

The Conformation and Vibrational Spectra of 1-Cyano-3-Butyne

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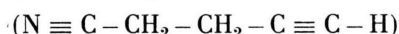
The infrared spectra of 1-cyano-3-butyne were recorded in the region $4000\text{--}50\text{ cm}^{-1}$ in the vapour and liquid states, as an amorphous and as two different crystalline solids at 90 K. In addition the compound was studied as a high pressure crystalline solid at ambient temperature. Raman spectra of the liquid, including polarization measurements, and of the amorphous and the two crystalline solids at 90 K, were obtained.

The spectra revealed the existence of two conformers, *anti* (C_s) and *gauche* (C_1 symmetry) in the vapour, liquid and in the amorphous solid. When annealed to *ca.* 140 K a metastable crystal containing one conformer (probably the *gauche*) was formed, when annealed to *ca.* 190 K a stable crystal was obtained having the other conformer (probably the *anti*). The latter conformer was present in the high pressure crystal.

Very accurate spectral data for each conformer were collected from the two crystalline solids, making complete assignments for the *anti* and *gauche* conformers feasible. The assignments were checked by a normal coordinate analysis. A simple diagonal force field was derived in which the same force constants were employed for the *anti* and *gauche* conformers. The mean amplitudes of vibration were calculated for both conformers.

Introduction

The present compound 1-cyano-3-butyne



(later to be called CB) is a hybrid between 1,2-dicyanoethane (succinonitrile) and 1,5-hexadiyne (bi-propargyl) and is isoelectronic with both of them. As a disubstituted ethane, CB is expected to exist as a mixture of two conformers in the vapour, liquid and in solution, but to crystallize as one single conformer.

Succinonitrile has been studied in considerable detail by vibrational spectroscopy [1, 2] and recently by electron diffraction [3]. The *gauche* conformer was the more stable one in the liquid and in a plastic solid, while the anisotropic crystal contained only the *gauche* conformer [1, 2]. In the vapour phase at 443 K *ca.* 74% of the molecules were present in the *anti* conformation [3].

In bipropargyl, the vapour phase consists of *ca.* 75% of *anti* at 293 K [4], furthermore the *anti*

conformer dominates in the liquid state, in solution and is the preferred conformer in the crystal [5]. The two derivatives, bromobipropargyl (1-bromo-1,5-hexadiyne) [6] and dibromobipropargyl (1,6-dibromo-1,5-hexadiyne) [7, 8], also crystallize in the *anti* conformer, but more of the *gauche* conformer is present in the vapour and in the liquid for these compounds.

Other related molecules which have been studied include 1-halo-2-cyanoethane [9–11]; for Cl, Br and I substituents, *gauche* has the lowest enthalpy in the liquid and this conformer is also present in the crystalline state. In 1,1,2,2-tetracyanoethane and 1,2-dichlorotetracyanoethane only small amounts of the *gauche* conformers were detected in solution, whereas the crystals of both compounds consisted of molecules in the *anti* conformations [12]. 1,2-Dicyanotetrafluoroethane [13] crystallized as *anti* conformer but considerable amounts of *gauche* were present in the vapour and in the liquid state.

When CB was studied in the solid state at low temperatures, we observed to our surprise that two different crystalline solids could be formed, one containing molecules in the pure *gauche*, the other molecules in the *anti* conformer. Such results are

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quite rare, but they permit the spectra of each conformer to be recorded simultaneously, making the spectral assignments much more reliable than what is usually the case for molecules with different conformations. In spite of this, considerable doubt remained concerning which spectrum should be attributed to which conformer in CB. A force constant calculation did not remove this problem which should be settled by electron diffraction of the vapour or preferably by X-ray crystallography on the stable crystal.

Experimental

Preparation of 1-cyano-3-butyne

To a freshly prepared solution of lithiumamide (from 1.9 g (0.28 mol) lithium wire in 250 ml ammonia) was added within 5 minutes at -30°C under vigorous stirring 10.3 g (0.25 mol) distilled acetonitrile. After 10 minutes 27.5 g (0.4 mol) propargylchloride is rapidly added, and after 1 h the reaction is terminated by addition of 15 g ammoniumchloride, followed by 250 ml of ether. The ammonia is evaporated, the remaining solution is poured on ice, and thoroughly extracted with ether. The combined organic layers are washed with 1 N HCl and dried over Na_2SO_4 . The solvent is removed by rotary evaporation, and the 1-cyano-3-butyne purified by distillation (b.p. $62-64^{\circ}\text{C}$, 15 torr; 1.1 g, 5.6%) and gas-chromatography (SE-30, 130°C).

Instrumental

The i.r. spectra were recorded with a grating spectrometer (Perkin-Elmer model 225) and a fast scan Fourier transform interferometer (Bruker model 114 c). The latter instrument was evacuable and equipped with beam splitters of germanium on KBr ($4000-500\text{ cm}^{-1}$) and of Mylar with thickness 3.5, 6.0, 12.0 and $23\text{ }\mu\text{m}$ for the far i.r. region ($600-30\text{ cm}^{-1}$). Detectors of TGS were used, and globar and mercury lamps employed above and below 150 cm^{-1} , respectively.

The vapour was recorded at a pressure of ca. 1 torr in a 1 m folded cell, but only the most intense bands were detected at room temperature. Solution spectra in CCl_4 were obtained using sealed cells with KBr, CsI and polyethylene windows, whereas the pure liquid was studied as a film be-

tween KBr plates. The low temperature spectra were recorded in conventional cryostats, cooled with liquid nitrogen and equipped with windows of CsI and polyethylene; the temperature was measured with calibrated iron-constantane thermocouples. The vapour was sprayed upon the inner window at ca. 90 K, subsequently annealed at higher temperatures and rapidly cooled to 90 K. High pressure spectra were recorded with a diamond anvil cell a 4 X beam condensor. The spectra were first run on the grating spectrometer. Due to the multiplex advantage highly improved spectra, including the far i.r. region [14] were recorded on the interferometer.

