

VIBRATIONAL SPECTRA, MOLECULAR STRUCTURE AND CONFORMATION OF ORGANIC AZIDES

Part VII. Azido-2-butyne*

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ABSTRACT

A new organic azide, azido-2-butyne, has been synthesized from bromo-2-butyne and tetramethylguanidinium azide and the ^1H and ^{13}C NMR data are reported. The structure has been determined by electron diffraction from the vapour. IR spectra have been recorded of the vapour, of the liquid, of the amorphous and crystalline solids at ca. 90 K and of the molecule trapped in nitrogen matrices at 15 K. Raman spectra of the cooled liquid and of the amorphous and crystalline solids at 90 K have also been obtained.

The spectroscopic results indicate that the molecule exists in only one conformation in all the states of aggregation and the electron diffraction results show this conformation to be *gauche* around the C-N bond with a dihedral angle of $37(10)^\circ$ from *syn* and the NNN angle $174(5)^\circ$ oriented *anti* to the C-N bond.

The following bond distances (r_a) and angles (\angle_{α}) between the heavy atoms are obtained assuming a linear butyne skeleton and $r_{\text{C}-\text{CH}_3} = 146.0$ pm; $r_{\text{C}\equiv\text{C}} = 120.8(6)$ pm, $r_{\text{C}-\text{CH}_2\text{N}_3} = 146.8(5)$ pm, $r_{\text{C}-\text{N}} = 147.4(15)$ pm, $r_{\text{N}=\text{N}} = 124.0(6)$ pm, $r_{\text{N}\equiv\text{N}} = 114.2(5)$ pm, $\angle_{\text{N}=\text{N}-\text{C}} = 116.5(14)^\circ$ and $\angle_{\text{N}-\text{N}-\text{C}} = 113.7(16)^\circ$.

INTRODUCTION

Although azido-2-butyne ($\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_2-\text{N}_3$) has been synthesized for the first time for this study, a preliminary report containing some of the spectroscopic and structural properties of this molecule has been published together with a brief survey of our studies on organic azides [1]. In the previous papers in this series we have reported the vibrational spectra and the molecular structure of 2-azido-1,3-butadiene [2], 2,3-diazido-1,3-butadiene

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[3], and the closely related molecules 3-azidopropyne [4] and azidoacetonitrile [5]. We have also reported the results of an ab initio study on the molecular structure and force field of the azido group [6].

3-Azidopropyne [4], which was also studied by ab initio methods, and azidoacetonitrile [5] both exist in only one conformation (*gauche*) in the vapour phase as well as in the liquid phase.

EXPERIMENTAL

Preparation

Azido compounds are known to be potentially explosive and appropriate caution should be applied.

Bromo-2-butyne was prepared from the corresponding alcohol using a general synthetic method for 1-bromo-2-alkynes [7]. Bromo-2-butyne (6.6 g, 0.05 mol) was added to a solution of tetramethylguanidinium azide [8] (15.8 g, 0.1 mol) in sulfolane (100 ml) at 55°C. After 1 h the product was sucked into a trap, cooled by liquid nitrogen, recondensed and dried by condensing through a U-shaped tube, which was partly filled with phosphorus pentoxide. Yield 2.4 g (52%); b.p. 92°C/760 Torr (extrapolated); $n_D^{20} = 1.4611$; $^1\text{H NMR}$ (200 MHz, CDCl_3): $\delta = 3.85$ (q, $J = 2.42$ Hz, 2H), 1.88 (t, $J = 2.42$ Hz, 3H); $^{13}\text{C NMR}$ (50.3 MHz, CDCl_3): $\delta = 83.81$ (C-2), 71.15 (C-3), 40.29 (C-1), 3.70 (C-4); UV [CH_3CN (log ϵ): 214 (2.87) nm.

Spectral studies

IR spectra of azido-2-butyne were recorded on a Perkin-Elmer model 225 spectrometer ($5000\text{--}200\text{ cm}^{-1}$) and with a Bruker IFS 114C FTIR interferometer ($4000\text{--}20\text{ cm}^{-1}$). Vapour phase spectra were obtained using cells of 10 cm and 1 m pathlengths equipped with windows of CsI and KRS5, respectively. Spectra were also obtained of the liquid at room temperature and of the solid at ca. 90 K before and after annealing to ca. 210 K using cryostats cooled with liquid nitrogen. Finally, IR spectra were recorded of the molecules trapped in a nitrogen matrix ($M/A \approx 1:500$) at ca. 15 K using a closed cycle displax unit from Air Products.

