

## THE VIBRATIONAL SPECTRA, MOLECULAR STRUCTURE AND CONFORMATION OF ORGANIC AZIDES

### Part II. 2-Azido-1,3-butadiene

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#### ABSTRACT

A sample of 2-azido-1,3-butadiene was synthesized from 4-bromo-1,2-butadiene and tetramethylguanidinium azide. Although the sample is highly explosive, we succeeded in making a structure determination by gaseous electron diffraction. IR spectra of the vapour, of the matrix isolated species in argon at 15 K, and of an amorphous and crystalline solid at 90 K were recorded. A Raman spectrum of the liquid, including semiquantitative polarization data, was obtained at 240 K.

The title compound was found to be planar with the CNN angle  $117^\circ$  oriented *syn* to the adjacent C=C double bond, the NNN angle was ca.  $177^\circ$  oriented *anti* to the C—N bond. The following bond distances ( $r_g$ ) were obtained: N—N(N), 114.3; N—N(C), 125.3; C—N, 143.4; C=C, 135.0; and C—C, 146.7 pm.

No additional conformers were observed in the vapour, liquid, amorphous or crystalline states.

#### INTRODUCTION

In the first paper in this series we reported a brief survey of spectroscopic and structural studies on organic azides [1], which have recently been synthesized in this laboratory [2–4]. The goal was to develop new synthetic routes for the preparation of unsaturated organic azides, to investigate their chemical reactions and to prepare these compounds for the purpose of structural and conformational studies by spectroscopic and electron diffraction techniques.

The vapour phase structures of  $\text{HN}_3$  [5],  $\text{CH}_3\text{N}_3$  [6],  $(\text{CH}_3)_3\text{SiN}_3$  [7],  $\text{ClN}_3$  [8],  $\text{NCN}_3$  [9],  $\text{CF}_3\text{N}_3$  [10] and  $\text{C}_6\text{H}_5\text{N}_3$  [11] have been reported, but generally very little work has been done on the smaller azides. In particular, no olefinic azides except azidoethane (vinyl azide) [12] has been studied by spectroscopic methods. The reason for this is obvious; all the

azides are explosive and they should be handled with the utmost caution. The unsaturated azides, containing one or more double or triple bonds, and the diazides, are found to be particularly dangerous. These compounds should be handled in the smallest possible quantities on vacuum lines; only vapours or solutions should be kept at room temperature; the liquids or solids should be kept as cool as possible. They should not be illuminated by argon ion laser light unless the temperature is near or below the freezing point.

In the present communication we report results for 2-azido-1,3-butadiene (later to be called AZBUT), obtained by gaseous electron diffraction and vibrational spectroscopy. In forthcoming papers from this laboratory the corresponding results for 2,3-diazido-1,3-butadiene [13], 3-azido-propyne [14], azido-acetonitrile [15], 1-azido-2-butyne [16] and 3-azido-propene [17] will be reported.

## EXPERIMENTAL

### *Preparative*

When an aqueous methanolic sodium azide solution of 4-bromo-1,2-butadiene was left standing for five days, a complete conversion to AZBUT took place [4]. A more convenient procedure, however, was to let tetramethylguanidinium azide react with 4-bromo-1,2-butadiene in a sulfolane solution. The postulated intermediate 4-azido-1,2-butadiene could not be isolated [4], but apparently rearranges to AZBUT. The physical and spectral properties of AZBUT for the purpose of identification have been described in detail elsewhere [4].

### *Electron diffraction*

The electron diffraction data were recorded on Kodak Electron Image plates with the Oslo diffraction apparatus [18] at a nozzle temperature of 293 K. Nozzle-to-plate distances of 48.5 and 20.5 cm were used, and four plates from each camera distance were employed in the final analysis. The electron wavelength was calibrated against benzene [19]. The electron diffraction patterns were measured with a Joyce Loebel densitometer. After data reduction [20], a calculated background was subtracted from the experimental data for each of the plates separately [21]. Intensities were obtained in the form  $sI_m(s)$ , and least squares analyses were performed on these intensity curves in the same way as described earlier [22].

### *Spectra*

IR spectra were obtained with a Perkin-Elmer model 225 spectrometer (4000–200  $\text{cm}^{-1}$ ) and with a Bruker model 114C Fourier transform spec-

trometer ( $4000\text{--}50\text{ cm}^{-1}$ ) Raman spectra were recorded on a Dilor RT-30 triple monochromator spectrometer equipped with a cooled photomultiplier and interfaced to the Aspect 2000 computer of the Bruker instrument. The 488 nm line of a CRL model 52 G argon ion laser was used for excitation.