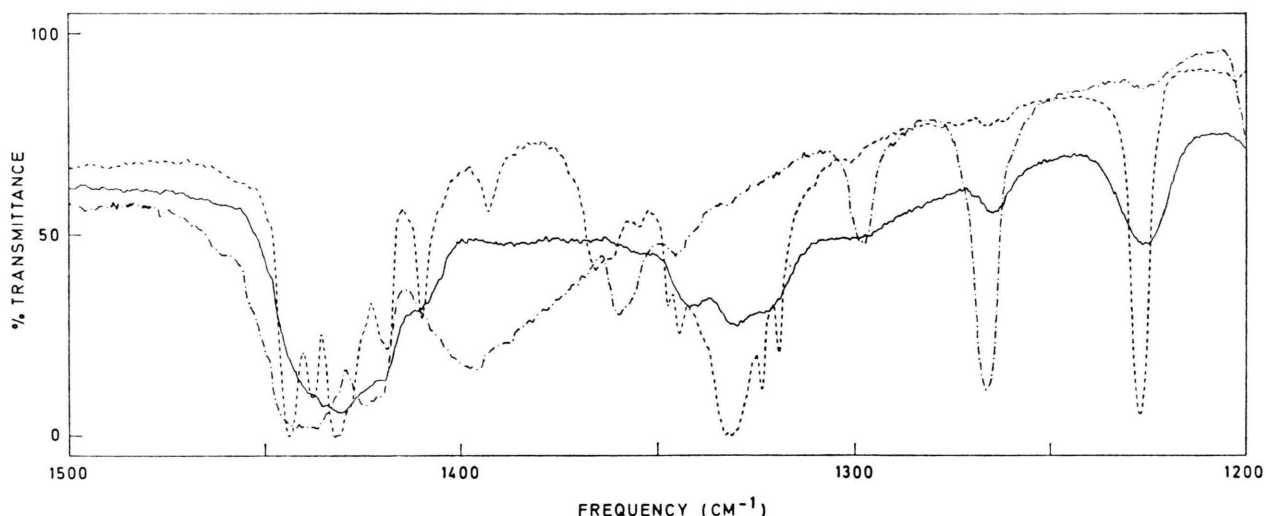
Raman spectra were recorded with a Cary 81 spectrometer, modified for perpendicular excitation [15] and illuminated with the 5145 and 4880 Å argon ion lines (CRL model 52 G). The pure liquid was recorded at room temperature and polarization data obtained. Spectra of the amorphous and annealed solids on a cooled copper plate were recorded with the same technique as used in infrared.

Results

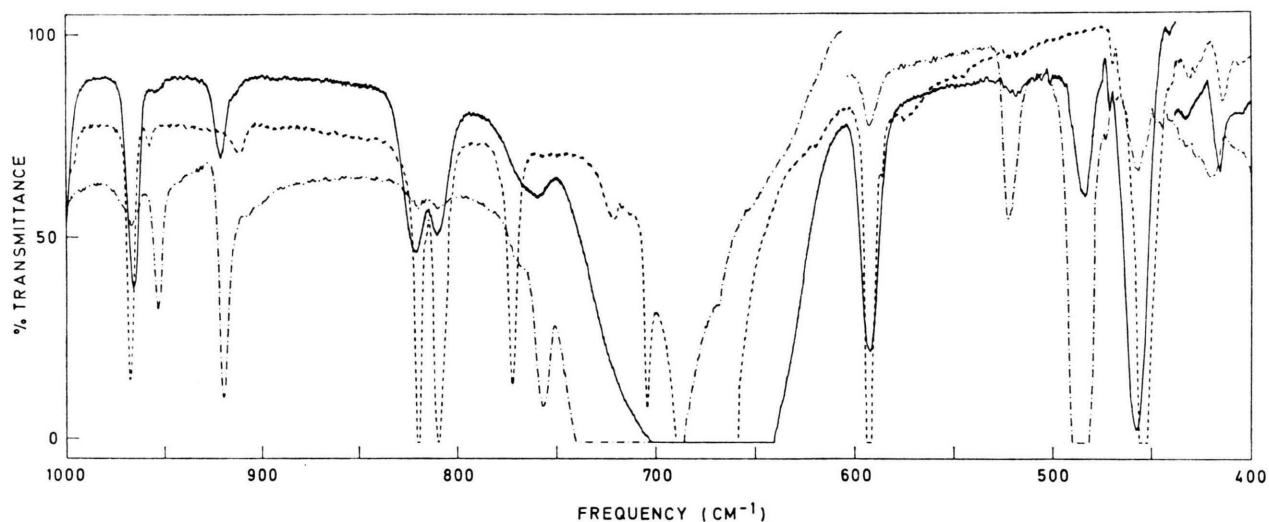
Infrared spectra recorded at ca. 90 K of the amorphous solid (solid line), the solid annealed to ca. 140 K and recooled to 90 K (dashed-dotted line) and the solid annealed to ca. 190 K and recooled to 90 K (dashed line) covering all the main bands in the region $1500-50\text{ cm}^{-1}$ are reproduced as four drawings in Figure 1. A Raman spectrum of the pure liquid is shown in Fig. 2, while spectra of the two crystalline solids (annealed to 140 and 190 K) recorded at 90 K are given in Figure 3. The wave numbers of the observed i.r. and Raman bands are listed in Table 1. Our assigned fundamental frequencies for the assumed *anti* and *gauche* conformers are listed in Table 2 together with the calculated values.

Low temperature spectra

As apparent from Fig. 1 and Table 1 the i.r. spectra of the solid deposit formed at 90 K by shock freezing the vapour, contained essentially all the bands appearing in the liquid and in the solution spectra. In spite of the low temperature these bands were quite broad (solid line of Figure 1). Undoubtedly, this solid phase consists of an amorphous glass in which both the molecular conformers, *anti* and *gauche*, are present.