The Raman spectra were recorded on a DILOR RTI 30 spectrometer (triple monochromator) interfaced to the Aspect 2000 data system of the Bruker FTIR. The 488 nm line of a CRL 52G argon ion laser was used for excitation. Spectra were obtained of the liquid in a capillary tube of 2 mm inner diameter inserted in a transparent Dewar [9] and cooled to ca. 260 K. No polarization data were collected. Further, Raman spectra of the solid formed by shock freezing the vapour on a copper block at ca. 90 K were obtained before and after annealing to ca. 175 K. As a safety precaution the laser power was kept below 40 mW on the sample.

Electron diffraction

The electron diffraction data were recorded on Kodak Electron Image plates with the Oslo apparatus [10] at a nozzle temperature of 293 K and nozzle-to-plate distances 48.5 and 20.5 cm. The electron wavelength was calibrated against benzene [11], optical densities were measured with a Joyce—Loebl densitometer, and the data were reduced in the usual way [12, 13] yielding two averaged intensity curves (one from each distance) in the form $sI_m(s)$. Five plates were selected from the long and short camera distances for the data averaging.

RESULTS

Vibrational spectra

The IR spectrum of azido-2-butyne isolated in a nitrogen matrix at ca. 15 K is given in Fig. 1. In Fig. 2 the spectrum of the liquid (room temperature) is shown and in Fig. 3 the spectrum at liquid nitrogen temperature of the crystalline solid obtained after annealing to ca. 210 K. Finally, the Raman spectra of the cooled liquid and of the amorphous and crystalline solids at ca. 90 K are given in Figs. 4, 5 and 6, respectively. The spectral data are collected in Table 1 and the assigned fundamentals are compared with the results of a normal coordinate calculation in Table 2.

It is immediately evident from the spectra of Figs. 1—6 and from Table 1 that none of the bands present in the spectra of the matrix isolated molecule, of the vapour or of the liquid are absent in the spectra of the crystalline solid. Further, only minor frequency shifts and correlation splittings are encountered between the spectra of the amorphous and crystalline solids. This strongly suggests that only one conformer is present in all states of aggregation.

Electron diffraction

The least squares refinements were carried out on the $sI_m(s)$ intensity curves; the composite of the two camera distance curves is shown in Fig. 7. A unit weight matrix was used. The molecular geometry was calculated from the geometry consistent r_α model [14] and root mean square amplitudes of vibration (l) and perpendicular correction coefficients (K) were constrained to the values calculated from an approximate force field. The set of l and K values was adjusted corresponding to the resulting torsional angle and torsional force constant as the analysis progressed.

The experimental radial distribution (RD) curve is compared with the theoretical curve for the *gauche* conformation in Fig. 8. As was the case for 3-azidopropyne [4] and azidoacetonitrile [5] the C—N torsional angle in azido-2-butyne could not be determined precisely, because the molecule exhibits a large amplitude motion and the ED data are insufficient to give an

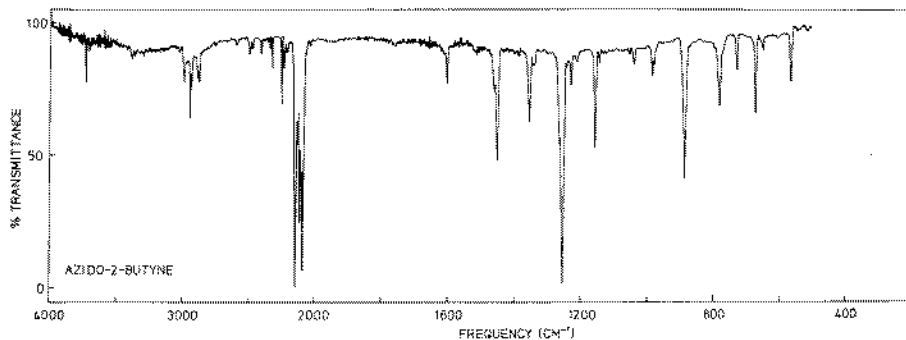


Fig. 1. The mid-IR spectrum of matrix isolated azido-2-butyne at ca. 15 K. Nitrogen matrix, $M/A \approx 1:500$.

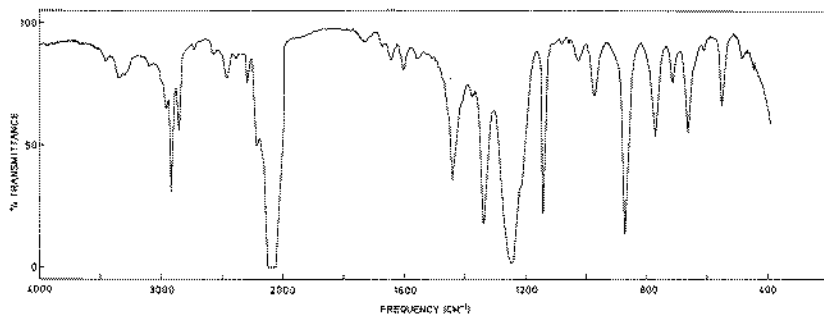


Fig. 2. The mid-IR spectrum of liquid azido-2-butyne, 0.012 mm thickness.