IR vapour phase spectra of AZBUT were recorded in cells of path length 9 cm ( $4000\text{--}400\text{ cm}^{-1}$ ) and 20 cm ( $700\text{--}50\text{ cm}^{-1}$ ) equipped with CsI and polyethylene windows, respectively, using ca. 50 torr pressure. Spectra of AZBUT isolated in an argon matrix (M/A  $\sim 1:1000$ ) were recorded at ca. 15 K, using a closed cycle cryostat from Air Products. Solid state spectra of the glassy solid formed by shock freezing the vapour on a CsI window at 90 K were recorded. The sample was subsequently annealed first to 160 K when the sample turned frosty, and later to 190 K when the crystalline sample changed appearance. After recooling each of the annealed samples to 90 K, the IR spectra were recorded and showed both samples to be crystalline, but with different band splittings, etc. For reasons of safety no IR spectra were recorded of AZBUT as a neat liquid.

Raman spectra of AZBUT were obtained in a capillary tube of 2 mm inner diameter. The tube was inserted in a transparent Dewar [23] and cooled to ca. 240 K (just above the freezing point) by a stream of cold nitrogen. In order to prevent decompositions and eventual explosions the laser power was kept below 50 mW at the sample. Under these conditions the sample seemed quite stable and no increased fluorescence or spectral instabilities were detected. Semiquantitative polarization measurements were carried out.

## RESULTS

### *Electron diffraction*

In Fig. 1 the composite of the averaged intensity curves from the long and short camera distances is shown. A unit weight matrix was used in the least

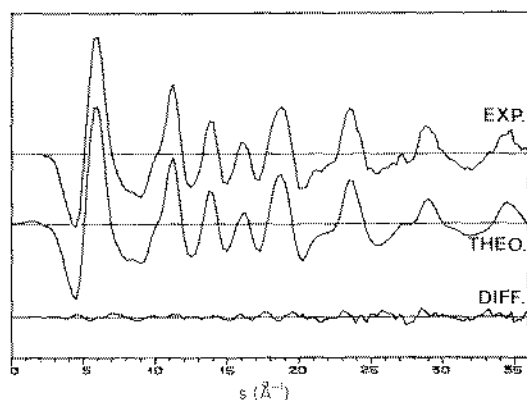


Fig. 1. 2-Azido-1,3-butadiene (AZBUT).  $sI_m(s)$  intensity curves. Experimental curve is the average for all plates and distances. Difference curve is exp. — theo.  $\Delta s = 0.25\text{ \AA}^{-1}$ .

squares analysis. The molecular geometry was calculated from the consistent  $r_{\alpha}$  model [24]. The mean square amplitudes of vibration ( $l$ ) and perpendicular correction coefficients ( $K$ ) were calculated from the force field commented upon elsewhere in this paper.

Among the parameters associated with hydrogen atoms some constraints had to be introduced. We have constrained the C—H distances to 111 pm and the five C—C—H angles to be equal. These are minor restrictions with respect to the molecule as a whole and they have practically no influence upon the parameter values obtained for the carbon nitrogen molecular skeleton.

The middle C—C distance was varied systematically while the C=C distances were assumed to have the same value. Because of the planarity of the molecule (see later) one might expect the two C=C—C angles to differ by a few degrees. Therefore, this difference was systematically investigated, and the later parameter and  $r(\text{C—C})$  was associated with an estimated error limit. For the simpler molecule vinyl azide two conformers have been found [12], a *syn* form with the azide group eclipsing the carbon carbon double bond, and an *anti* form with the azide group rotated 180° around the C—N bond relative to the *syn* form. Radial distribution curves corresponding to the (1)*syn* and to the (1)*anti* form of AZBUT are shown in Fig. 2. Clearly, there is very little, if any, of the *anti* form present. Furthermore, the least squares analysis suggests that the *syn* is the only conformer present in detectable amounts. Intermediate forms were also searched for, but excluded.

Apparently AZBUT is quite rigidly planar without unusually large amplitude motions. In Table 1 the geometrical parameters as obtained from the least squares analysis are given. Correlation coefficients larger than 0.6 are also included in Table 1. The experimental and theoretical intensity and radial distribution curves are shown in Figs. 1 and 2, respectively. The interatomic distances and their  $l$ -values are listed in Table 2.

