

THE VIBRATIONAL SPECTRA, MOLECULAR STRUCTURE AND CONFORMATION OF ORGANIC AZIDES

Part III. 2,3-Diazido-1,3-butadiene*

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ABSTRACT

A sample of 2,3-diazido-1,3-butadiene has been synthesized from 1,4-dibromo-2-butyne and tetramethylguanidinium azide. The highly explosive sample has been studied by gaseous electron diffraction and by IR spectroscopy. Only incomplete Raman spectra have been recorded due to sample decomposition in the laser beam. The title compound is found to be planar with the CNN angle equal to 114.5° , oriented *syn* to the adjacent C=C double bond; the NNN angle is ca. 167° , oriented *anti* to the C–N bond. The following bond distances (r_d) are obtained: N–N(N), 114.1; N–N(C), 124.2; C–N, 143.2; C=C, 134.8; and C–C, 148.5 pm. The vibrational spectra are tentatively assigned in terms of C_{2h} molecular symmetry, supported by force constant calculations.

INTRODUCTION

In the two previous papers in this series we have reported a brief survey of our studies on organic azides [1] and the molecular structure and an interpretation of the vibrational spectra of 2-azido-1,3-butadiene [2].

It was concluded that 2-azido-1,3-butadiene (AZBUT) has a planar structure with the CNN linkage *syn* and the NNN linkage "bent away" from the adjacent C=C bond. No additional conformers were detected in any of the states of aggregation.

2,3-Diazido-1,3-butadiene (DAZBUT) is among the most explosive azides we have studied so far and it should be handled with the utmost caution. The compound was, however, sufficiently stable as a vapour and as a capillary film at ambient temperature to allow gaseous electron diffraction and IR spectral recordings to be made. It was nearly impossible to observe a Raman spectrum since the sample decomposes rapidly, even at reduced

*Parts I and II of this series are given as ref. 1 and 2, respectively.

temperatures, when irradiated by the 488 or the 514.5 nm lines of an argon ion laser. The molecular structure and the incomplete vibrational spectra of DAZBUT are reported in the present paper.

EXPERIMENTAL

Preparative

In aqueous ethanolic sodium azide solution, 1,4-dibromo-2-butyne reacts to form 1,4-diazido-2-butyne. When the latter compound, dissolved in benzene, chloroform or in aqueous acetone solution, is heated to 310–340 K, DAZBUT is gradually formed by a rearrangement reaction [3]. Details of the synthesis and the physical and spectroscopic properties of DAZBUT valuable for characterisation have been reported [3].

Electron diffraction

The electron diffraction data were recorded with the Oslo diffraction apparatus [4] at a nozzle temperature of 293 K. Due to its low vapour pressure (1 Torr at room temperature) this compound was not well suited for an electron diffraction experiment with the ordinary equipment. A new nozzle construction was therefore employed. Data from both the usual nozzle-to-plate distances of 48.5 and 25.5 cm, were collected, and five plates from each camera distance were selected for further analysis. However, only the long camera data were employed in the final least squares run.

Calibration, intensity measurements, data reduction and the least squares analysis of the intensity curves have been described previously [2].

Spectral studies

The IR and Raman spectrometers were described earlier [2]. DAZBUT appeared to be more unstable than any of the saturated and unsaturated azides that we have studied so far and this is reflected in the spectral qualities. A mid-IR spectrum of the vapour recorded at ambient temperature appeared stable with time. A small crystal was put between KBr plates and melted (m.p. 303 K) in the IR beam to form a capillary melt. No explosions occurred in the IR beam and a reproducible melt spectrum was obtained. Low temperature, solid state IR spectra were obtained at 90 K when the sample was deposited on CsI (4000–200 cm^{-1}) and polyethylene (700–50 cm^{-1}) windows. Spectra of the polycrystalline samples were obtained after annealing to 210 K. The sample was mixed with nitrogen in a 1:1000 ratio, deposited on a CsI window at ca. 15 K and a matrix isolation spectrum was recorded between 4000 and 300 cm^{-1} .

Large difficulties were encountered in recording the Raman spectra, since the laser light can initiate explosions as well as slow decompositions of

DAZBUT. A crystallite of a few mg was initially mounted in a capillary tube kept at room temperature and illuminated with 20–30 mW 488 nm radiation. Decomposition was detected since the fluorescence rapidly increased in the spectrum, and after some time a violent explosion damaged parts of the collecting optics.