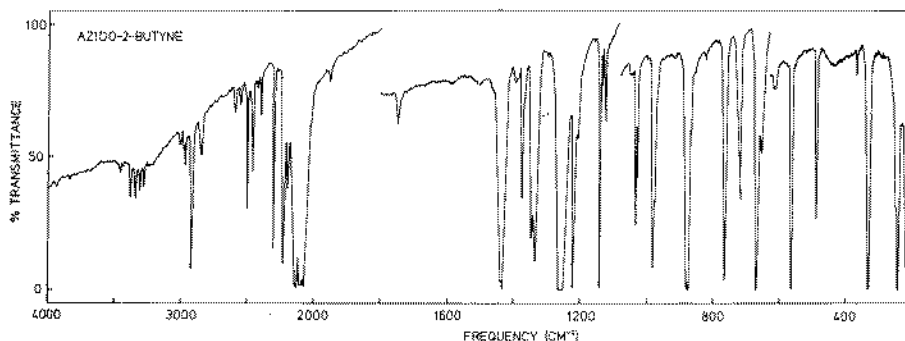


Fig. 3. The mid-IR spectrum of polycrystalline azido-2-butyne at ca. 90 K.

indication of whether the torsional potential is symmetric or not around the torsional angle minimum, τ_0 . There was no significant change in the overall fit to the observed RD curves when the C-N torsional angle and the torsional amplitude were varied within wide regions. However, the torsional amplitude

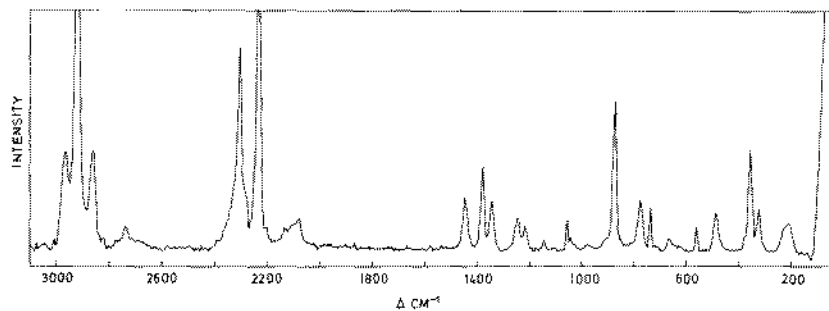


Fig. 4. Raman spectrum of azido-2-butyne as a liquid at ca. 260 K.

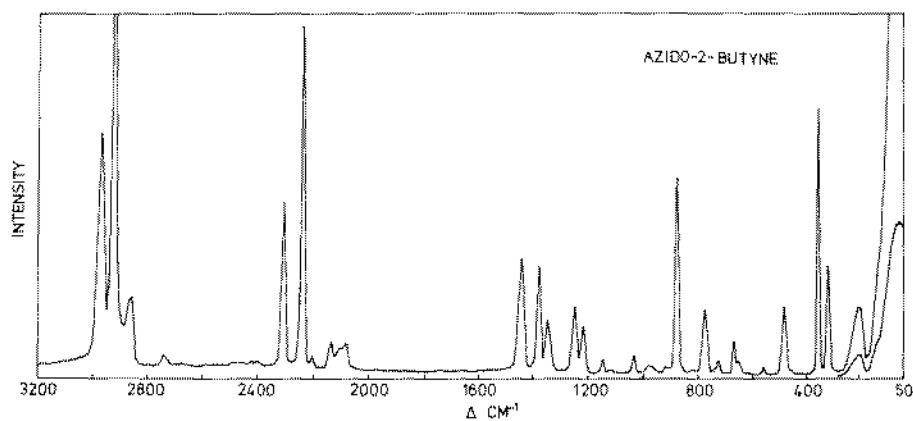


Fig. 5. Raman spectrum of amorphous azido-2-butyne at ca. 90 K.