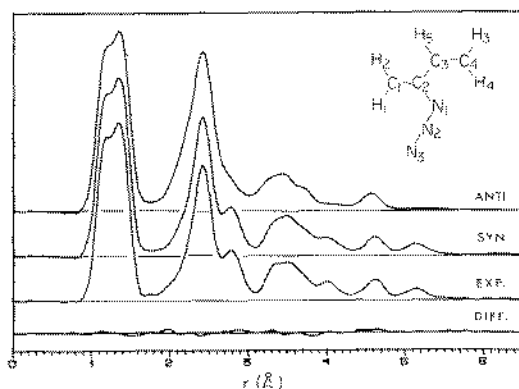


Fig. 2. Radial distribution curves for the separate *anti* and *syn* conformers, and the experimental curve of AZBUT. The latter two are the curves calculated from the intensity curves in Fig. 1, after multiplication by  $(f_{\text{C}}(s) * f_{\text{N}}(s))^{-1}$  and using theoretical data for the unobserved area  $s < 2.0 \text{ \AA}^{-1}$  and a damping coefficient  $0.0020 \text{ \AA}^{-2}$ . The position of the most important distances can be found in Table 2.

TABLE 1

2-Azido-1,3-butadiene<sup>a</sup>. Final results from least squares refinement of the electron diffraction data at 20°C

No.	Parameter <sup>b</sup>	$r_a/L_\alpha^c$
1	$r(C_1-C_2)^d$	135.0(4)
2	$r(C_2-C_3)$	146.7(8) <sup>e</sup>
3	$r(C_2-N_1)$	143.4(7)
4	$r(N_1-N_2)$	125.3(6)
5	$r(N_2-N_3)$	114.3(4)
6	$\langle r(C-H) \rangle^f$	111.0 <sup>g</sup>
7	$C_1-C_2-N_1$	125.0(1.3)
8	$C_1-C_2-C_3$	123.7(1.1)
9	$C_2-C_3-C_4$	2.4(1.5)
10	$C-N-N$	116.8(1.1)
11	$N-N-N$	176.5(3.5)
12	$\langle C-C-H \rangle^f$	122.3(2.1)
	$R_{lc}/R_{sc}^h$	7.5/14.2

Correlation coefficients >0.6:

$$(4/5) = 0.63,$$

$$(7/8) = -0.72,$$

$$(10/11) = 0.72$$

<sup>a</sup>Results for the C-N *syn* conformation shown in Fig. 2. <sup>b</sup>Atomic numbering in Fig. 2. <sup>c</sup>Distances in pm and angles in degrees. Error limits are  $2\sigma$  where  $\sigma$  includes uncertainties in experimental conditions and in parameters used in the data reduction. <sup>d</sup>All bonds are designated —, no distinction in this column between single and double bonds. <sup>e</sup>Systematically varied, error limit estimated. <sup>f</sup>Average value for the five C-H distances/C=C-H angles. <sup>g</sup>Assumed. <sup>h</sup>R-factor for long camera (lc) and short camera (sc) data in %.

TABLE 2

2-Azido-1,3-butadiene. Interatomic distances for the most important distances, CC, CN and NN, and their root mean square amplitudes of vibration in pm (calculated)

Distance <sup>a</sup>	$r_a$	$l$	Distance <sup>a</sup>	$r_a$	$l$
C-H	111	7.7	$C_1 \cdots C_2$	248	6.2
$N_1-N_2$	114	3.4	$C_1 \cdots N_3$	276	11.7
$N_2-N_3$	125	3.9	$C_2 \cdots N_1$	279	10.6
$C_1-C_2$	135	4.1	$C_2 \cdots N_3$	331	7.0
$C_2-N_1$	143	4.8	$C_1 \cdots N_3$	348	16.4
$C_2-C_3$	147	4.7	$C_3 \cdots N_3$	352	7.1
$C_2 \cdots N_2$	228	7.5	$C_2 \cdots C_4$	372	6.4
$N_1 \cdots N_3$	239	4.6	$C_1 \cdots N_2$	401	10.6
$C_3 \cdots N_1$	239	6.7	$C_3 \cdots N_3$	462	7.8
$C_1 \cdots N_1$	246	6.2	$C_4 \cdots N_3$	513	11.1

<sup>a</sup>Atomic numbering in Fig. 2.

### Spectral results

A part of the IR vapour spectrum ( $1000\text{--}400\text{ cm}^{-1}$ ) is given in Fig. 3. The unannealed, amorphous solid spectrum is shown in Fig. 4 and the corresponding spectrum of the crystalline solid, annealed to 160 K is given in Fig. 5. Finally, a Raman spectrum of the cooled liquid is reproduced in Fig. 6. The maxima of the observed IR and Raman bands are listed in Table 3.