(1a)

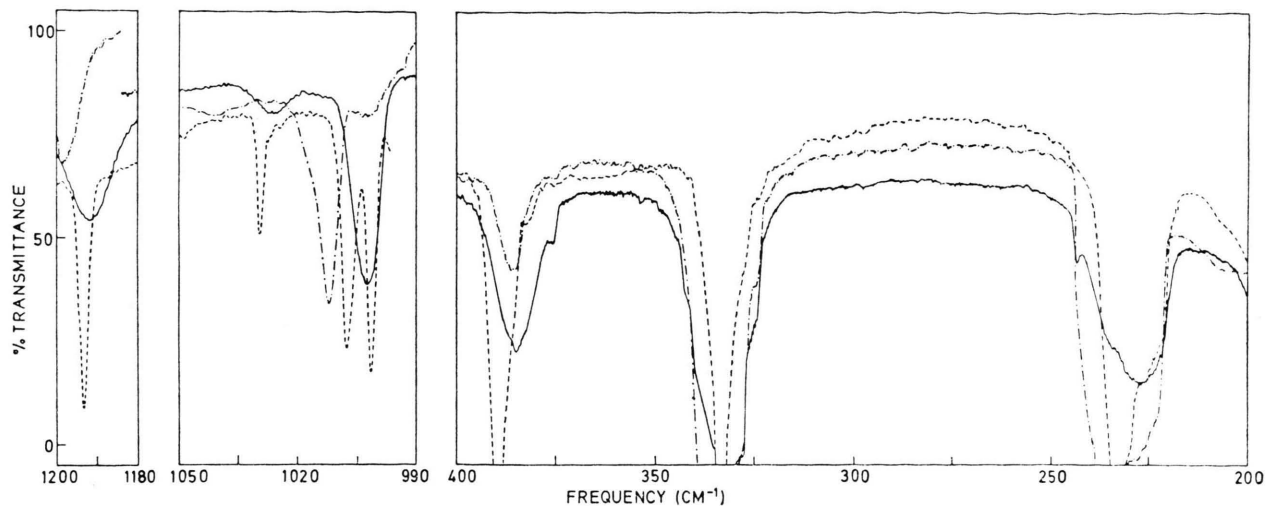


(1b)

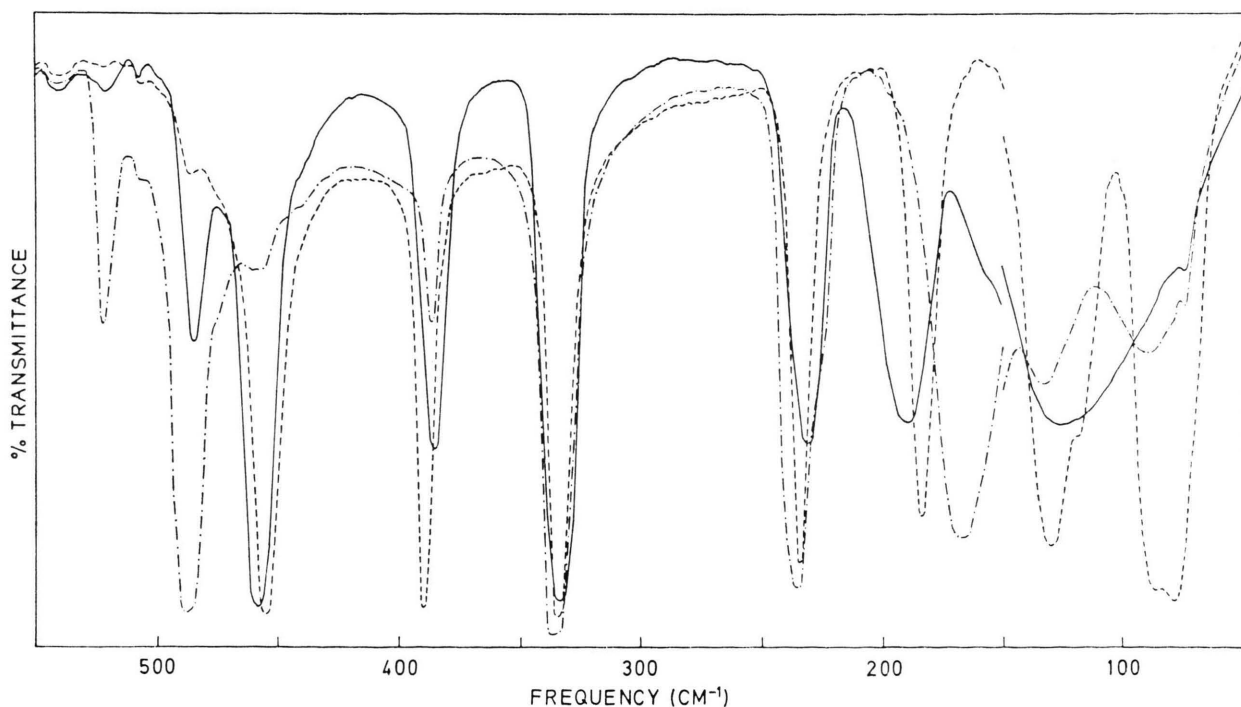
Fig. 1. The infrared spectra of 1-cyano-3-butyne (CB) recorded at 90 K; unannealed sample (amorphous) solid line, sample annealed at ca. 140 K (crystal A) dashed-dotted line, sample annealed at ca. 190 K (crystal B) dashed line. The top, upper middle and lower middle curves were recorded with a grating spectrometer (PE 225), the bottom curve with a Fourier transform spectrometer (Bruker 114 C); 50–150 cm^{-1} 12 μ beamsplitter, 250 scans, 2 cm^{-1} resolution; 150–500 cm^{-1} 3.5 μ beamsplitter, 250 scans, 2 cm^{-1} resolution.

When the temperature was slowly raised, various spectral changes started to occur at ca. 120 K. The bands became sharper and some bands increased while others decreased in intensities. At higher temperatures the conversion occurred at a faster rate, the dotted-dashed curves (Fig. 1) were recorded after 15 minutes annealing at ca. 140 K and sub-

sequent rapid cooling to 90 K (crystal A). A number of bands present in the amorphous phase had vanished in this spectrum, the remaining bands were enhanced with smaller band widths. If crystal A was maintained at ca. 140 K during the recording, the spectrum appeared quite similar although the bands had slightly larger widths.