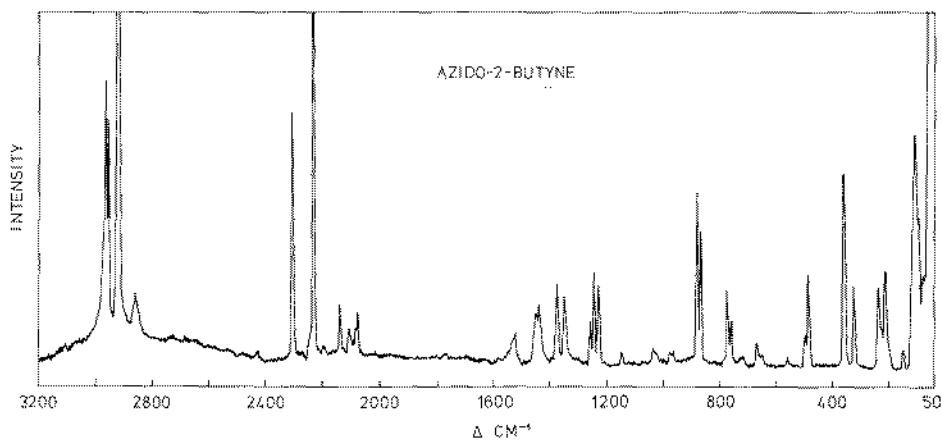


Fig. 6. Raman spectrum of polycrystalline azido-2-butyne at ca. 90 K.

TABLE 1

Vibrational spectral data^a for azido-2-butyne^b

Infrared					Raman			Inter-pretation
Nitrogen matrix 15 K	Vapour	Liquid 250 K	Amorph. solid 90 K	Cryst. solid 90 K	Liquid 250 K	Amorph. solid 90 K	Cryst. solid 90 K	
	3012 Q, vw	~3000 vw	~3000 vw	3007 vw	3005 vw			
2983 w	2983 Q, w			2978 vw			2976 w, sh	ν_1
	2970 } w, B	~2965 w, br	2964 w, br	2965 w	2965 m	2968 ms	2966 m	ν_2, ν_3
	2954 }			2958 vw, sh			2958 m	
2939 m	2944 }							
2929 w	2938 Q } m, AB	2924 m	2920 m	2919 s	2921 vs	2921 s	2921 s	ν_4, ν_5
	2932 }							
		~2910 w, sh						
2880 w	2881 }							
2869 w	2877 Q } m, AB	2861 m	2855 m	2853 w	2860 m	2860 m	2860 w	
	2872 }			2840 w				
2316 w		2304 w	2303 m	2302 s	2305 m	2307 m	2305 m	
2246 m	~2235 w	2233 m	2233 m	2229 s	2233 s	2235 s	2232 s	ν_6
2227 w		~2215 w, sh	2215 w	~2220 w, sh				
2209 vw	~2190 w	~2180 m, sh	2198 w	2199 w	~2200 vw	2200 w	2198 vw	
2203 vw				2194 w				
2143 vs	2130 vs, br	~2110 vs, br	2134 vs	2135 vs	2130 w	2133 w	2140 w	ν_7
2126 m								
2108 s			~2105 s, br	2106 vs	~2105 w, sh	~2100 w	2105 w	
2100 m								
2088 s	~2090 vs, br		2079 s	2079 vs	2080 w	2079 w	2078 w	
				2055 m				
				2045 w				
				2032 vw				
		1460 w, sh						
1454 w	~1460 vw	1444 m	1439 m	1448 s	1445 mw	1443 mw	1450 mw	ν_8, ν_9, ν_{10}
1446 m				1436 s			1438 mw	

			1418 w, sh								
				1392 vw	1393 vw						
			1378 w	1376 w	1373 m	1377 mw	1378 mw	[1379 mw 1374 mw	ν_{11}		
					~1365 w, sh						
1350 m	1345 1341 Q 1337]		1340 s	1347 m 1339 m	1345 s 1335 s	1345 mw	1349 w ~1335 w, sh	1348 mw 1344 vw, sh	ν_{12}		
1341 vw											
1334 vw											
1258 m											
1249 vs	1251 s, bd		1248 vs	1246 vs	1256 vs 1250 vs 1229 s	1245 w	1248 w	1256 w 1244 mw	ν_{13}		
1222 w											
1205 vw			1215 m, sh	1214 m	1221 s 1206 m	1214 w	1217 w	1226 mw	ν_{14}		
1151 m	1152] 1141]-w, B		1145 s	1145 s	1141 s	1144 w	1145 vw	1149 vw	ν_{15}		
1138 w					1137 w 1131 w 1123 m						
1120 vw							~1115 vw				
				1088 vw 1064 vw							
1050 vw			1047 vw	1047 vw	~1045 vw	~1045 vw					
1034 w			1030 w	1031 w	[1032 m 1027 m	1030 vw	1033 vw	1032 vw	ν_{16}, ν_{17}		
979 w					[981 m 975 m	975 vw	977 vw	977 vw	ν_{18}		
973 w	980 w		978 m	978 m	975 m	975 vw	977 vw	977 vw	ν_{18}		
			~910 vw	916 vw	916 vw	910 vw	917 vw				
882 m					880 s 876 s 864 w 852 vw						
877 m, sh	880 m		874 s	875 s	876 s 864 w 852 vw	874 m	875 m	[882 m 869 m	ν_{19}		
					822 vw						
				816 vw	822 vw		~820 vw				
780 w, sh											
775 m	772 w		776 m	774 m	765 s	776 mw	775 w	[775 mw 763 w	ν_{20}		
723 w	729 Q, w		720 mw	722 mw	720 mw	725 vw					
668 m	672 w		668 m	669 m	670 m	666 w	670 w	671 w	ν_{21}	HCCH	