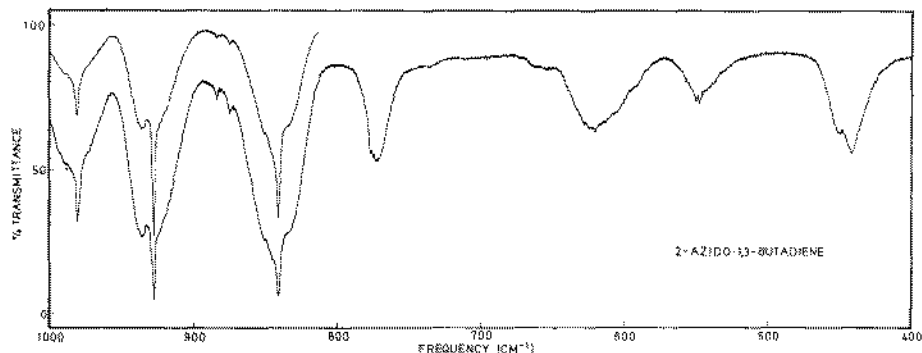


Fig. 3. IR vapour spectrum of AZBUT, path 9 cm. The band at  $775\text{ cm}^{-1}$  is due to chloroform.

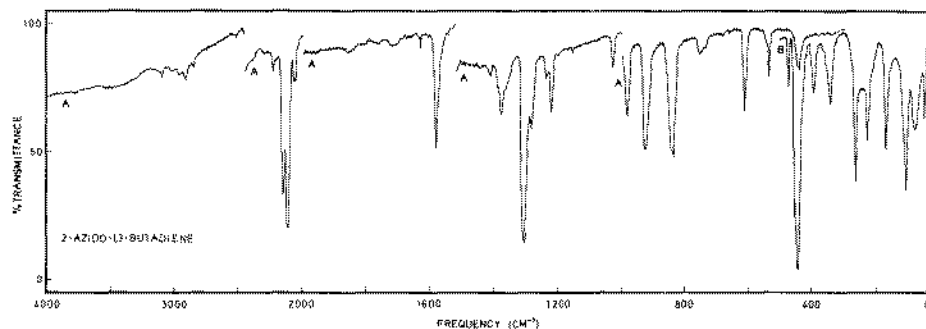


Fig. 4. IR spectrum of AZBUT as an unannealed amorphous solid at 90 K.

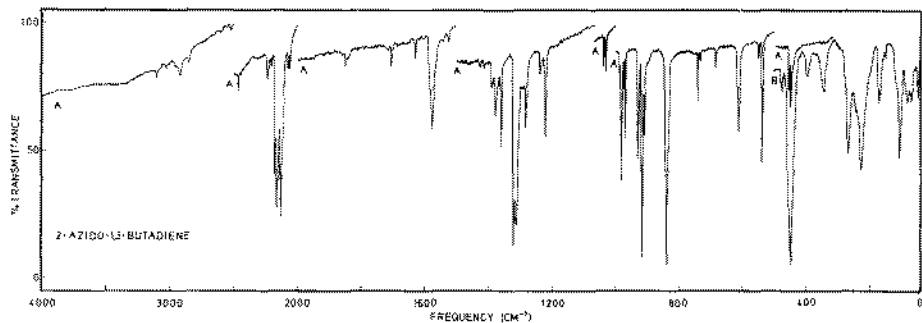


Fig. 5. IR spectrum of AZBUT as an unannealed crystalline solid at 90 K.

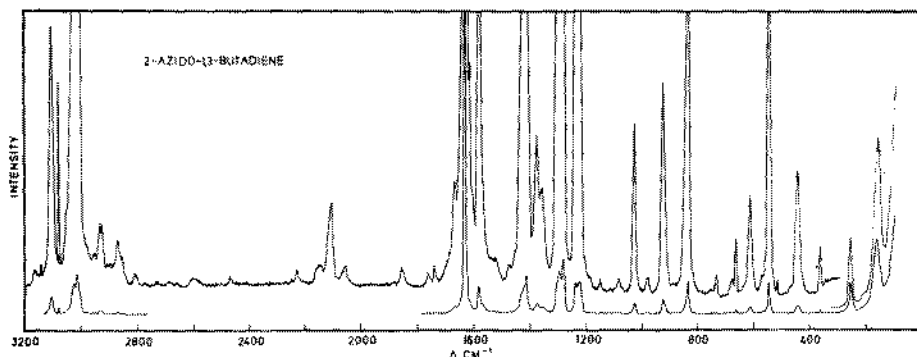


Fig. 6. A Raman spectrum of liquid AZBUT, cooled to 240 K. The weak bands at 758, 668 and 366  $\text{cm}^{-1}$  are due to chloroform.

