 430 w 468 vw 465 w 422 w 429 m 433 s 430 m P 436 w v ₁₉ 269 w 274 w 271 vs P? 278 s v ₂₀ 251 w,sh 203 m 207 s D 215 m v ₄₁ 165 m 169 w D 164 w 179 w 121 m v ₂₁ 165 m 169 w D 164 w 179 w 121 m v ₂₁ 143 w P 120 m v ₂₁ 147 vw 143 w P 120 m v ₂₁ 165 w P? 95 w v ₂₂ 80 w 59 w lattice modes					692 m	
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638 vs 636 vs 646 vs 633 s 643 m P? 635 m		675 w,sh	668 m	672 w,sh	668 m }	crystal
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$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$						10/ 1// 50/ 5/
569 w,Q 572 w 569 s 573 w D 572 vw v ₃₈ 522 vw,sh 517 m,sh 519 s 519 vs P 523 m v ₁₈ 511 m 507 s 508 s 509 w,sh D 513 w v ₃₉ 504 m,sh 481 w,sh 472 s 476 s 472 w D 479 w v ₄₀ 481 w,sh 472 m,C 468 vw 465 w 465 w 464 w,sh 468 vw 465 w 430 m P 436 w v ₁₉ 422 w 269 w 274 w 271 vs P? 278 s v ₂₀ 203 m 207 s D 215 m v ₄₁ 179 w 165 m 169 w D 164 w 179 w 147 vw 143 w P 120 m v ₂₁ 105 w P? 95 w v ₂₂ 80 w 59 w lattice modes						
522 vw,sh 517 m,sh 519 s 519 vs P 523 m v ₁₈ 511 m 507 s 508 s 509 w,sh D 513 w v ₃₉ 504 m,sh 481 w,sh 472 m,C 472 s 476 s 472 w D 479 w v ₄₀ 464 w,sh 468 vw 465 w 430 w 429 m 433 s 430 m P 436 w v ₁₉ 422 w 269 w 274 w 271 vs P? 278 s v ₂₀ 203 m 207 s D 215 m v ₄₁ 165 m 169 w D 164 w 179 w 147 vw 143 w P 120 m v ₂₁ 105 w P? 95 w v ₂₂ 80 w 59 w lattice modes	,	572 w	569 s	573 w D	572 vw	V20
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504 m,sh 481 w,sh 472 m,C 464 w,sh 468 vw 465 w 430 w 429 m 433 s 430 m P 436 w v ₁₉ 422 w 269 w 274 w 271 vs P? 278 s v ₂₀ 251 w,sh 203 m 207 s D 215 m v ₄₁ 179 w 165 m 169 w D 164 w 147 vw 143 w P 120 m v ₂₁ 105 w P? 95 w v ₂₂ 80 w 59 w lattice modes	311 m	507 s	508 s	509 w sh D	513 w	Vao
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	504 m sh	207 5	200 5	200,511 2	010	7.39
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$						
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		472 s	476 s	472 w D	470 w	Via
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		7/2 3	470 3	4/2 W D	417 W	V4()
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	707 W,SII)		168	165 w		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	420 m)		400 VW	403 W		
422 w 269 w 274 w 271 vs P? 278 s v_{20} 251 w,sh 203 m 207 s D 215 m v_{41} 165 m 169 w D v_{42} 147 vw 143 w P 120 m v_{21} 105 w P? 95 w v_{22} 80 w 3 1attice modes	430 W	420 m	422 c	420 m D	126	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	422	429 111	433 8	430 III F	430 W	v_{19}
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	422 W	260	274	271 D2	270 .	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		209 W	214 W		210 8	v_{20}
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		202			215	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		203 m		207 S D		v_{41}
164 w		165		160 - D	1/9 W	
147 vw 143 w P 120 m v ₂₁ 105 w P? 95 w v ₂₂ 80 w 59 w lattice modes		165 m		169 W D	164	v_{42}
105 w P? 95 w v ₂₂ 80 w				4.40	,	
80 w 59 w lattice modes		147 vw				
59 w lattice modes				105 w P?		v_{22}
53 w						lattice modes
					53 w	

^a Infrared data not obtained below 300 cm⁻¹ in the vapour state and 220 cm⁻¹ in the solid state. ^b s=strong, m=medium, w=weak, v=very, sh=shoulder, bd=broad, P=polarized, D=depolarized, A, B and C are vapour contours, FR=Fermi resonance.