TABLE 1 (continued)

Infrared					Raman			Interpretation
Nitrogen matrix 15 K	Vapour	Liquid 250 K	Amorph. solid 90 K	Cryst. solid 90 K	Liquid 250 K	Amorph. solid 90 K	Cryst. solid 90 K	
645 vw	638 vw	646 vw 620 vw	654 w 642 vw 618 vw	655w ~645 vw 618 vw		654 vw	656 vw	
560 w	568 556 Q 544	556 m	560 m	563 m	559 vw	564 vw	563 vw 499 w	ν_{22}
	496 484	489 w	489 w	487 w	486 mw	488 w	488 mw	ν_{23}
	~375 w		363 w	365 w	378 vw 357 m	363 m	366 m	ν_{24}
	~315 w		328 m	333 m	325 mw	327 mw	331 mw	ν_{25}
				244 m	~230 w, sh	~235 m, sh	245 mw	ν_{26}
	~200 w			217 w	205 w	210 m, br	222 mw	ν_{27}
					~140 w	~145 w	158 w	ν_{28}
							118 m 66 vs	

^aWeak bands in the regions 4000–3000, 2800–2300 and 2000–1500 cm^{-1} have been omitted. ^bAbbreviations: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder; A, B and C denote band contours.

TABLE 2

Calculated and observed fundamental modes of vibration for azido-2-butyne compared with the observed modes of the C—CH₂—N₃ fragment in 3-azidopropyne and azidoacetonitrile

No.	Approximate description	Calculated LSFF ^b	Observed LSFF ^a		
			Azido-2-butyne	3-Azido-propyne ^c	Azidoacetonitrile ^d
ν_1	CH ₂ antisym str	3023	2983 ^e	2985	2996
ν_2	CH ₃ antisym str	2958	2959		
ν_3	CH ₃ antisym str	2958	2959		
ν_4	CH ₂ sym str	2926	2938		
ν_5	CH ₂ sym str	2919	2938	2923	2939
ν_6	C≡C str	2242	2235		
ν_7	N=N str	2104	2130	2129	2115
ν_8	CH ₃ antisym def	1448	1460		
ν_9	CH ₂ antisym def	1448	1460		
ν_{10}	CH ₂ def	1438	1460	1453	1430
ν_{11}	CH ₃ sym def	1377	1378 ^e		
ν_{12}	N=N str	1336	1341	1340	1335
ν_{13}	CH ₂ wag	1260	1251	1247	1265
ν_{14}	CH ₂ twist	1225	1215 ^e	1214	1217
ν_{15}	C—C antisym str	1150	1146		
ν_{16}	CH ₃ rock	1032	1030 ^e		
ν_{17}	CH ₃ rock	1032	1030 ^e		
ν_{18}	CH ₂ rock	945	980	949	925
ν_{19}	C—N str	901	880	868	875
ν_{20}	C—C sym str	762	772		
ν_{21}	NNN bend	678	672	693	685
ν_{22}	N=N torsion	556	556	555	555
ν_{23}	C—C—N bend	479	490	501	525
ν_{24}	C≡C—C bop	359	375		
ν_{25}	C≡C—C bip	314	315		
ν_{26}	C≡C—C bop	211	230 ^e		
ν_{27}	C—N=N bend	193	200	160	199 ^e
ν_{28}	C≡C—C bip	110	140 ^e		
ν_{29}	C—N torsion	49			
ν_{30}	CH ₃ torsion	—			

^aWavenumbers from vapour except when noted. ^bLocal symmetry force field, see text.