In the synthesis of AZBUT, tetramethylguanidinium azide was dissolved in chloroform which was subsequently pumped off under vacuum for 2 hours. However, the very intense IR band at 775  $\text{cm}^{-1}$  (vapour) and the Raman bands at 668 and 336  $\text{cm}^{-1}$  (liquid) of chloroform appeared as weak impurity peaks in the spectra (Figs. 3–6). At a conservative estimate the concentration of chloroform in AZBUT was less than 1%.

#### *Vapour phase*

After AZBUT was synthesized and the spectra recorded, it was still uncertain if electron diffraction data could be obtained due to the hazards. Therefore, the IR vapour contours were carefully calculated for various possible geometries, including: *syn* and *anti* positions of the  $\text{N}_3$  group relative to *anti*-butadiene as well as relative to the unlikely *syn*-butadiene. Because of conjugation it was believed a priori that the azide group would lie in the butadiene plane. Since the vapour phase structure of AZBUT was shown beyond doubt to be *syn* of the  $\text{N}_3$  group relative to *anti*-butadiene (see above), the alternative interpretations will not be discussed. The calculations [25] revealed the PR separations to be 12, 10 and 16  $\text{cm}^{-1}$  for the *A*, *B* and *C*-type bands, respectively. As is apparent from Fig. 3 and the data of Table 3, these predictions are in good agreement with the experimental results. The best resolved vapour contours are those at 1590 (*B*), 1034 (*A/B*) and the *C*-type bands at 981, 928 and 841  $\text{cm}^{-1}$ .

#### *Crystal phase*

A comparison between the IR spectra of Figs. 4 and 5 reveal that the spectrum of the annealed crystalline solid has sharper bands, frequency shifts and certain cases of crystal splitting compared to the spectrum of the unannealed, amorphous solid. It is highly significant, however, that none of the IR bands

TABLE 3

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

IR				Raman liquid	Interpretation
Vapour	Ar matrix 15 K	Amorphous 90 K	Crystal 90 K		
3119 } 3116 Q } 3113 Q } 3108 }	m, A <sup>b</sup>	3101 w	3101 w	3105 m	$\nu_1, \nu_2 A'$
				3074 vw	
3043 } 3037 Q } 3032 }	w, A	3023 vw	3028 vw	3027 s, P	$\nu_3 A'$
~3025 w, sh			3014 vw	3015 vw	3014 s
~2170 m, sh	2172 m	~2170 s, sh	3001 vw	3005 m, sh	$\nu_5 A'$
2156 vs	2156 s	2156 vs	2176 vs		comb. FR
2131 vs, sh	2125 s	2125 vs, br	{ 2163 vs 2153 vs	2151 w, P	comb. FR
2121 vvs	2114 vs	2115 vs, br	2134 vs	~2120 mw, sh, P	comb. FR
2065 m, br	2079 w	2074 w, br	2120 s	2111 m, P	$\nu_6 A'$
	2061 w	2060 w, br	2077 w	~2070 w, sh	$\nu_7 + \nu_{19} A'$
			2060 w	2059 w, P	$\nu_{13} + \nu_{15} A'$
				1672 mw, P	$2\nu_{16} A'$ FR
1645 } 1634 }	w, B	1638 vw	1633 w	1635 vvs, P	$\nu_7 A'$
					1618 m, P
			1608 vw	1606 w	$\nu_{29} + \nu_{26} A'$
1595 } 1585 }	vs, B	1591 s	1584 vs	1584 s, P	$\nu_8 A'$
					~1570 m, sh
			1550 vw	1550 vw	$\nu_{11} + \nu_{20} A'$
			1530 w	~1525 vw, br, P	$\nu_{12} + \nu_{20} A'$
				~1475 vw, P?	$\nu_{13} + \nu_{20} A'$
				~1455 vw	$\nu_{11} + \nu_{21} A'$
~1435 vw?			1430 w	1430 m, P	$\nu_{12} + \nu_{21} A'$
~1420 vw?	1417 vw	1415 w	1416 w	1415 s, P	$\nu_9 A'$
	1390 w	1388 m, sh	1391 m	~1390 vw, sh	$\nu_{13} + \nu_{21} A'$ FR
1390 } 1381 Q } 1375 }	s, A	1381 m	1379 s	1381 s	$\nu_{10} A'$
~1365 m, sh			~1365 m, sh	1362 s	1359 w, br, P
1316 } 1313 Q } 1311 Q } 1305 }	vs, B	1313 s	1308 vs	1304 m, P?	$\nu_{22} + \nu_{25} A'$ FR
			1310 vs	1308 vs	1313 vs, br
~1275 m	1283 w	1285 m	{ 1285 m 1283 w, sh	1284 s, P	$\nu_{12} A'$
	1244 vw	1240 w	1241 w	1238 s, P	$2\nu_{17}$ FR
1232 } 1227 Q } 1221 }	m, A	1224 w	1222 m	1223 m	$\nu_{13} A'$
			1208 vw	1202 vw	1202 vw
			1171 vw	1171 vw	comb.
			1155 w	1155 w	comb.
1164 w, br				1154 w, P	$\nu_{17} + \nu_{18} A'$
1141 } 1135 Q } ~1130 }	m, A/B	1127 vw	1111 vw, br	~1110 vw, br	
~1090 vw					1082 vw
			1043 vw, br	1042 m	$\nu_{17} + \nu_{19} A'$
1039 } 1034 Q } 1027 }	m, A/B	1031 w	1029 m, br	1034 m	$\nu_{14} A'$