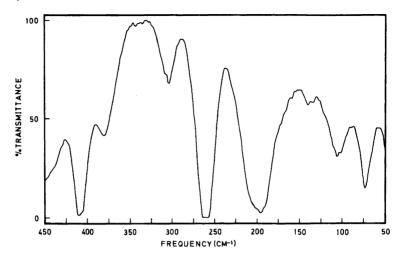


Fig. 5. Far infrared spectrum of cis-1,2-diethynylcyclobutane dissolved in benzene, path 1 mm.

Table 3. Infrared and Raman spectral data for cis-1,2-diethynylcyclobutane (cm⁻¹).a

Infrared			Raman		Interpretation	
Vapour	Solution	Solid, 90 K	Liquid	Solid, 90 K		
~3360 m,sh						
3338 vs						
3332 vs,Q }	3304 vs	3280 vs		3284 m	v_1, v_2	
3325 vs						
3325 vs						
3312 m,Q				3274 w,sh		
3306 m,sh J						
3010 s						
3004 vs,Q }	2996 s	2998 s	2997 m	2995 m	v_3	
2297 s	~2985 m.sh	2984m,sh	~2980 m,sh	2984 m	v_4	
2983 s,sh}	2705 111,311	270411,311	2700 111,311	2704 111	٧4	
2968 s						
2962 vs,Q }	2954 s	2955 s	2956 vs	2953 s	v_5	
2953 s J	****			* 0 #4		
2951 vs,Q	2940 m,sh	\sim 2910 m,sh	2943 s	2941 s	v_6	
2942 s	2020 1	2020	2020 1	2012		
2931 m,Q }	\sim 2920 m,sh	\sim 2920 m,sh	\sim 2920 m,sh	2913 s	v_7	
2924 m						
2888 m	2901 m,sh	\sim 2900 w,sh	2905 m	\sim 2900 w,sh		
2885 m,Q	2870 m	2870 m	2870 m	2870 m	ν_8	
2879 m J 2125 m	2116 m	2112 m	2116 vs,P	2110 vs		
2123 III		~1460 w	2110 VS,F	2110 VS	v_9, v_{10}	
1461 m ()	~1460 w,sh 1453 m	~1460 w 1454 w	\sim 1455 w,sh	~1455 w,sh	17	
1461 m,Q 1453 m	1433 111	1434 W	1433 W,SII	-1433 W,511	v_{11}	
1433 m 1447 m.O }	1442 m	1441 m	1443 m	1445 w	V	
1447 m,Q }	1442 111	1441 111	1443 III	1 44 3 W	v_{12}	
1440 III)						