(1c)



(1d)

The Raman spectrum of crystal A (formed by annealing at 140 K) is shown by the solid line of Figure 3. As apparent from the figures and from Table 1 the i.r. and Raman bands of crystal A generally coincided, and many Raman bands present in the liquid (Fig. 2) had vanished. Undoubtedly,

a crystalline solid of CB was formed in which only one of the two conformers was present.

When the sample of crystal A was heated above ca. 145 K further spectral changes started to occur in i. r. and Raman. The amorphous bands which had vanished in crystal A, started slowly to reappear,

Table 1. Vibrational spectral data ^a (cm⁻¹) for 1-cyano-3-butyne.

Liquid	Amorphous ^b		Crystal B ^c		Crystal A ^d		High pressure		Interpretation	
	Raman	IR	Raman	IR	Raman	IR	IR	IR	Anti f	Gauche f
3298 vs g	3292 m, P 3273 w, D?	3280 vs	3283 vw	3287 w } 3280 vs } 3262 m } 3256 m }	3282 s	3235 vs	3238 w	3300 vs	$\nu_1 a'$	ν_1
3075 vw										
2980 w	2978 m, D	2976 w	2977 w	2976 s	2978 w	2976 m	2976 w	3006 m	$\nu_{18} a''$	ν_{18}
2948 s	2959 s, P?	2958 vvw	2956 m	2960 s	2964 m	* h	*	2980 s	$\nu_{18} a''$	ν_{18}
2936 s	2936 vs, P } 2921 w, ? }	2940 m	2936 s	2942 s } 2935 w }	2939 vs	2941 w	2946 s } 2924 s }	2919 s	$\nu_2 a'$	ν_2
2870 w			2860 vw		2860 w, br		2860 w	2860 w, br	$\nu_3 a'$	ν_3
2850 w	2857 m, P	2848 vw	2860 w	2850 m	2860 w	2846 w	2860 w			
2270 vw	2300 w, P	2286 vw		2288 m } 2284 m }	2289 vw	2278 m		2245 s	$\nu_4 a'$	ν_4
2251 s	2253 vs, P 2200 vw, P? 2164 vw, P?	2252 s	2253 s	2248 s	2252 s 2201 vw 2150 vw	2252 s	2251 s		$\nu_5 a'$	ν_5
2120 w	2124 vs, P 2079 w, P 2021 vw, P	2120 m	2124 s 2084 vw	2118 m	2122 s	2118 m	2117 s 2079 vw			
1439 vs	1445 s, D?	1440 vs		1444 s } 1437 s }	1442 s	1443 vs } 1437 vs }	1441 w	1439 s	$\nu_6 a'$	ν_6
1431 vs	1436 s, D?	1430 vs	1436 w	1432 vs } 1428 s }	1428 w	*	*	1432 s	$\nu_7 a'$	ν_7
	1418 vw	1420 vs		1421 w } 1419 w }		1424 m } 1420 m }	1422 m	*		
		1410 vw 1390 vw		1410 s 1393 w		*		1418 m 1388 w		
1350 w	1354 m, P?		1356 w	1367 m } 1362 m }	*	1360 m } 1357 m }	1357 m	1346 vw	$\nu_{20} a''$	ν_8
1342 s	1343 m, D	1342 w	1343 w	1348 w } 1344 m }	1338 w	1346 w	1345 w	1334 m		
1323 s	1325 s, P?	1330 s } 1324 w }	1323 w	1332 vs } 1324 m }	1323 m	*	*	1321 s	$\nu_8 a'$	
1300 vw	1297 w, D?	1298 vw	1300 vw	1319 m }						
1284 w				*	*	1301 w } 1298 m }	1300 m	*		ν_9
1265 m		1264 w			*	1267 s	1274 w	1280 w		
1228 m	1231 s, P	1226 m	1227 w	1227 s 1227 s	1227 s	*	*	1227 s	$\nu_9 a'$	ν_{10}

1192 w	1194 m, D?	1192 m	1191 w	1193 s 1150 vw	1196 m	1198 m	*	1195 s 1150 vw	$\nu_{21} a''$	ν_{20}
	1158 vw		1126 vw							
	1121 vw	1026 w	1030 w	1029 s	1029 s	*	*	1038 s	$\nu_{10} a'$	ν_{11}, ν_{21}
	1027 s, D		1018 vw	*	*	1018 w 1012 s	1017 m			
	1016 m, P									
1004 m	1002 m, P	1003 s	1008 w	1008 s 1002 s	1007 m	*	*	1003 s	$\nu_{11} a'$	
966 w	967 m, D	968 s	964 w	968 s	969 w	968 w	967 vw	972 s	$\nu_{22} a''$	ν_{22}
	955 m, P	950 w	959 w	958 w	954 w	956 m	955 m			
922 w	920 w, P?	922 m	920 vw	912 vw	915 vw?	920 s	915 vw	*	ν_{12}	
	908 vw					908 vw		912 vw		
822 m	826 s, P	822 m	823 w	820 s	833 m	*	*			
807 m	811 vs, P	808 m	813 m	810 s	813 s	*	*	822 s	$\nu_{12} a'$	
	763 w	767 vw		772 s	773 w	*	*	767 w	$\nu_{23} a''$	
758 w		760 w				757 s		*	ν_{23}	
	700 w, P?			720 w 704 w		722 vw	720 w 706 w, br			
648 vs, br	680 m, D?			683 vs 674 m	682 m	710 vs		698 vs 625 vs	$\left\{ \begin{array}{l} \nu_{13} a' \\ \nu_{24} a'' \end{array} \right\}$	ν_{13}, ν_{24}
	662 s, D	670 vs, br	675 w, br	669 vs	675 m					
591 m	592 w, D	592 s	595 w	592 vs	595 m	*	*	601 m	$\nu_{14} a'$	ν_{14}
519 vw	519 m, P	518 w	521 w	*	*	522 m	521 m	*		ν_{15}
484 m	485 m, P	484 m	486 w	*	*	484 vs	489 m	*		
454 s	457 s, P	458 s	460 w	456 vs	459 s	*	*	456 s	$\nu_{15} a'$	
374 m i	383 s, D	385 s	386 m	389 vs	389 s	386 m	386 w	386 s	$\nu_{25} a''$	ν_{16}
324 s i	330 vs, D	334 vs	333 m	334 vs	334 s	334 vs	336 s	335 s	$\nu_{26} a''$	ν_{25}
221 m i	229 vs, D	229 s	232 s	234 vs	238 s	235 vs 227 m, sh	233 m	246 s	$\nu_{16} a'$	ν_{26}
177 m i	182 s, D?	187 s	185 m	183 s	183 s	*	*	196 w	$\left\{ \begin{array}{l} \nu_{17} a' \end{array} \right\}$	ν_{17}
134 w i		125 m, br		*	*	166 s, br				ν_{27}
				130 m 118 w	134 w, br	133 m	114 w		$\nu_{27} a''$	dipole
98 w, br i	100 w, D?					90 m, br				lattice
				86 m 78 m						

^a The vapour data are incomplete and are omitted. Weak bands in the region 2800–2250 cm⁻¹ are omitted.