In a 50% solution in CCl_4 , the sample polymerized rapidly when exposed to 20 mW of 488 nm radiation. In a 20% CCl_4 solution at room temperature, the Raman spectrum could be recorded for 10–20 min, but decomposition and increased fluorescence occurred. A 30% solution in CS_2 was cooled to 250 K in a capillary by a stream of cold nitrogen. The sample decomposed with time but a spectrum could be recorded for ca. 1/2 h. If the sample was cooled below 250 K DAZBUT started to precipitate from the solution. The cooled CS_2 solution was illuminated with 30 mW of the 632.8 nm radiation from a helium-neon laser but no spectrum was obtained.

RESULTS

Vibrational spectra

An IR vapour spectrum of DAZBUT, recorded at full pressure in a 1 m cell is shown in Fig. 1. Because of the low pressure (ca. 1 Torr) the spectrum was not intense and in addition the vapour contours are poorly resolved and cannot be used to distinguish between bands belonging to different symmetry species. A spectrum of DAZBUT as a liquid is given in Fig. 2, while the IR spectra of the annealed crystalline solid at 90 K are given in Figs. 3 (mid-IR) and 4 (far-IR). The IR data are listed in Table 1 and the incomplete Raman results are given in the same table.

Electron diffraction

As mentioned, the explosion hazards and the low vapour pressure of DAZBUT made the recording of the electron diffraction data quite difficult.

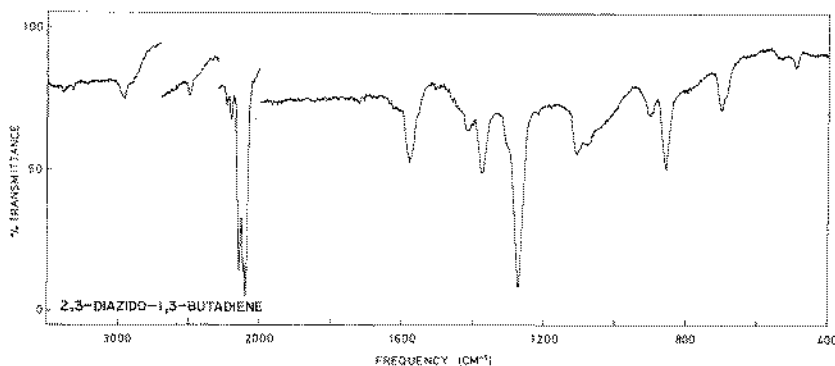


Fig. 1. The mid-IR spectrum of 2,3-diazido-1,3-butadiene (DAZBUT) in the vapour phase, 1 m path.

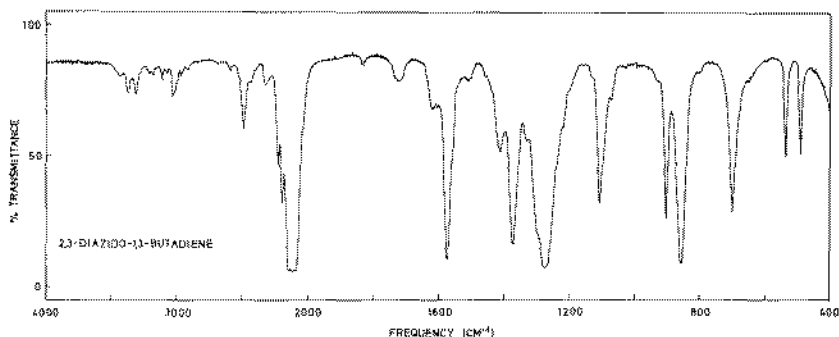


Fig. 2. The mid-IR spectrum of 2,3-diazo-1,3-butadiene (DAZBUT) as a capillary melt.

