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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-diethynylcyclobutane 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).

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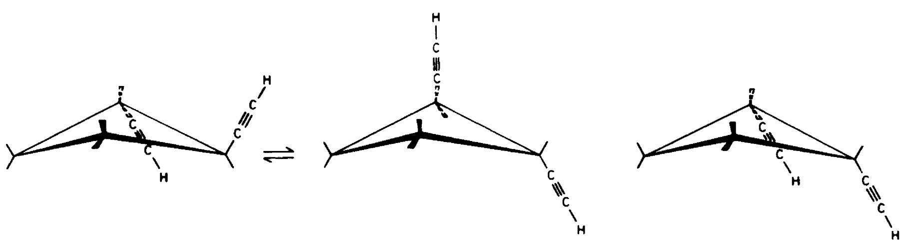
For many years we have been studying the spectra of compounds which may exist in more than one conformation. In a loose sense this work is an extension of our earlier work on bipropargyl,[1,2] which can be seen clearly if one mentally substracts the two carbon atoms which are not attached to acetylenic 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 1,1,2-trichloro-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



ee-trans *aa-trans* *ae-cis*

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	C_s	21A′+21A″	1	C_2	22A+20B	1
Non-planar ring	C_1	42A	1 (ae)	C_2	22A+20B	2 (aa, ee)

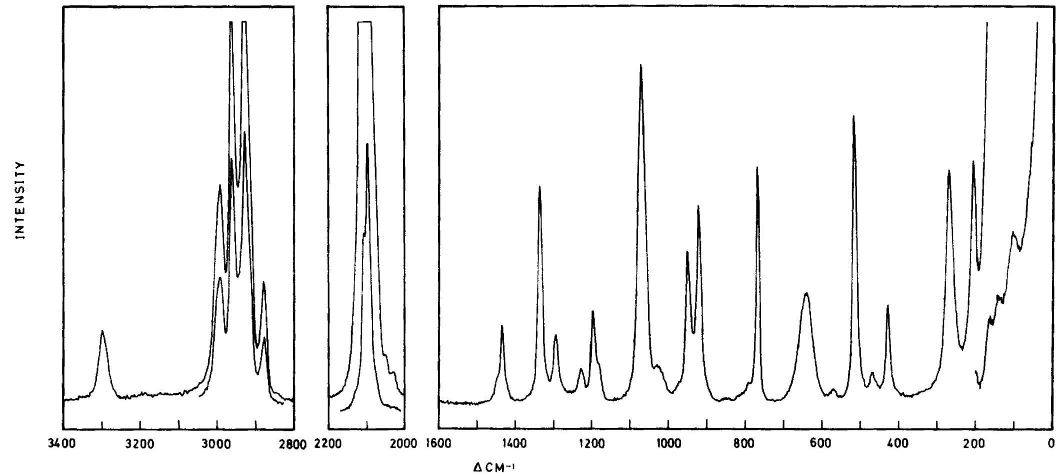

Fig. 2. Raman spectrum of *trans*-1,2-diethynylcyclobutane as a liqquid.