TABLE 3 (continued)

IR					Raman	Interpretation
Vapour	Ar matrix 15 K	Amorphous 90 K	Crystal 90 K	liquid		
990 } 981 Q } s, C 973 } 936 } 928 Q } s, C 920 }	981 m	985 s, br	{ 985 vs 974 vs	983 w, D	$\nu_{22} a''$	
	931 m	929 s	{ 933 s 930 s	929 m, D	$\nu_{23} a''$	
	925 m	~920 s, sh	{ 919 vs 912 m	~920 w, sh, P?	$\nu_{15} a'$	
850 } 841 Q } s, C 834 } 777 } 775 Q } m 772 } ~735 w }	845 s 839 s	845 s, br 839 vs	842 vs 839 s	848 m, sh, D 838 s, P	$\nu_{24} a''$ $\nu_{16} a'$	
	769 vw 765 vw	~755 m	746 m	758 vw, br, D	imp. $\text{CHCl}_3$	
	728 vw	742 w ~685 w, br 665 vw	737 w 688 w 665 vw	739 w, D 682 w, D 668 w, P	$\nu_{25} a''$ $\nu_{26} a''$ imp. $\text{CHCl}_3$	
~620 m, br	620 w	616 s	616 s	~630 w, sh 617 m, P 577 vw, P	$\nu_{18} + \nu_{30}$ $\nu_{17} a'$	
554 } 550 Q } mw 548 Q } 542 }	547 vw	549 w 542 m	551 w 542 s	551 vs, P	$\nu_{18} a'$ $\nu_{27} a''$	
				475 vw, D?		
450 } 441 } m ~380 vw		449 m, br 396 vw	{ 456 m 448 m 396 vw	446 m, br, P	$\nu_{28} + \nu_{29}$ FR $\nu_{19} a'$ FR	
~345 vw 254 w		345 vw 264 w 228 vw 170 w 106 w ~80 vw	345 vw 268 w 228 w 170 w 106 w { 83 vw 69 vw	366 w, P 348 vw, D 260 s, P 167 vs, P?	imp. $\text{CHCl}_3$ $\nu_{28} a''$ $\nu_{20} a'$ $\nu_{21} a'$ $\nu_{29} a''?$ $\nu_{30} a''?$	

<sup>a</sup>Bands in the regions  $4000-3150\text{ cm}^{-1}$ ,  $3000-2200\text{ cm}^{-1}$  and  $2000-1700\text{ cm}^{-1}$  have been omitted. <sup>b</sup>Abbreviations: s, strong; m, medium; w, weak; v, very; FR, Fermi resonance; br, broad; sh, shoulder; P, polarized; D, depolarized. A, B and C denote vapour phase band contours; comb denotes combination bands for which different alternatives are available.

in the spectrum of the vapour or in the spectrum of the amorphous solid vanish in the spectrum of the crystalline solid. This strongly suggests that only one conformer of AZBUT (known from electron diffraction to be the *syn*) is present not only in the vapour phase, but also in the liquid, amorphous and crystalline states as well.

The detection limit for an eventual second conformer of AZBUT can be estimated to be 8% by electron diffraction, but probably less than 5% from the IR spectra.

## DISCUSSION

*Structure*

Unlike vinyl azide there is no appreciable amount of any C—N *anti* conformer in AZBUT. An obvious reason is that in an *anti* form of AZBUT the outer nitrogen atom would be very close to one of the hydrogen atoms.