^cFrom ref. 4. ^dFrom ref. 5. ^eWavenumber from liquid phase.

appeared to be smaller than in 3-azidopropyne [4] and in azidoacetonitrile [5]. In addition to the large amplitude motion around the C—N bond, a nearly free rotation of the methyl group was indicated. The theoretical RD curve in Fig. 8 and the calculated root mean square amplitudes of vibration, listed in Table 3, are based upon the force field specified in Table 4 and the torsional force constants, $F_\tau(\text{C—N}) = 0.09$ and $F_\tau(\text{CH}_3) = 0.01$ mdyn Å rad⁻².

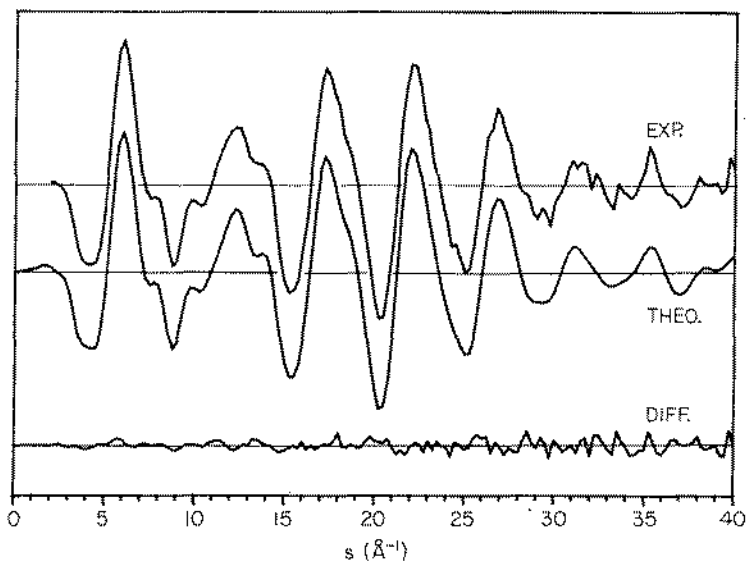


Fig. 7. Azido-2-butyne, intensity curves in the form $sI_{\text{m}}(s)$. Experimental curve is the composite of all plates and camera distances. Theoretical curve was calculated from parameters in Tables 3 and 4. All curves are on the same scale. $\Delta s = 0.25 \text{ \AA}^{-1}$.

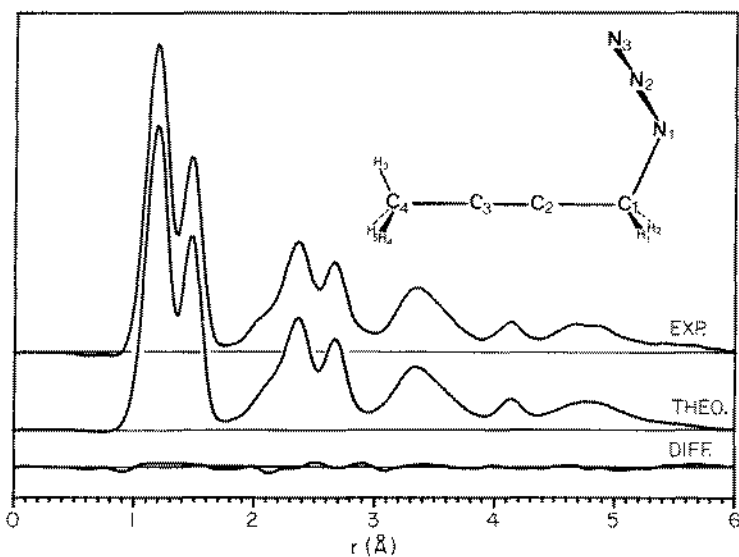


Fig. 8. Azido-2-butyne, radial distribution curves calculated from the intensity curves in Fig. 7 after multiplication by $(f_N'(s) \times f_C'(s))^{-1}$, using theoretical data for unobserved area $s < 2.0 \text{ \AA}^{-1}$ and a damping factor $B = 0.002 \text{ \AA}^2$. All curves are on the same scale.