^b Recorded at 90 K.

^c Annealed to ca. 140 K and recooled to 90 K.

^d Annealed to ca. 190 K and recooled to 90 K.

^e Pressure estimated to ca. 20 kbar.

^f Anti and gauche conformers may be interchanged, see text.

^g Abbreviations used: s, strong; m, medium; w, weak; v, very; br, broad; P, polarized; D, depolarized.

^h Asterisks indicate vanishing bands.

ⁱ On CCl₄ solution.

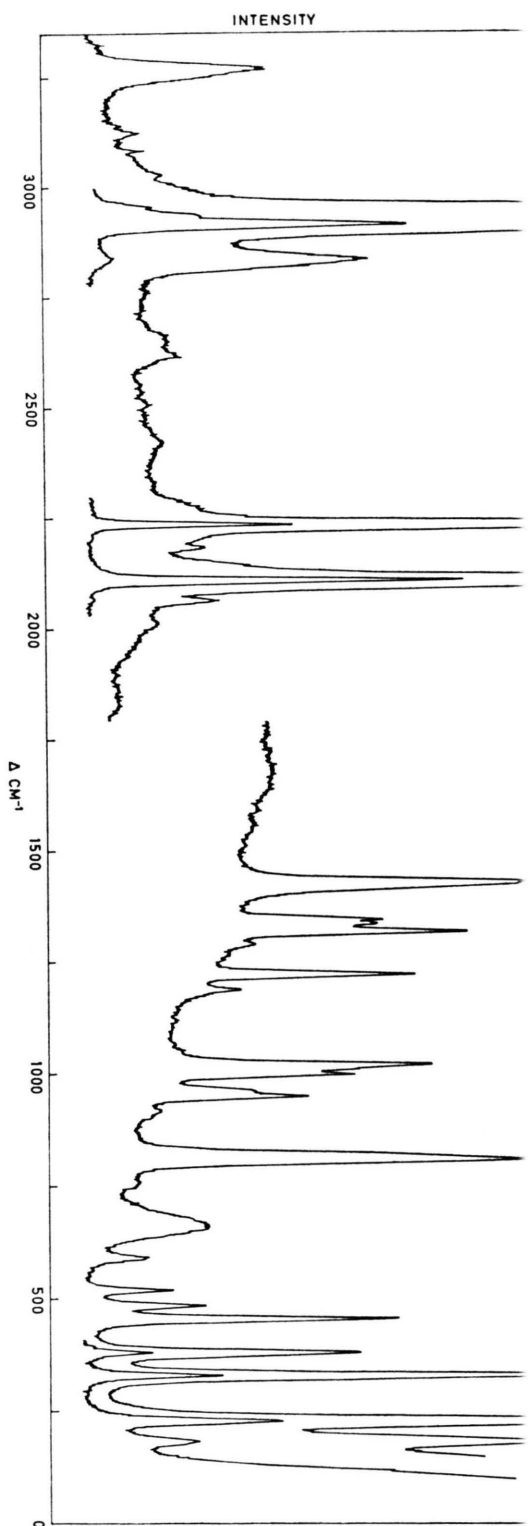


Fig. 2. Raman spectrum of liquid 1-cyano-3-butyne (CB).