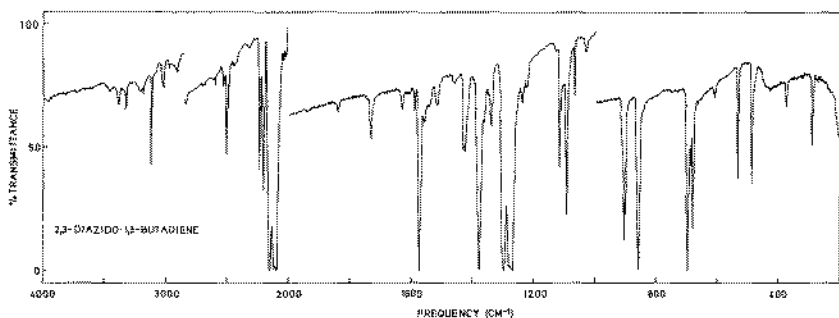


Fig. 3. The mid-IR spectrum of 2,3-diazo-1,3-butadiene (DAZBUT) as a crystalline solid at ca. 90 K, annealed at 210 K.

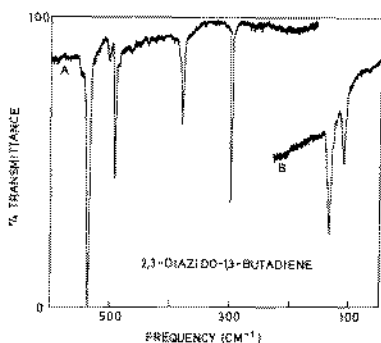


Fig. 4. The far-IR spectrum of 2,3-diazo-1,3-butadiene (DAZBUT) as a crystalline solid at ca. 90 K, annealed at 210 K.

A new doughnut-shaped nozzle constructed for samples with low vapour pressures had not been thoroughly tested when the sample was recorded. Later calibration runs with benzene revealed certain parameter deviations, particularly in the short camera distance data.

The intensity data were fitted to a theoretical curve based upon geometrically consistent r_{α} parameters [5], using a unit weight matrix in the least

squares refinements. Because of the higher symmetry the geometry of DAZBUT should be easier to determine than that of the corresponding monoazide (2-azido-1,3-butadiene) [2]. However, the experimental difficulties influenced the quality of the data. In particular, the short distance camera data showed features which could not be reproduced by the theoretical curve without unreasonable parameter adjustments and a simultaneous deterioration of the fit to the long distance camera data. The resulting geometry parameters obtained from both sets of data were not significantly different from those obtained from the long camera data alone. Accordingly, only the latter data were used in the final refinements and are presented in the tables and figures.

The long distance camera data are shown in Fig. 5 and the radial distribution curves based upon the corresponding *s*-region are given in Fig. 6, together with separate curves for other possible conformers. Geometry parameters are listed in Table 2, while the calculated vibrational root mean square amplitudes are given in Table 3.

DISCUSSION

Structure

The only conformation which could be positively detected for 2-azido-1,3-butadiene [2] is the (1) *syn* form. Therefore, it is not surprising that DAZBUT seems to exist in the (1) *syn*- (4) *syn* form only.

Because of the experimental conditions, the geometry parameters of DAZBUT have large uncertainties. However, they resemble the corresponding parameters of 2-azido-1,3-butadiene as can be seen from Table 4. The parameters associated with the butadiene part of the molecule also show close similarities with other 2,3-disubstituted butadienes. According to the results listed in Table 4 the $X-C_2-C_3$ angle is considerably smaller in both the azides than for $X = Cl$ [6] and CH_3 [7]. This may be explained by the N_3 group eclipsing the carbon-carbon double bond. On the other hand the $C-N-N$ angle in DAZBUT being 114.5° (Table 2) is quite close to our values found for the $C-N-N$ angles in 3-azidopropyne (114.5°) [8], 1-azido-2-butyne (116.5°) [9], in azidoacetonitrile (115.5°) [10] and in 3-azidopropene (115.1°) [11]. In the last four compounds the azido group does not eclipse, but is rather situated *gauche* to the $C\equiv C$, $C\equiv N$ or $C=C$ linkage [1]. Moreover the bond distances and bond angles of the azido group are quite similar in DAZBUT and in 3-azidopropyne [8]: $r(N_1-N_2)$, $r(N_2-N_3)$ and $(N-N-N)$ being 124.9(7), 113.7(6) pm and $169.2(4.1)^\circ$ in the latter and 124.2(12), 114.1(9) pm and $166.7(5.6)^\circ$ in DAZBUT, (see also Table 1 in ref. 1).