TABLE 3

Azido-2-butyne: interatomic distances (r_a) and calculated^a root mean square amplitudes of vibration (l) in pm^b

Distance	r_a	l	Distance	r_a	l
C ₁ -H ₁	111	7.8	N ₃ ··C ₁	332	8.8
C ₄ -H ₃	111	7.9	N ₃ ··C ₂	344	22.7
N ₂ -N ₃	114	3.5	N ₁ ··C ₃	351	12.6
C ₂ -C ₃	121	3.6	N ₁ ··C ₃	351	22.5
N ₁ -N ₂	124	4.0	N ₂ ··H ₁	373	23.4
N ₁ -C ₁	147	5.1	N ₃ ··C ₃	395	33.4
C ₁ -C ₂	147	4.7	C ₁ ··C ₄	413	5.9
C ₃ -C ₄	148	4.6	N ₁ ··H ₂	427	10.9
C ₃ ··H ₄	210	10.7	C ₂ ··H ₁	465	14.4
C ₂ ··H ₂	212	10.6	N ₂ ··C ₄	471	27.5
N ₁ ··H ₂	213	10.5	N ₂ ··H ₄	472	36.9
N ₂ ··C ₁	224	7.2	N ₃ ··H ₄	472	52.8
N ₁ ··N ₃	238	4.5	C ₄ ··N ₁	489	15.6
N ₁ ··C ₂	245	9.9	C ₄ ··N ₃	491	42.7
C ₂ ··C ₄	268	5.1	N ₁ ··H ₄	512	26.5
C ₁ ··C ₃	268	5.0	N ₂ ··H ₃	520	38.2
N ₂ ··C ₂	272	16.7	N ₂ ··H ₅	531	26.5
N ₂ ··H ₁	280	18.1	N ₂ ··H ₅	536	35.1
N ₃ ··H ₂	318	10.6	N ₃ ··H ₃	543	54.6
C ₂ ··H ₄	319	12.4	N ₁ ··H ₅	549	18.3
C ₃ ··H ₁	322	12.3	N ₃ ··H ₅	556	52.2

^aCalculated from force field in Table 4 (see text). ^bAtomic numbering as shown in Fig. 8.

Numerous geometrical constraints had to be imposed on the molecular model. First, the 2-butyne skeleton was assumed to be linear (there was no detectable deviation from linearity) and the methyl group to have C_{3v} symmetry with CCH angles of 111° . The C—H distances were taken to be the same as in the methylene group where further the four CCH and NCH angles were assumed to be equal. In accordance with the results for other azides [2—5, 15—17] the geometry of the azide group was assumed to be *trans*. These constraints had virtually no influence on the other geometrical parameters. Second, the nearly equally long bonds C—CH₃, C—CH₂— and C—N obviously cannot be determined simultaneously. Consequently, the C—CH₃ bond distance was constrained to 146 pm while the C—CH₂N₃ distance was varied systematically. The final results are given in Table 5, where the correlation coefficients larger than 0.5 have also been included.

TABLE 5

Azido-2-butyne: final results (r_a in pm, \angle_a in degrees) from the least squares refinements of the electron diffraction data at 293 K

No.	Parameter	Value
1	$r(N_2-N_3)$	111.2(5) ^a
2	$r(N_1-N_2)$	124.0(6)
3	$r(N-C)$	147.4(15) ^b
4	$r(C_1-C_2)$	146.8(5)
5	$r(C_2-C_3)$	120.8(6)
6	$r(C_3-C_4)$	146.0 ^c
7	$\langle r(C-H) \rangle$	111(3)
8	$\angle(N-N-N)$	174(5) ^d
9	$\angle(N-N-C)$	116.5(14)
10	$\angle(N-C-C)$	113.7(16)
11	$\left. \begin{array}{l} \langle \angle C-C_1-H \rangle \\ \langle \angle N-C-H \rangle \end{array} \right\}$	110 ^c
12	$\langle \angle C-C_4-H \rangle$	111 ^c
13	$\tau(C-N)$	37(10)
14	$\angle C-C-C$	180 ^c
	R^{lc}/R^{sc}	6.7/10.8
Correlation coefficients > 0.5:		
$C_{1,7} = -0.7$	$C_{8,9} = 0.5$	$C_{9,10} = 0.5$
$C_{9,13} = -0.5$	$C_{10,13} = -0.7$	

^aUncertainties given in parentheses are three times the standard deviation (including estimates of systematic errors and correlation). ^bValue found by systematic variation, uncertainty estimated. ^cAssumed. ^dThe NNN linkage is bent *trans* to the C-N bond. ^e R factors for long and short camera data in %.

be caused by dipolar packing effects (dipole moment 3.05 D [18]), but otherwise only the *gauche* conformation has been found in all states of aggregation. This is in agreement with the results of our *ab initio* calculations of the C-N torsional potential in 3-azidopropyne (see Fig. 10 in ref. 4) giving barriers to rotation of ca. 6.5 and 8.5 kJ mol⁻¹ in the *syn* and *anti* positions, respectively.