The structure of AZBUT is as expected from other butadienes and other azides. For example the double bonded carbon carbon distance of 135.0(4) pm is practically equal to the value in butadiene, 134.9(1) pm [26], and the single carbon carbon bond was found to be equal in both cases, 146.7 pm. The azide group seems to have distance parameters comparable with those of the simpler azides. In the present molecule the N<sub>1</sub>—N<sub>2</sub> and the N<sub>2</sub>—N<sub>3</sub> distances are 125.3(6) and 114.3(4) pm, respectively, and the NNN angle 176.5° is in good agreement with other experimental results [5, 8—11]. We are convinced that the deviation from linearity of the azide group is real. An acceptable agreement between the experimental and theoretical radial distribution curves could not be obtained with reasonable adjustments of the other geometrical parameters under the N—N—N linearity constraint. Nonlinear N—N—N fragments of approximately 170° are also in agreement with recent theoretical results from *ab initio* Hartree—Fock calculations on a series of azides [27].

One might expect the sterically crowded situation in AZBUT to be reflected in the C=C—C, C=C—N and C—N<sub>1</sub>—N<sub>2</sub> angles. The C=C—N angle is indeed large, 125.0(1.3)°, the C=C—C angle to the unsubstituted vinyl group opens 2.4(1.5)°, but the C=C—C angle at the substituted site is quite close to the value in 1,3-butadiene, 124.4(1)° [26] and the C—N<sub>1</sub>—N<sub>2</sub> angle is not significantly different from what we have found in other azides [13—17].

*Spectral assignments*

The IR and Raman spectra of AZBUT have been interpreted on the basis of the observed IR vapour contours, the Raman polarization data, and on similarities with the spectra of 2-chloro-1,3-butadiene (chloroprene) [28]. In addition force constant calculations were carried out.

The assigned fundamentals are listed in Table 4 together with the results of the force constant calculations and the "approximate motion" appearing as the largest contribution to the potential energy distribution.

A large part of the in-plane modes of AZBUT are characteristic group frequencies and their positions require no comments. The azide stretching fundamental at 2121 cm<sup>-1</sup> is extremely intense in the IR and of medium intensity in the Raman; the position and intensities are common for all the azides. There are a large number of combination bands in Fermi resonance with the fundamental. The other azide stretching mode has given rise to intense IR and Raman bands around 1250 cm<sup>-1</sup> in the saturated as well as in the unsaturated

TABLE 4

Observed and calculated vibrational fundamentals of 2-azido-1,3-butadiene in  $\text{cm}^{-1}$  (AZBUT)

	IR vapour	Raman liquid	Calc. Q. Chem.	Calc. LSFF <sup>a</sup>	Interpretation
$a'$ $\nu_1$	3115 m	3105 m	3120	3114	asym $\text{CH}_2$ stretch
$\nu_2$	3113 m		3120	3112	asym $\text{CH}_2$ stretch
$\nu_3$	3037 w	3027 s	3047	3044	C—H stretch
$\nu_4$	3025 w	3014 s	3039	3040	sym $\text{CH}_2$ stretch
$\nu_5$	3002 vw <sup>a</sup>	3005 s	3035	3022	sym $\text{CH}_2$ stretch
$\nu_6$	2121 vvs	2111 m	2145	2111	N=N stretch
$\nu_7$	1639 w	1635 vvs	1666	1641	sym C=C stretch
$\nu_8$	1590 vs	1584 s	1600	1604	asym C=C stretch
$\nu_9$	1420 vw	1415 s	1437	1426	sym $\text{CH}_2$ scissor
$\nu_{10}$	1381 vw	1378 m	1397	1378	asym $\text{CH}_2$ scissor
$\nu_{11}$	1312 vs	1297 s	1362	1313	C—H bend
$\nu_{12}$	1275 m	1284 s	1287	1298	C—C/C—N stretch
$\nu_{13}$	1227 m	1224 m	1218	1234	N=N stretch
$\nu_{14}$	1034 m	1030 m	1031	1030	$\text{CH}_2$ rock
$\nu_{15}$	920 s <sup>a</sup>	920 w	931	922	$\text{CH}_2$ rock
$\nu_{16}$	839 vs <sup>a</sup>	838 s	846	852	C—N stretch
$\nu_{17}$	620 m	617 m	641	623	NNN bend
$\nu_{18}$	550 mw	551 vs	518	555	CCC bend
$\nu_{19}$	445 m	446 m	455	443	CCN bend
$\nu_{20}$	254 w	260 s	214	254	CCC bend
$\nu_{21}$		167 vs	133	156	CNN bend
$a''$ $\nu_{22}$	981 s	983 w		978	<i>trans</i> wag
$\nu_{23}$	928 s	929 m		917	$\text{CH}_2$ wag
$\nu_{24}$	841 s	848 m		848	$\text{CH}_2$ wag
$\nu_{25}$	735 w	739 w		731	<i>cis</i> wag
$\nu_{26}$	685 w <sup>a</sup>	682 w		667	$\text{CH}_2$ twist
$\nu_{27}$	548 mw			536	CNNN torsion
$\nu_{28}$	345 vw	348 vw		356	C—N b.o.p.
$\nu_{29}$	106 w <sup>a</sup>			113	C—C torsion
$\nu_{30}$	80 vw <sup>a</sup>			79	C—N torsion