				1,2-Dietnynyicyc	hobutane	313
	1437 w,sh	1437 w,sh				
1340 m	1737 W,311	1 4 57 W,511				
1340 m 1334 m,Q }	1330 m	1331 m	1331 w	1332 w		
1334 m,Q	1550 III	1331 111	1551 W	1332 W	v_{13}	
1326 111	1220 var. ob					
١	1320 vw,sh					
1315 w	1304 m	1306 m	1205 - D	1205		
1307 w	1304 111	1300 111	1305 m,P	1305 m	v_{14}	
~1280 vs	~1275 w,sh	1202 m hd				
~1200 VS	~12/3 w,sii	1292 m,bd			v_{15}	
1256 s	~1245 s,bd					
1248 s	1245 S,00					
1243 s,sh	1238 s	1240 m	1237 w	1242 w	37 .	
1243 s,sii 1214 w	1207 m	1240 m 1205 w	1206 m	1208 m	<i>v</i> ₁₆	
~1185 vw	1207 III	1203 W	1200 111	1200 III	v_{17}	
1170 m	1155 m	~1170 w	1170 w	1174 w	V	
1170 m 1118 m	1106 m	1098 m	11/0 W	11/7 W	<i>v</i> ₁₈	
~1090 vw	~1090 vw	1070 111			v_{19}	
1000 VW	~1085 vw	~1080 w	1082 s,P	1084 s	V- a	
	1070 w	~1070 w	~ 1070 m,sh	1071 m	V ₂₀	
	1051 w	1070 W 1052 W	1054 m	1071 m 1052 m	<i>V</i> ₂₁	
983 w	~ 995 w	988 w	996 m	994 w,bd	V ₂₂	
939 w,Q	938 m	942 m	938 m.P	945 m	v ₂₃ v ₂₄	
,,,Q	$\sim 920 \mathrm{vw,sh}$	~ 920 vw	921 vs	923 s	v ₂₄ v ₂₅	
892 w.Q	888 m	892 m	889 w	892 w	v ₂₅ v ₂₆	
841 w	~ 835 w	0, 2 m	00) "	0,2 11	*26	
797 w	~ 790 vw	~ 790 w	794 s,P	791 m,bd	<i>v</i> ₂₇	
746 w,Q	747 m	752 m	749 m	752 w	v_{28}	
718 w,sh	, , ,	, o 2 iii	, ,, ,,,	, o ~	* 28	
710 s	702 m	710 s			v_{29}	
, 20 0		692 s	(693 w,sh	. 29	
~ 675 w	673 s	670 s	672 m,sh	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		
		661 s	,	666 m,bd		
630 vs	632 vs	638 vs	640 m,bd		V30. V31.	v_{32}, v_{33}
		624 s	,	633 w	507 51	327 33
578 m		,		,		
572 m,Q	573 m	578 m	572 m,P	577 w	v_{34}	
567 m					51	
,	520 vw					
500 m						
492 s,Q	495 s	501 m	496 m,P	503 w	V ₃₅	
485 m						
	461 m	465 m	462 w	467 w	v_{36}	
		432 vw				
408 w,Q	410 m	410 m	407 s	409 m	v_{37}	
	$\sim 305 \text{ vw}$					
	262 m		261 m	269 m	v_{38}	
	204 m		204 m,sh	216 m,sh	V ₃₉	
	190 m		191 s	200 s	V ₄₀	
			125 s	150 s,bd	v_{41}	
	$\sim 105 \text{ vw}$		$\sim 110 \text{ m,sh}$	113 m	v_{42}	
				78 m		

^a For meaning of abbreviations, see Table 2.

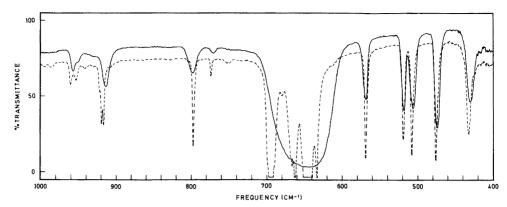


Fig. 6. Infrared spectra of trans-1,2-diethynylcyclobutane as an unannealed (solid curve) and annealed solid (dashed curve) at 90 K.

volatile enough and certainly not stable enough at elevated temperatures to attain the pressures necessary for such observations to be made. We did attempt polarization measurements with the cis compound, but its instability forced us to run the liquid phase spectra with the less intense helium-neon laser. The necessity of using axial illumination gives polarization measurements of lesser quality. And, even with this laser, there was some evidence of polymerization during the course of the determination. Thus, we have only labelled a few of the bands which were obviously polarized because of the uncertainty in this determination. Finally, as mentioned earlier, variations in the spectra on phase changes are of the sort to be associated with hydrogen bonding differences, not with changes in ring conformation or conformational abundance.