The conformational preference of the *gauche* to the *anti* or *syn* positions in azido-2-butyne, azidoacetonitrile and 3-azidopropyne may be rationalized in terms of Coulombic attraction/repulsion between the π -electron system of the C \equiv C triple bond and that of the azide group. It can be seen from Table 6 that for all three molecules the dihedral angle around the C-N bond is significantly less than 60°. There are no steric reasons for this so there must be a Coulombic attraction between the two groups. Usually the bonding properties and the charge distribution of covalent azides are discussed in terms of two resonance structures:



TABLE 6

Comparison of some of the geometrical parameters (pm, deg.) of azido-2-butyne with related molecules

Molecule	r _{C-CH₃}	r _{C≡C}	r _{C-CH₂X}	r _{C-N}	r _{N=N}	r _{N≡N}	∠CCN	∠CNN	∠NNN	τ ^a	Ref.
CH ₃ -C≡C-CH ₃	146.7(1)	121.3(1)									23
CH ₃ -C≡C-CH ₂ Cl	145.8(20)	120.7 ^b	146.0(20)								22
N≡C-CH ₂ -N≡N≡N			146.5(15)	147.6(6)	124.5(5)	113.5(4)	113.4(10)	115.4(11)	173(3)	52(5)	5
HC≡C-CH ₂ -N≡N≡N		121.6(7)	148.1(13)	146.4(13)	124.9(7)	113.7(6)	114.6(12)	114.5(16)	169(4)	37(8)	4
CH ₃ C≡C-CH ₂ -N≡N≡N	146.0 ^b	120.8(6)	146.8(5)	147.4(15)	124.0(6)	114.2(5)	113.8(16)	116.5(14)	174(5)	37(10)	This work
H-N≡N≡N					124.3(5)	113.4(2)			171(5)		15
CH ₃ -N≡N≡N				146.8(5)	121.6(4)	113.0(5)		116.8(3)	180 ^b		24
CF ₃ -N≡N≡N				142.7(5)	125.0(7)	111.7(4)		111.8(11)	175(4)		17
N≡C-N≡N≡N				135.5(2)	126.1(1)	112.7(2)		114.5(2)	169.2(16)		16
CH ₂ -O-CH ₂ -C-(CH ₂ N ₃) ₂				147.0(9)	124.0 ^c	114.2	111.4(12)	119.2(10)	180 ^b		25

^aTorsional angle measured from the *syn* position. ^bAssumed. ^cGiven as NN_{av.} = 1.191(2) and NN_{diff.} = 0.098(2).

Gross atomic charge calculations on the Hartree—Fock SCF level with large basis sets on HN_3 [6, 19] and ClN_3 [20] show that the charge distribution of the azide group is best described by structure (a). The reasons for the *gauche* being the stable conformer are then obvious and easily visualized by a simple Newman projection.

Spectral interpretation

The assignment and interpretation of the vibrational spectra of azido-2-butyne are based on analogies with closely related molecules such as 3-azidopropyne [4], azidoacetonitrile [5] and chloro- and bromo-2-butyne [21]. The characteristic methyl group vibrations hardly need any comments and the $\text{C}\equiv\text{C}$ and the antisymmetric and the symmetric $\text{C}-\text{C}$ stretching vibrations are found at nearly the same wavenumbers as in chloro- and bromo-2-butyne [21]. This is also true for the four $\text{C}\equiv\text{C}-\text{C}$ bending modes. Further, most of the $\text{C}-\text{CH}_2-\text{N}_3$ vibrations are situated close to the corresponding modes in 3-azidopropyne [4] and azidoacetonitrile [5] as illustrated in Table 2.

As seen, we have assigned all the vibrational fundamentals except the $\text{C}-\text{N}$ and the methyl torsional modes. The first of these modes has been calculated to be around 50 cm^{-1} using the SQM force field (see later). The barrier to rotation of the methyl group is obviously very low but probably somewhat higher than in chloro-2-butyne, where an upper limit was estimated as 400 J mol^{-1} [22]. Still, a barrier of this magnitude corresponds to virtually free internal rotation.

Force constant calculations

The normal modes of vibration for azido-2-butyne were calculated from an approximate, local symmetry force field (LSFF) constructed from a scaled quantum mechanical (SQM) force field for the *gauche* conformation of azidoethane [6] and from a LSFF for the halonitriles as previously described [4]. Only the diagonal CH_2 wag and twist force constants and the $\text{N}=\text{N}$ torsional force constant have been modified from the transferred values. The results of the normal coordinate calculations are given in Table 2.

The definition of the internal coordinates and the corresponding force constants can be obtained from Table 10 in ref. 4 by deleting the coordinates $S_{16}-S_{21}$ (and columns 16–21 in the force constant matrix) and instead including the coordinates and force constants given in Table 4.

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