Spectral interpretations

The electron diffraction data reveal that in the vapour phase all the heavy atoms lie in a plane and that both the $C-N-N$ angles are oriented *syn* to the

TABLE 1

IR and Raman spectral data^{a,b} for 2,3-diazido-1,3-butadiene (DAZBUT)

IR			Raman		Interpretation	
Vapour	Matrix, 14 K	Liquid	Solid, 90 K	Liquid		Solid, 90 K
		~3445 w, br	~3460 vw			
			3400 vw			
		3380 w	3391 w			
		3319 w	3331 w			
		3223 vw	3220 w			
		3192 vw	3194 w			
		3122 w	3125 mw	3120		$\nu_1 a_g, \nu_{25} b_u$
		3085 vw				
	3034 w	3034 w	3040 w			
	3025 w	3020 w	3030 w	3018		$\nu_2 a_g, \nu_{26} b_u$
		~2975 vw	2981 vw			
	2920 vw	~2030 vw	2918 vw			
	2848 vw	~2850 vw	2847 vw			
	2622 vw	2603 vw	2609 vw			
		~2530 vw	2540 vw			
2500 w	2518 w	2498 m	2509 m			
			2493 vw			
		~2440 vw	~2450 vw			
			~2430 vw			
	2358 vw	~2345 vw	2333 vw			
		~2330 vw				
2246 w	2256 w	2238 m	2242 m			
	2243 vw		2236 w, sh			
2212 w	2218 w	2205 m	2211 m			
	2208 vw					
	2177 w					
2156 s	2163 s	2152 vs	2176 s			FR
	2158 s		2161 s			
	2150 w		2144 m			FR
2124 s	2133 s	~2125 vs, sh	2128 vs			FR
				2118		$\nu_3 a_g$
	2113 vs	~2115 vs, sh				
2105 vs			2106 vs			$\nu_{27} b_u$
	2102 m	2098 vs				
	2090 vw		2074 vw			
	2052 vw	~2045 w, sh	2053 vw			
			2033 vw			
			~1940 vw			
	1844 vw	1837 vw	1840 vw			
		1725 w	1733 w			
		1635 vw	1633 vw			
		1620 w		1627	1625	$\nu_4 a_g$
		1605 vw				
			1593 vw			
	1587 w	1577 m				
1582 s	1580 s	1574 s	1577 s			$\nu_{28} b_u$

TABLE 1 (continued)

IR				Raman		Interpretation
Vapour	Matrix, 14 K	Liquid	Solid, 90 K	Liquid	Solid, 90 K	
	1572 vw	1570 m	1569 w			
	1565 vw	1565 vw, sh	1563 vw			
		1557 vw, sh	1558 vw			
			1548 vw			
			1520 w, br			
			~1460 vw, br			
			1432 m			
1417 w	1421 vw	~1415 m	1426 m	1415	1420	$\nu_5 a_g$
	1411 w					
1378 m	1380 m	1375 s	1381 vs			$\nu_{29} b_u$
	1372 vw	1365 w, sh	1365 w			
	1364 vw		1353 vw			
		1335 w	1341 w	1340	1340	$\nu_6 a_g$
1300 m	1303 m	~1300 s, sh	1301 vs			FR
			1281 ms, sh			FR
			1277 s, sh			FR
1275 vs	1277 s	1272 vs	1273 vs			$\nu_{30} b_u$
	1248 vw	~1240 w, sh	1242 vw	1238	1243	$\nu_7 a_g$
	1235 vw	1222 vw	1227 vw			
		~1200 vw				
		~1135 vw				
1109 m	1115 m	1109 m	1118 m			$\nu_{31} b_u$
	1109 vw	~1095 mw, sh	1094 m			FR
	1097 w					
1080 w	1079 w	1073 w	1069 w			
			1033 vw			
		~935 vw		938	935	$\nu_8 a_g$
	917 vw					
906 w	908 s	904 s	{ 907 vs 904 s			$\nu_{32} b_u$
860 m	{ ~865 m, sh 857 s	856 vs	861 vs			$\nu_{19} a_u$
				855	868	$\nu_{14} b_g$
				840	843	$\nu_9 a_g$
	803 vw	802 vw				
704 m	700 s	700 s	699 vs			$\nu_{33} b_u$
			689 mw			
690 w	~685 vw	~680 m, sh	682 s			$\nu_{20} a_u$
538 vw	541 w	537 m	536 m			$\nu_{21} a_u$
495 w	492 m	492 m	491 m			$\nu_{34} b_u$
			377 w			$\nu_{22} a_u$
			292 m			$\nu_{35} b_u$
				185	190	$\nu_{13} a_g$
			125 m			$\nu_{36} b_u$
			97 w			$\nu_{23} a_u$

^aBands in the 4000–3500 cm^{-1} region have been omitted. ^bAbbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad; FR, Fermi resonance.