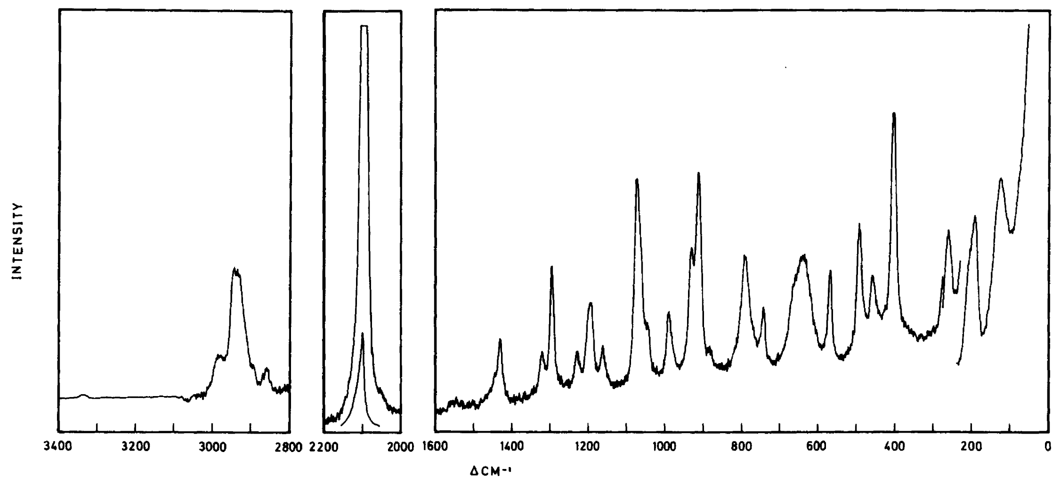

Fig. 3. Raman spectrum of *cis*-1,2-diethynylcyclobutane as a liquid.

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 CCl_4 solution (4000–400 cm^{-1}), and in cyclohexane solution (400–50 cm^{-1}). The *cis* isomer was studied in CCl_4 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 non-planar 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

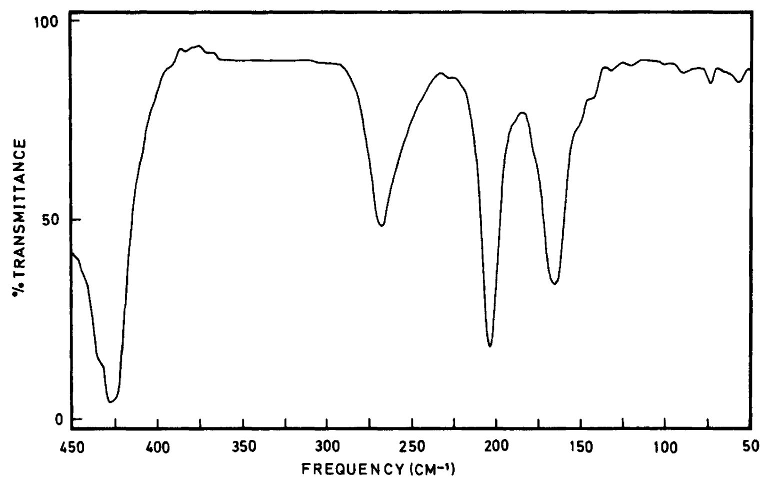

Fig. 4. Far infrared spectrum of *trans*-1,2-diethynylcyclobutane dissolved in cyclohexane, path 1 mm.

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	ν_1, ν_{23}
3324 vs		3272 vs		3276 w	
3310 m,sh					
		3257 w			
3304 m,sh					
3010 s,sh				3304	
	2994 s	2999 s	2993 m,sh,D		ν_{24}
3002 vs C				2998 m	
2994 s					
	2986 s,sh	2987 s	2983 s,P	2985 m	ν_2
2987 s					
2970 s		2955 s		2955 m,sh	
2966 s,A	2954 s		2953 vs,P		ν_3
2959 s		2951 s,sh		2953 m	
2945 m	2934 m,sh	2940 w,sh		2940 m	
2919 w,sh	2910 w,sh	2923 w	2920 vs,P	2924 s	ν_{25}
2893 w		2894 w		2898 w	ν_{26}
2889 m		2867 w		2868 w	
	2874 m		2872 m P		ν_4
2884 m		2858 w		2861 w	
				2145 w	
		2131 vw			
2128 m,bd	2119 m		2116 vs,sh,P?	2120 vs	ν_5, ν_{27}
		2120 w			
			2106 vs,P	2109 vs	FR
				2090 m	
1469 w	1460 w	1453 w	1458 w,sh,P	1455 w	ν_6
1459 w,sh		1434 m		1440 w	
1452 m A	1446 m		1445 s D		ν_{28}
1446 w		1431 w,sh		1437 w	
		1378 m			
1352 m		1359 w		1355 w	
	1345 m		1344 vs P		ν_7
1344 m		1350 w		1349 s	
1311 m		1307 w			
1307 m A	1302 m		1301 m D	1306 m	ν_{29}
1301 m		1301 m			
1275 w,sh	1270 m,bd	1281 m,bd			ν_8
1261 s					
1255 s		1267 w			
1251 s					
		1240 w		1244 w	
1231 w,sh	1234 w		1233 w,D		ν_{30}
		1233 m		1235 w	
		1217 m		1215 vw	
1203 w	1200 w		1203 s P		ν_9
		1203 w		1203 m	
1185 w,sh	1182 w,bd	1192 w	1188 m P	1190 w	ν_{10}
1110 w		1093 w	1095 vw,D	1097 w	ν_{32}
				1087 s	
			1075 vs P		ν_{11}
				1080 m	