Conformation of substituents. If the ring is non-planar one acetylenic group must always be axial and the other equatorial in the cis isomer. However, in the trans isomer the two substituents are either both axial or both equatorial (Fig. 1).

To repeat a point just made in connection with the conformation of the ring, we note that there is no simplification of the spectra, no disappearance of either infrared or Raman bands upon crystallization of the *trans* isomer. To illustrate this point, the regions of the infrared spectra of amorphous and crystalline *trans*-1,2-diethynyl-cyclobutane which are shown in Fig. 6 display as usual a great change near 630 cm⁻¹ associated ^{1,2} with the \equiv C-H bending frequencies when the sample crystallizes. Otherwise the spectra are

very similar. Our interpretation is that only one conformer is present in the liquid. It is very probably the conformer with the two acetylenic groups in equatorial positions as expected ³ and this prediction is supported by our normal coordinate calculations.

As seen from Table 4 the observed infrared and Raman bands believed to be fundamentals agree much better with those calculated for the ee than for the aa conformer. Particularly, the b fundamentals v_{35} , v_{36} and v_{38} , but also the a fundamentals v_{12} , v_{14} and v_{21} agree well with the calculated ee modes, but they can hardly be fitted to the aa frequencies. All together 14 bands assigned as fundamentals in the trans isomer agree best with the calculated ee frequencies, 4 agree best with the aa values, while the remaining bands can be equally well correlated with both sets. We feel that these data firmly support our conclusion that trans-diethynyl cyclobutane exists in the ee conformation in the vapour, liquid and crystalline states. A possible second conformer (aa) is probably present in less than 5 % abundance.

Spectra and vibrational assignment. The C_2 axis of the trans isomer coincides with the B-axis of inertia. The vapour phase infrared bands of species a are expected to have type B band contours and bands of species b are expected to have type A/C hybrid band contours. While in general the band contours were not of much help in the assignment, those bands with really prominent central maxima (3002, 1452, 1307, 797 and 472 cm⁻¹) were all assigned to species b fun-

Table 4. Observed and calculated fundamentals for trans- and cis-1,2-diethynylcyclobutane.

	trans			cis		
	Calc. (aa)	Obs. ^a	Calc. (ee)	Calc.	Obs.	
a						
v_1	3301	3300	3301	3301	3304	
v_2	2973	2983 ^b	2973	3301	3304	
v_3	2949	2954	2926	2993	2996	
V ₄	2897	2874	2893	2974	2985	
V ₅	2122	2116 ^b	2122	2957	2954	
V ₆	1444	1460	1460	2939	2941 ^b	
<i>'</i> 7	1312	1345	1314	2917	2913 b	
v ₈	1291	1275 ^d	1274	2896	2870	
'8 '9	1225	1200	1226	2125	2116	
v ₁₀	1078	1188 b	1151	2123	2116	
/10 /11	1067	1075 b	1061	1456	1453	
V ₁₂	1001	948 ^b	965	1443	1442	
/12 /13	910	926	925	1325	1330	
v 13 V 14	812	911	1283	1304	1330	
/14 /15	759	771	762	1280	1275	
	637	640	637	1248	1238	
¹ 16	637	640	626	1233	1207	
′17	522	522	525	1145	1155	
['] 18	436	429	430	1117	1106	
/19 /	274	269	369	1084	1082 b	
² 20	181	143 <i>b</i>	149	1076	1070	
² 21	82	105 b	93	1042	1051	
/22	62	103	73	1042	1031	
•						
2 3	3301	3300	3301	977	996 ^b	
² 24	2994	2994	2992	954	938	
² 25	2965	2920 ^b	2952	917	921 ^b	
' 26	2919	2893	2917	842	888	
' 27	2126	2116 ^b	2125	796	794	
2 8	1445	1446	1449	738	747	
² 29	1320	1302	1292	699	702	
'30	1236	1234	1271	638	632	
' 31	1188	1161	1155	637	632	
' 32	1038	1110^{-d}	1109	636	632	
'33	1011	1063	1018	635	632	
'34	946	955	933	568	573	
³ 35	868	796	809	504	495	
⁷ 36	713	640	639	472	461	
V37	638	640	637	416	410	
V ₃₈	636	572	580	273	262	
/38 /39	511	507	521	222	204	
V ₄₀	445	472	502	202	190	
V ₄₁	223	203	225	115	125	
V ₄₂	145	165	182	89	113 °	