<sup>a</sup>Wavenumbers from spectrum of the amorphous phase.

azides. In AZBUT this mode can be slightly shifted because of conjugation with the butadiene system and is assigned to the band at  $1224 \text{ cm}^{-1}$ . The results from electron diffraction as well as quantum chemical calculations on a series of azides [27] reveal more than 10 pm difference in bond lengths between the two N—N bonds. The eigenvectors resulting from the normal coordinate analysis reveal that these two azide fundamentals should preferably be called N=N and N=N stretch, rather than NNN antisymmetric and symmetric stretch.

The IR and Raman bands around 1365, 1304 and  $1238 \text{ cm}^{-1}$  are all of species  $a'$  and are in part very intense. They have all been explained as com-

bination bands or overtones in Fermi resonance with  $\nu_{10}$ ,  $\nu_{12}$  and  $\nu_{13}$ . It thus appears that the two azide modes  $\nu_6$  and  $\nu_{13}$  are both surrounded by combination bands in Fermi resonance with the fundamentals.

As is apparent from Tables 3 and 4 the  $a'$  modes can all be assigned with considerable confidence. The bands around  $620\text{ cm}^{-1}$  are assigned as  $\nu_{17}$  involving the azide bending-in-plane (bip), whereas the corresponding out-of-plane (bop), or rather the CNNN torsion, is situated around  $548\text{ cm}^{-1}$ , both in good agreement with other azides. The four characteristic and fairly well localized azide frequencies: N≡N stretch, N=N stretch, NNN bip and NNN bop for a number of azides are summarized in Table 2 of ref. 1.

The out-of-plane modes  $\nu_{22}$ ,  $\nu_{23}$  and  $\nu_{24}$  can immediately be assigned to prominent IR bands with C-type vapour contours and depolarized Raman counterparts while  $\nu_{25}$ ,  $\nu_{26}$  and  $\nu_{28}$  are attributed to the weak IR bands at  $735$ ,  $685$  and  $345\text{ cm}^{-1}$ , all with weak or very weak, depolarized Raman components. More uncertain are the  $a''$  modes  $\nu_{27}$ ,  $\nu_{29}$  and  $\nu_{30}$ . We believe that the  $\nu_{27}$  mode together with  $\nu_{10}(a')$  forms the band complex at  $540\text{--}550\text{ cm}^{-1}$ ; the former is the more intense in the IR and vice versa in the Raman effect. As mentioned before,  $\nu_{27}$  corresponds to the CNNN torsion (or NNN bop) and in other azides e.g. methylazide [29], this mode is very weak in the Raman effect.

The remaining two  $a''$  fundamentals corresponds to the C—C and the C—N torsions. In 2-chloro-1,3-butadiene the C—C torsion has been observed around  $100\text{ cm}^{-1}$  [28] and we tentatively assign the weak IR bands at  $106\text{ cm}^{-1}$  to  $\nu_{29}$ . Finally, the C—N torsional mode,  $\nu_{30}$ , is attributed to the very weak IR bands around  $80\text{ cm}^{-1}$  in good agreement with the force constant calculations.

### *Force constant calculations*

We have adopted three force fields for calculating the normal modes of vibration and other vibrational quantities: (a) A standard valence force field for butadiene extended with force constants transferred from methylazide [30], (2) a symmetry force field constructed from scaled force constants from quantum chemical calculations on 1,3-butadiene [31] and on azidoethene [27] and (3) a symmetry force field constructed by adding the above mentioned constants for azidoethene to a slightly adjusted local-symmetry force field (LSFF) for 1,3-butadiene [32]. The results of the latter two calculations are listed in Table 4. It must be emphasized that the "theoretical" force constants have not been adjusted to the wavenumbers of AZBUT. The symmetry force field will be presented together with our results for 2,3-diazido-1,3-butadiene [13].

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