		1071 w		1070 w	
1070 w	1063 w	1062 w	1064 s,sh		ν_{33}
		1060 m		1062 w	
1033 w		1023 w	1036 w P		
1023 w	1021 w	1020 w	1024 w D	1022 w	
982 vw	981 vw	986 vw	978 w,sh D	982 vw	
963 vw	955 w	961 w	955 s D	960 s	ν_{34}
956 vw		953 w	948 w,sh P?	950 w,sh	ν_{12}
915 w		922 s			
912 w	926 vw		925 vs P	926 vs	ν_{13}
906 w		920 m			
	911 m	917 m	917 vw?	916 w,sh	ν_{14}
			858 vw P	859 vw	
823 vw	821 vw		814 vw P		
801 w					
797 w, C	796 w	798 s	795 w D	800 w	ν_{35}
792 w,sh					
	771 vw	774 w	772 vs P	774 m	ν_{15}
736 vw?		750 w			
		694 vs		692 m	Interactions
		680 vw			in the
	675 w,sh	668 m	672 w,sh	668 m	crystal
		666 s			
		663 vs			
638 vs		646 vs			
636 vs	640 vs	633 s	643 m P?	635 m	ν_{16}, ν_{17}, ν_{36}, ν_{37}
632 vs					
582 w,sh					
569 w,Q	572 w	569 s	573 w D	572 vw	ν_{38}
522 vw,sh	517 m,sh	519 s	519 vs P	523 m	ν_{18}
511 m					
	507 s	508 s	509 w,sh D	513 w	ν_{39}
504 m,sh					
481 w,sh					
472 m,C	472 s	476 s	472 w D	479 w	ν_{40}
464 w,sh					
		468 vw	465 w		
430 w					
	429 m	433 s	430 m P	436 w	ν_{19}
422 w					
	269 w	274 w	271 vs P?	278 s	ν_{20}
			251 w,sh		
	203 m		207 s D	215 m	ν_{41}
				179 w	
	165 m		169 w D		ν_{42}
				164 w	
	147 vw		143 w P	120 m	ν_{21}
			105 w P?	95 w	ν_{22}
				80 w	
				59 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.

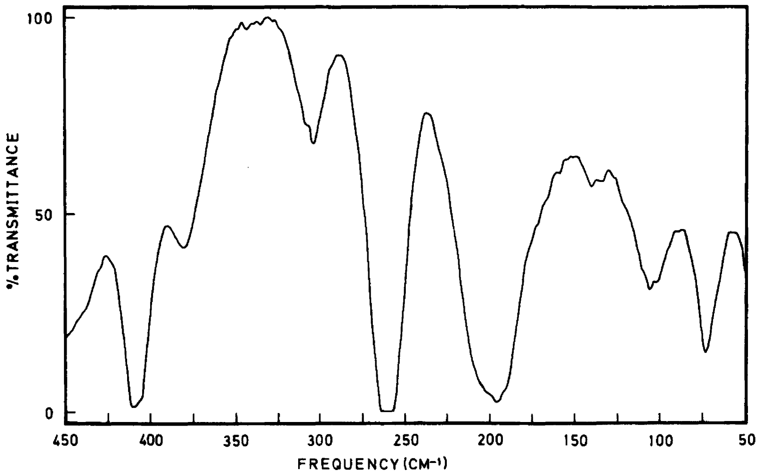

Fig. 5. Far infrared spectrum of *cis*-1,2-diethynylcyclobutane dissolved in benzene, path 1 mm.