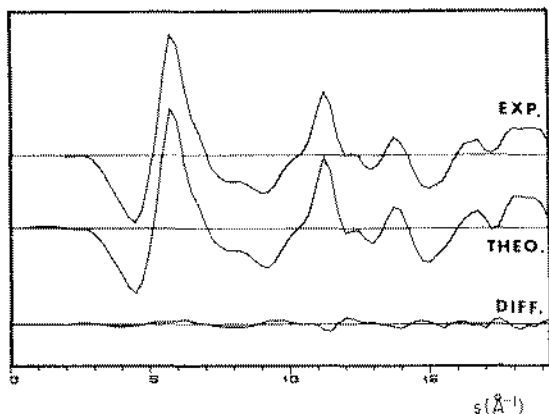


Fig. 5. 2,3-Diazo-1,3-butadiene (DAZBUT). Intensity curves in the form $sI_m(s)$. Only the long camera curve shown, $\Delta s = 0.25 \text{ \AA}^{-2}$.

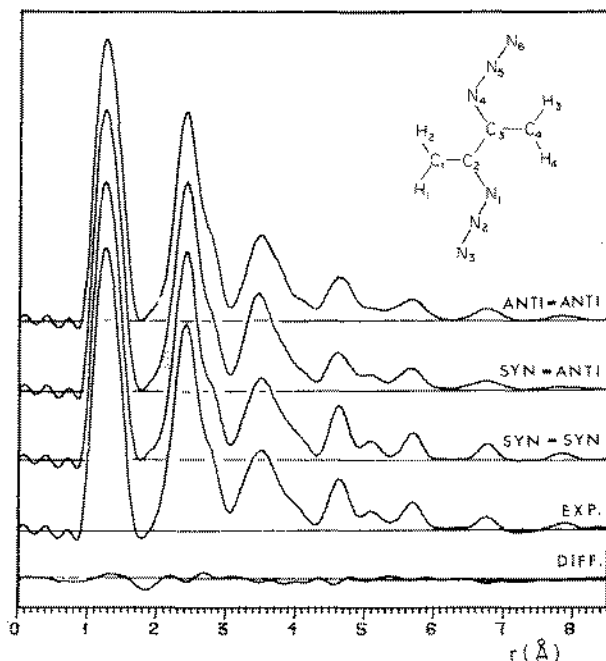


Fig. 6. Radial distribution curves for 2,3-diazo-1,3-butadiene (DAZBUT) corresponding to the experimental intensity curves in Fig. 5, to the (1)*anti*-(4)*anti* conformer and to the conformations (1)*syn*-(4)*anti* and (1)*syn*-(4)*syn*. Difference curve is exp. - theo. A modification function $(f'_C(s)f'_N(s))^{-1}$, theoretical data for unobserved area $s < 2.0 \text{ \AA}^{-1}$ and $B = 0.0035$ were used in the transformation of the intensity curves.

TABLE 2

Final results from least squares analysis of the electron diffraction data at 293 K for 2,3-diazido-1,3-butadiene (DAZBUT) (conformation (1)*syn*-(4)*syn*^a)

No.	Parameter ^b	r_a/L_α^c
1	$r(C_1-C_2)$	134.8(18)
2	$r(C_2-C_3)$	148.5(30)
3	$r(C_2-N_1)$	143.2(24)
4	$r(N_1-N_2)$	124.2(12)
5	$r(N_2-N_3)$	114.1(9)
6	$\langle r(C-H) \rangle^d$	111.0 ^e
7	$\angle C_1-C_2-N_1$	124.1(1.7)
8	$\angle C_1-C_2-C_3$	124.1(1.4)
9	$\angle C-N-N$	114.5(2.3)
10	$\angle N-N-N$	166.7(5.6) ^f
11	$\angle C-C-H^d$	119.5(3.6)
	R^g	6.9