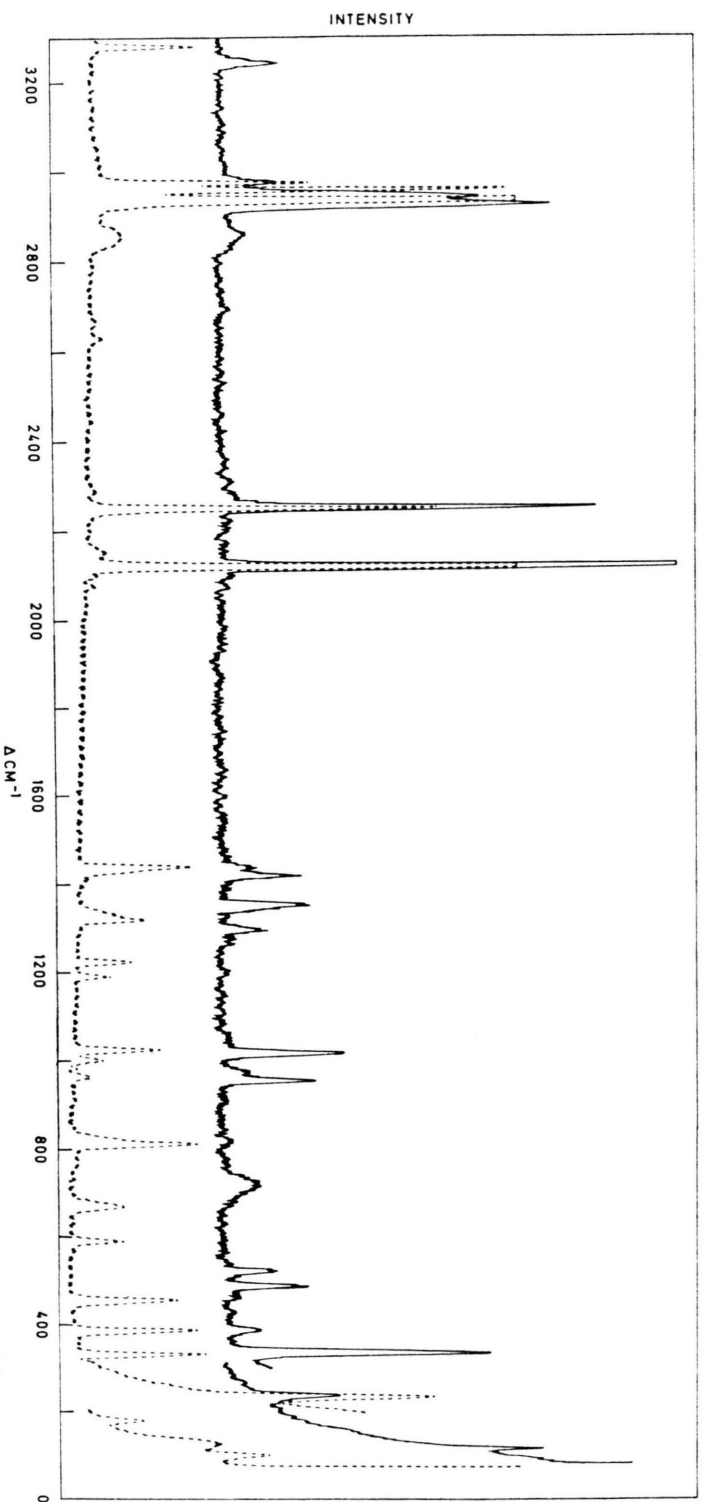


Fig. 3. Raman spectra of 1-cyano-3-butyne (CB) recorded at 90 K; sample annealed at ca. 140 K (crystal A) solid curve; sample annealed at ca. 190 K (crystal B) dashed curve.

Table 2. Observed (ν_{obs} , cm^{-1}) and calculated (ν_{calc} , cm^{-1}) fundamentals for 1-cyano-3-butyne.

Species and No.		Anti conformer		Gauche conformer ^a	
		ν_{obs}	ν_{calc} ^b	ν_{obs}	ν_{calc} ^b
a'	ν_1	3298	3326	3298	3326
	ν_2	2870	2855	2936	2918
	ν_3	2850	2845	2850	2848
	ν_4	2251	2231	2251	2230
	ν_5	2120	2136	2120	2136
	ν_6	1439	1594	1439	1564
	ν_7	1431	1388	1418	1463
	ν_8	1323	1311	1350	1315
	ν_9	1228	1285	1300	1272
	ν_{10}	1027	1068	1265	1206
	ν_{11}	1004	1000	1016	1016
	ν_{12}	807	991	922	891
	ν_{13}	648	653	648	658
	ν_{14}	591	480	519	557
	ν_{15}	454	430	484	424
	ν_{16}	221	221	374	385
	ν_{17}	177	139	177	197
a''	ν_{18}	2948	2922	2980	2924
	ν_{19}	2936	2917	2870	2851
	ν_{20}	1342	1218	1192	1205
	ν_{21}	1192	1216	1016	1036
	ν_{22}	966	961	955	1026
	ν_{23}	763	806	758	828
	ν_{24}	648	638	648	639
	ν_{25}	374	399	324	306
	ν_{26}	324	301	221	224
	ν_{27}	134	129	134	104

^a The fundamentals are numbered as for the *anti* conformer (C_s symmetry).

^b Calculated on the basis of the force field in Table 3.

those present in crystal A started to vanish. At higher temperatures the conversion was more rapid, the dashed curves of Fig. 1 (i.r.) and 3 (Raman) were recorded after 30 minutes annealing at ca. 190 K and rapid quenching to 90 K (crystal B). Again the spectra recorded at ca. 190 K or at still higher temperatures below the melting point were quite similar to those recooled to 90 K apart from slightly broader bands.

The striking difference between the spectra of crystal A and crystal B clearly revealed that opposite conformers were present in the two crystals. A number of clear-cut examples can be seen in the spectra, e.g. the intense i.r. bands (weaker in Raman) at 1267 cm^{-1} in crystal A and at 1227 cm^{-1} in crystal B. Each band had negligible signal in the antagonist crystal spectra, while both bands were present in the amorphous spectra. Therefore, crystal A and crystal B contained opposite con-

formers with nearly no impurity of the other conformer. On the other hand several bands coincide or nearly coincide in the two crystal spectra, e.g. the bands around 229, 276, 324, 2120, 2251 and various bands in the 3000 cm^{-1} region, to be discussed below.

When crystal B was formed after annealing at temperatures above 145 K we were not able to reach crystal A again. In several experiments the sample containing crystal B was kept at different temperatures from 145 K to 120 K for ca. 1 h, but no conversion to crystal A was ever achieved. Unless an eventual conversion from crystal B to crystal A is extremely slow, which seems unlikely since the opposite transition takes place readily, we are forced to assume that crystal A represents a metastable phase. It can apparently be formed from the thermodynamically unstable amorphous glass, but not from the stable crystal B.

To our knowledge, such behaviour between two crystalline states, each having molecules in a different conformer, is very rare. However, we have recently observed quite similar features for the six *trans*-1,4-dihaloxyclohexanes [16, 17] in which apparently metastable crystals containing the *aa* conformers could be formed by annealing the amorphous glass. When the stable crystals of these compounds (containing the *ee* conformer) were formed, we did not again obtain the "*aa* crystal" by cooling, in complete agreement with the present observations for CB. The transitions from the amorphous phase to crystal A and further to crystal B took place at lower temperatures and were more complete for CB than for most of the *trans*-1,4-dihaloxyclohexanes [16, 17]. Since the phase changes for CB as well as the cyclohexanes all appeared irreversible, exact temperatures for the transitions could not be determined.

High pressure crystal

When CB was compressed in the diamond anvil cell at ambient temperature, a spontaneous crystallization occurred at ca. 20 kbar nominal [18] pressure clearly visible in a polarization microscope. The i.r. spectrum of the high pressure crystal was greatly simplified compared to that of the liquid and was similar to that of crystal B. No spectrum like that of crystal A was ever obtained by compressing. Therefore, the high pressure crystal was apparently the same as the stable low temperature

crystal B and contained the same conformer. Most of the i.r. bands were shifted to higher wave numbers with pressure in agreement with the general experience in high pressure spectroscopy.