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	ν_1, ν_2
3325 vs					
3325 vs					
3312 m,Q				3274 w,sh	
3306 m,sh					
3010 s					
3004 vs,Q	2996 s	2998 s	2997 m	2995 m	ν_3
2297 s					
2983 s,sh	~2985 m,sh	2984m,sh	~2980 m,sh	2984 m	ν_4
2968 s					
2962 vs,Q	2954 s	2955 s	2956 vs	2953 s	ν_5
2953 s					
2951 vs,Q	2940 m,sh	~2910 m,sh	2943 s	2941 s	ν_6
2942 s					
2931 m,Q	~2920 m,sh	~2920 m,sh	~2920 m,sh	2913 s	ν_7
2924 m					
2888 m					
2885 m,Q	2901 m,sh	~2900 w,sh	2905 m	~2900 w,sh	
2879 m	2870 m	2870 m	2870 m	2870 m	ν_8
2125 m	2116 m	2112 m	2116 vs,P	2110 vs	ν_9, ν_{10}
	~1460 w,sh	~1460 w			
1461 m,Q	1453 m	1454 w	~1455 w,sh	~1455 w,sh	ν_{11}
1453 m					
1447 m,Q	1442 m	1441 m	1443 m	1445 w	ν_{12}
1446 m					

	1437 w,sh	1437 w,sh			
1340 m					
1334 m,Q	1330 m	1331 m	1331 w	1332 w	ν_{13}
1328 m					
	1320 vw,sh				
1315 w	1304 m	1306 m	1305 m,P	1305 m	ν_{14}
1307 w					
~1280 vs	~1275 w,sh	1292 m,bd			ν_{15}
1256 s	~1245 s,bd				
1248 s					
1243 s,sh	1238 s	1240 m	1237 w	1242 w	ν_{16}
1214 w	1207 m	1205 w	1206 m	1208 m	ν_{17}
~1185 vw					
1170 m	1155 m	~1170 w	1170 w	1174 w	ν_{18}
1118 m	1106 m	1098 m			ν_{19}
~1090 vw	~1090 vw				
	~1085 vw	~1080 w	1082 s,P	1084 s	ν_{20}
	1070 w	~1070 w	~1070 m,sh	1071 m	ν_{21}
	1051 w	1052 w	1054 m	1052 m	ν_{22}
983 w	~ 995 w	988 w	996 m	994 w,bd	ν_{23}
939 w,Q	938 m	942 m	938 m,P	945 m	ν_{24}
	~ 920 vw,sh	~ 920 vw	921 vs	923 s	ν_{25}
892 w,Q	888 m	892 m	889 w	892 w	ν_{26}
841 w	~ 835 w				
797 w	~ 790 vw	~ 790 w	794 s,P	791 m,bd	ν_{27}
746 w,Q	747 m	752 m	749 m	752 w	ν_{28}
718 w,sh					
710 s	702 m	710 s			ν_{29}
		692 s		693 w,sh	
~ 675 w	673 s	670 s	672 m,sh		
		661 s		666 m,bd	
630 vs	632 vs	638 vs	640 m,bd		ν_{30}, ν_{31}, ν_{32}, ν_{33}
		624 s		633 w	
578 m					
572 m,Q	573 m	578 m	572 m,P	577 w	ν_{34}
567 m					
	520 vw				
500 m					
492 s,Q	495 s	501 m	496 m,P	503 w	ν_{35}
485 m					
	461 m	465 m	462 w	467 w	ν_{36}
		432 vw			
408 w,Q	410 m	410 m	407 s	409 m	ν_{37}
	~ 305 vw				
	262 m		261 m	269 m	ν_{38}
	204 m		204 m,sh	216 m,sh	ν_{39}
	190 m		191 s	200 s	ν_{40}
			125 s	150 s,bd	ν_{41}
	~ 105 vw		~ 110 m,sh	113 m	ν_{42}
				78 m	

[a] For meaning of abbreviations, see Table 2.