^a Wave numbers given are IR solution values except when noted. ^b Raman liquid values. ^c Raman solid values. ^d IR vapour values.

damentals. The bands at 1348 and 426 cm⁻¹ which clearly do not contain central maxima were assigned to fundamentals of species a.

As in the case of 1,5-hexadiyne, 1,2 for both compounds studied, the ≡C-H stretching region of the liquid phase spectrum is a little unusual since all three compounds deviate from the characteristic pattern for a terminal alkyne. Usually the liquid phase spectrum has a strong peak near 3315 cm⁻¹ with a weak shoulder near 3300 cm⁻¹, the shoulder probably arising from the CH stretching of an acetylenic hydrogen which is hydrogen-bonded to the triple bond of another molecule.⁶ In the pure liquid both of these compounds show only a strong singlet at or near 3300 cm⁻¹, implying complete or nearly complete association in the liquid phase. In a dilute solution in an inert solvent, the equilibrium is expected to shift toward the monomer; in spectra of such a solution we do observe the expected behaviour.

For both compounds the assignments, with the aid of the normal coordinate assignments were quite straightforward. For the *trans* isomer, the criteria of polarized and depolarized bands and of infrared vapour contours needed to be satisfied as well as the numerical predictions.

The assignments proposed for the two diethynylcyclobutanes are listed in Tables 2 and 3 and only a few uncertainties will be mentioned. Two very strong Raman bands were observed at 2116 and 2106 cm⁻¹ of the *trans* isomer. The former band, also observed in the IR, was attributed to coinciding $C \equiv C$ stretching modes v_5 and v_{27} , found at 2116 cm⁻¹ in the *cis* isomer. Thus, the 2106 cm⁻¹ band which is the more intense, was interpreted as a combination band of species A, enhanced by Fermi resonance.

In spectra of both compounds strong infrared vapour bands around 1250 cm^{-1} were interpreted as overtone and combination bands of the C=C-H bending modes, as commonly observed for acetylenes. Also, very intense infrared bands observed between 640 and 700 cm⁻¹ of the crystalline compounds are characteristic of the C=C-H bending modes interacting in the crystal. The mode v_{14} of the trans isomer was assigned to the infrared and Raman bands around 915 cm⁻¹, although the Raman band at 858 cm⁻¹ which had no infrared counterpart agreed slightly better with the calculated frequency of 879 cm⁻¹.

Because of the chemical instability of cis-1,2-diethynylcyclobutane, its infrared and Raman spectra were not as completely studied as those

for the *trans* isomer. Since there is no symmetry in this molecule, the infrared vapour contours or the Raman polarization measurements are not informative. We believe that our assignments are essentially correct, since they are in good agreement with the results of the normal coordinate analysis.

FORCE CONSTANT CALCULATIONS

Force fields for the two title compounds were constructed by transferring force constants without modification from ethynylcyclohexane ⁷ and from cyclobutane. We derived the latter force field (a 25 parameter VFF) by a least squares procedure from the spectroscopic data given by Miller et al.⁸

As seen from Table 4 the agreement between the observed and calculated fundamental frequencies is quite satisfactory. The few obvious discrepancies are those for the bending modes at the substituted sites of the cyclobutane ring. Only small changes in the force constants are necessary in order to obtain a perfect agreement between the observed and calculated fundamental modes of vibration. For the sake of brevity the force constants are not presented here, but they are available from the authors (Oslo) upon request.

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