Discussion

Presence of the two conformers

The crucial problem remains to be settled, which conformer is present in the metastable crystal A and which in the stable crystal B as well as in the high pressure crystal? Various, partly conflicting arguments are listed below.

1. The *anti* and *gauche* conformers of CB belong to point groups C_s and C_1 , respectively, all fundamentals for both conformers being i.r. and Raman active. The *gauche* conformer should have 27 fundamentals of the same species (Raman polarized), while the *anti* conformer should have 17 of species a' (Raman polarized) and 10 of species a'' (Raman depolarized). Since the depolarized Raman bands were observed among those present in crystal B, this conformer might therefore be *anti*. However, the existence of depolarized Raman bands is an uncertain criterium since *gauche* bands may have polarization ratios close to 6/7.

2. The *anti* conformer might exhibit C_{2h} pseudo symmetry, considering the strong relationship to succinonitrile and bipropargyl, giving widely different intensities in i.r. and in Raman. Neither the crystal A nor the crystal B bands, however, indicated any degree of pseudo symmetry.

3. The weak i.r. vapour spectrum prevented any conclusions to be based upon *PR* separation of bands belonging to the *anti* or *gauche* conformers.

4. CB has no characteristic conformation – dependent modes like e.g. the C-Hal stretch in halo-paraffins for which the conformation can be correlated with the band position. It has been claimed that the CH_2 scissoring modes in 1,2-dihaloethanes [19] give rise to a degenerate *anti* band at a higher wave number than the *gauche* band. In CB, however, the highest scissoring mode at 1439 cm^{-1} is common to both conformers. The band at 1431 cm^{-1} is present in crystal B, the band at 1418 cm^{-1} is strong in crystal A and weak in crystal B. If applied to CB, the correlation [19] might indicate the 1431 cm^{-1} and 1418 cm^{-1} bands to belong to *anti* and *gauche*, respectively.

5. Unlike $C \equiv C-H$, the $C \equiv N$ group has a very large bond dipole moment. In succinonitrile the *anti* and *gauche* conformers have very different dipole moments, leading to a large stabilization of *gauche* in the condensed phases relative to the vapour, and in polar solvents relative to unpolar ones [1–3]. Similar stabilizations of the *gauche* conformer with polar solvents were observed for the 1-halo-2-cyanoethanes [9–11]. In bipropargyl, however, very small effects were detected [5]. For CB we observed that the i.r. bands at 454 , 591 , 1004 and 1228 cm^{-1} present in crystal B were slightly enhanced relative to those at 484 , 922 and 1265 cm^{-1} (crystal A) in the pure liquid compared to CCl_4 solution. Consequently, the bands in crystal B might belong to the *gauche* conformer.

6. The vibrational bands present in crystal A and in crystal B were correlated with the fundamentals assigned to the *anti* and *gauche* conformers of succinonitrile [1, 2] and bipropargyl [5]. Since CB has less symmetry than the latter molecules, no easy comparison between the spectra could be achieved, and one alternative assignment was as likely as the other.

7. Force fields were constructed by transferring force constants from related molecules (see below). Although the results were not conclusive, they seemed to favour the crystal A and B bands as *gauche* and *anti*, respectively.

8. Cyanosubstituted ethanes with large differences in dipole moments between the *anti* and *gauche* conformers like succinonitrile [1, 2] and 1-halo-2-cyanoethane [9–11] have highly stabilized *gauche* conformers in the condensed phases and crystallize as *gauche*.

Tetracyanoethane, however has a preferred *anti* conformer as an exception to this rule [12]. In 1,2-dicyano-tetrafluoroethane the dipole difference is smaller and the *anti* conformer is preferred [13], the favourable fluorine-fluorine *gauche* interactions [20] also favour the *anti* conformer. In bipropargyl [4, 5] *anti* is the preferred conformer in all the states of aggregation. Chemical intuition indicates that the low bond moment of the $C \equiv C-H$ group would lead to small dipole differences between the *anti* and *gauche* conformers in CB in spite of the polar $C \equiv N$ group. Consequently, the *gauche* stabilization in the condensed phases should be small. Thus, the crystal B conformer is likely to be *anti*, since it

is slightly more abundant in the liquid state and in solution than that of crystal A (*gauche*).

With conflicting results from the various arguments 1–8, we have tentatively attributed the crystal A and B bands to *gauche* and *anti*, respectively, although nearly equally good arguments can be favoured for the opposite conclusion.

Force constant calculations

The structural parameters were taken identical to those of the normal coordinate analysis of bipropargyl [4], except for the $C \equiv N$ distance, which was adopted from succinonitrile (1.17 Å) [2].

The initial force field approximation was chosen as a diagonal force field in terms of valence coordinates including redundancies around the CH_2 groups. These coordinates include all stretchings (10 coordinates), bendings (12) and linear bendings (3 pairs), along with one torsion. The numerical values for the majority of the force constants (see Table 3) were transferred from bipropargyl [4]; the $C \equiv N$ stretching constant was taken from cyanoacetylene [21]; finally the torsion constant was adjusted to be compatible with the observed low frequencies of the present work. Identical force constant values were applied to the two conformers.

It was possible to assign the observed frequencies in satisfactory agreement with the calculated magnitudes. The frequency *shifts* from one conformer to the other, on the other hand, show a confusing picture. It is in fact impossible to decide conclusively from this analysis to which conformer the two sets of experimental assignments should be

attributed. But the analysis does not contradict the preferred choice, which is discussed above.

Several attempts were made in order to improve the force field with respect to calculated frequency shifts for the two conformers. Many interaction terms were successively introduced through these systematical efforts. In conclusion all these refinements failed to solve the problem. Hence the original approximation was taken as the best force field for the purpose of checking the assignment of frequencies. The virtue of its great simplicity was taken into account when the conclusion was made.

The calculated frequencies are included in Table 2.

Spectral interpretations

The fundamentals assigned to crystal A and B (believed to be *gauche* and *anti*, respectively) in Table 2 are both listed according to C_s symmetry ($17 a' + 10 a''$) for the sake of easy comparison.