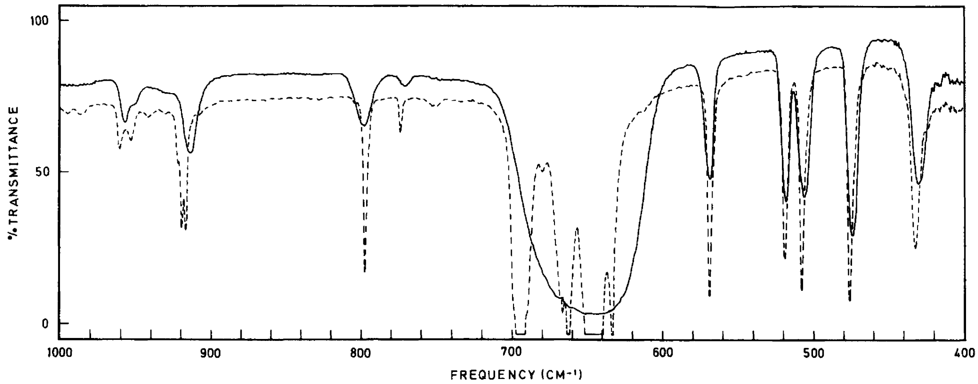

Fig. 6. Infrared spectra of *trans*-1,2-diethynylcyclobutane as an unannealed (solid curve) and annealed solid (dashed curve) at 90 K.

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-diethynylcyclobutane which are shown in Fig. 6 display as usual a great change near 630 cm^{-1} associated [1,2] with the ≡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 ν_{35}, ν_{36} and ν_{38}, but also the *a* fundamentals ν_{12}, ν_{14} and ν_{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					
ν_1	3301	3300	3301	3301	3304
ν_2	2973	2983 [b]	2973	3301	3304
ν_3	2949	2954	2926	2993	2996
ν_4	2897	2874	2893	2974	2985
ν_5	2122	2116 [b]	2122	2957	2954
ν_6	1444	1460	1460	2939	2941 [b]
ν_7	1312	1345	1314	2917	2913 [b]
ν_8	1291	1275 [d]	1274	2896	2870
ν_9	1225	1200	1226	2125	2116
ν_{10}	1078	1188 [b]	1151	2123	2116
ν_{11}	1067	1075 [b]	1061	1456	1453
ν_{12}	1001	948 [b]	965	1443	1442
ν_{13}	910	926	925	1325	1330
ν_{14}	812	911	1283	1304	
ν_{15}	759	771	762	1280	1275
ν_{16}	637	640	637	1248	1238
ν_{17}	637	640	626	1233	1207
ν_{18}	522	522	525	1145	1155
ν_{19}	436	429	430	1117	1106
ν_{20}	274	269	369	1084	1082 [b]
ν_{21}	181	143 [b]	149	1076	1070
ν_{22}	82	105 [b]	93	1042	1051
b					
ν_{23}	3301	3300	3301	977	996 [b]
ν_{24}	2994	2994	2992	954	938
ν_{25}	2965	2920 [b]	2952	917	921 [b]
ν_{26}	2919	2893	2917	842	888
ν_{27}	2126	2116 [b]	2125	796	794
ν_{28}	1445	1446	1449	738	747
ν_{29}	1320	1302	1292	699	702
ν_{30}	1236	1234	1271	638	632
ν_{31}	1188	1161	1155	637	632
ν_{32}	1038	1110 [d]	1109	636	632
ν_{33}	1011	1063	1018	635	632
ν_{34}	946	955	933	568	573
ν_{35}	868	796	809	504	495
ν_{36}	713	640	639	472	461
ν_{37}	638	640	637	416	410
ν_{38}	636	572	580	273	262
ν_{39}	511	507	521	222	204
ν_{40}	445	472	502	202	190
ν_{41}	223	203	225	115	125
ν_{42}	145	165	182	89	113 [c]

[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≡C stretching modes ν_5 and ν_{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.[1,2] The mode ν_{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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