From the two low temperature crystal i.r. and Raman spectra and the high pressure i.r. spectrum, the bands can be assigned to the respective conformers with considerable confidence, although various uncertain cases still remain. The $C-H$, $C \equiv N$ and $C \equiv C$ stretching modes for both conformers coincided (except ν_{18}) as expected for typical group frequencies. In addition, the bands at 1439, 1192, 698, 324 and 221 cm^{-1} undoubtedly belonged to both conformers. Furthermore, the bands at 1418, 1350, 1342, 416 and 374 cm^{-1} were much more intense in one crystal spectrum than in the other. They have been attributed to a fundamental of one conformer coinciding with a combination band belonging to the other conformer.

We were forced to assign the *gauche* band at 1016 cm^{-1} to two coinciding vibrational modes ν_{11} and ν_{21} (the calculated values were 20 cm^{-1} apart) since no other bands were available. The intense acetylenic $C-H$ bending modes were strongly shifted with the state of aggregation and three of the four modes (one *anti* and two *gauche*) overlapped. All the polarized Raman bands were assigned as *gauche* fundamentals or as a' modes of the *anti* conformer. The a'' modes had depolarized or unknown polarization ratios. A few apparently depolarized Raman bands were assigned as a' fundamentals.

Considering that diagonal force fields, generally transferred from related molecules were employed, with the same force constants for both conformers,

Table 3. Force constants (mdyne/Å) of the diagonal force field.

Stretchings

$\equiv C-H$:	5.93;	$C-H(CH_2)$:	4.53
$C \equiv C$:	14.0;	$C \equiv N$:	15.8
$\equiv C-C-$:	7.33;	$-C-C-$:	5.0

Bendings

CCH:	0.40;	CCC:	0.50;	HCH:	0.30
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Linear bendings

CCH, CCN, CCC:	0.15
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Torsion

CCCC:	0.20
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the overall fit must be considered satisfactory. The largest deviations were observed for ν_6 (CH_2 scissor) due to the neglect of interaction terms. Also, for other fundamentals like ν_{15} (*gauche*) at 484 cm^{-1} , ν_{23} (*gauche*) at 758 cm^{-1} and ν_{20} (*anti*) at 1342 cm^{-1} the discrepancies were not acceptable. If the *anti* and *gauche* conformers had been interchanged, however, the deviations between the observed and calculated values would have been considerably larger.

Practically all the strong or medium intense i. r. and Raman bands were interpreted as fundamentals. Various weak or very weak bands not considered as fundamentals were interpreted as binary combinations but are not listed in Table 1. The strong to medium intense bands around 822 cm^{-1} were interpreted as an *anti* combination band of species A' in Fermi resonance with ν_{12} .

Mean amplitudes of vibration

The mean amplitudes of vibration [22] were computed for all the types of interatomic distances in both conformers at the temperatures of absolute zero and 298 K. They are of great interest in modern gas electron-diffraction studies, as had been demonstrated for the related molecule bipropargyl [4].

In the course of this computation the simple force field was refined in the following way. Differ-

Table 4. Mean amplitudes of vibration (\AA) for the skeletal distances independent of the angle of internal rotation; 298 K.

Distance	<i>anti</i> -CB	<i>gauche</i> -CB	Bipropargyl [4]
$\text{C}_1 - \text{C}_2$	0.043	0.043	—
$\text{C}_2 - \text{C}_3$	0.050	0.049	0.048
$\text{C}_3 - \text{C}_4$	0.043	0.043	0.043
$\text{C}_4 \equiv \text{C}_5$	0.037	0.037	0.037
$\text{C}_1 \equiv \text{N}$	0.035	0.035	—
$\text{C}_1 \dots \text{C}_3$	0.066	0.071	—
$\text{C}_2 \dots \text{C}_4$	0.068	0.071	0.071
$\text{C}_3 \dots \text{C}_5$	0.049	0.049	0.048
$\text{C}_2 \dots \text{C}_5$	0.094	0.103	0.103
$\text{C}_3 \dots \text{N}$	0.095	0.101	—

Table 5. Mean amplitudes of vibration (\AA) for the skeletal distances dependent on the angle of internal rotation; 298 K. (Equilibrium distance in Cb, r, in \AA .)

Distance	(r)	CB	Bipropargyl [4]
$\text{C}_1 \dots \text{C}_4$ (<i>anti</i>)	(3.75)	0.068	0.071
$\text{C}_1 \dots \text{C}_4$ (<i>gauche</i>)	(2.88)	0.152	0.141
$\text{C}_1 \dots \text{C}_5$ (<i>anti</i>)	(4.87)	0.084	0.089
$\text{C}_1 \dots \text{C}_5$ (<i>gauche</i>)	(3.65)	0.152	0.210
$\text{C}_4 \dots \text{N}$ (<i>anti</i>)	(4.85)	0.085	—
$\text{C}_4 \dots \text{N}$ (<i>gauche</i>)	(3.62)	0.153	—
$\text{C}_2 \dots \text{N}$ (<i>anti</i>)	(6.00)	0.093	—
$\text{C}_2 \dots \text{N}$ (<i>gauche</i>)	(4.15)	0.208	—

ent force fields were applied for the two conformers in order to make them fit accurately the experimental assignments. That was achieved by an adjustment of the symmetry force constant matrix from the approximate calculation, maintaining the normal coordinate transformation matrix (L matrix) unchanged.

For the sake of brevity we only give here a number of mean amplitudes for selected interatomic types and only at 298 K. The most important ones are those of the molecule skeleton. Table 4 shows the calculated values for the distances independent of the angle of rotation around the $\text{C}_2 - \text{C}_3$ bond. The dependent skeleton distances with the associated mean amplitudes are collected in Table 5. The calculated mean amplitudes for the related distances in bipropargyl [4] are included for comparison (Tables 4 and 5). As expected the *anti* mean amplitudes are invariably smaller than their *gauche* partners. The mean amplitudes of the $\text{C} - \text{H}$ bonded distances were obtained as 0.074 \AA and 0.079 \AA for the $\equiv \text{C} - \text{H}$ and CH_2 groups, respectively.

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