^aAzido groups eclipsing the adjacent C=C bond. ^bAtomic numbering in Fig. 6. All bonds are designated—; there is no distinction in this column between single, double or triple bonds. ^cDistances in pm and angles in degrees. Error limits are 2σ where σ includes uncertainties in experimental conditions and in parameters used in the data reduction. ^dAverage value of the four C—H bonds/CCH angles. ^eAssumed value. ^fThe N—N—N angle is bent away from the adjacent C=C bond. ^gR-factor (%).

adjacent C=C bond. Thus DAZBUT belongs to point group C_{2h} and the 36 vibrational modes divide into $13a_g$, $5b_g$, $6a_u$ and $12b_u$ leading to a mutual exclusion between IR and Raman lines. In agreement with the results for 2-azido-1,3-butadiene [2], no significant spectral changes occurred when the amorphous solid of DAZBUT was annealed in the IR cryostat. Thus, we assume that no additional conformer exists and the spectra of DAZBUT have been interpreted in terms of C_{2h} symmetry in all states of aggregation.

As is apparent from Table 1, many of the observed Raman bands (some of which are uncertain, see above) coincide with weak IR bands. For the C—H stretching vibrations, the a_g modes ν_1 and ν_2 are accidentally degenerate with the b_u modes ν_{25} and ν_{26} . The Raman bands assigned as the a_g modes ν_4 — ν_8 apparently coincide with weak IR active combination bands or overtones.

The complete lack of Raman polarization data and the means to distinguish between the IR active a_u and b_u fundamentals, renders the assignments in Tables 1 and 5 highly tentative. The interpretation is strongly dependent upon the results of the force constant calculations. It appears from Table 5 that the agreement between the observed and calculated frequencies is quite satisfactory. More importantly, the assignment of the "butadiene-vibrations" agrees well with those suggested for 2,3-dihalo-1,3-butadienes [12, 13].

The large number of IR peaks not assigned as fundamentals can all be explained by binary combinations of *gerade* and *ungerade* modes. Particularly, for the strong bands in the vicinity of the $N\equiv N$ and $N=N$ stretching fundamentals of b_u symmetry at ca. 2100 and 1270 cm^{-1} , respectively,

TABLE 3

Interatomic distances and calculated r.m.s. amplitudes of vibration (pm) for the most important CC, CN and NN distances in 2,3-diazido-1,3-butadiene (DAZBUT)

Distance ^a	<i>r</i>	<i>l</i>
N ₂ -N ₃	114	3.4
N ₁ -N ₂	124	4.0
C ₁ -C ₂	135	4.2
C ₂ -N ₁	143	4.8
C ₂ -C ₃	149	4.6
C ₂ ··N ₂	226	6.9
N ₁ ··N ₃	236	4.5
C ₃ ··N ₁	241	7.2
C ₁ ··N ₁	245	6.4
C ₁ ··C ₃	250	6.0
C ₁ ··N ₂	269	11.2
C ₄ ··N ₁	278	11.5
C ₂ ··N ₃	331	8.4
C ₁ ··N ₃	350	15.7
C ₃ ··N ₂	351	7.2
N ₁ ··N ₄	367	7.7
C ₁ ··C ₄	373	6.1
C ₄ ··N ₂	399	11.8
C ₃ ··N ₃	463	7.7
N ₂ ··N ₄	463	8.9
C ₄ ··N ₃	509	12.3
N ₂ ··N ₅	568	8.7
N ₁ ··N ₆	570	10.8
N ₃ ··N ₅	677	9.7
N ₃ ··N ₆	787	10.1

^aAtomic numbering in Fig. 6.

TABLE 4

Comparison between various geometrical parameters^a of 2,3-diazido-1,3-butadiene (DAZBUT) and some related butadienes

Parameter	2,3-Diazido- 1,3-butadiene (DAZBUT) ^b	2-Azido- 1,3-butadiene (AZBUT) ^c	2,3-Dichloro- 1,3-butadiene ^d	2,3-Dimethyl- 1,3-butadiene ^e
r(C=C)	134.8(18)	135.0(4)	133.7(2)	134.9(6)
r(C-C)	148.5(30)	146.7(8)	147.2(4)	149.1(6)
C=C-C	124.1(17)	123.7(11)	126.1(3)	122.0(20)
C-C-X	111.8(15)	111.3(12)	115.2(3)	117.9(15)
C=C-X	124.1(14)	125.0(13)	118.7(3)	120.1(18)

^aDistances in pm, angles in degrees. ^bFrom this work. ^cFrom ref. 2. ^dFrom ref. 6. ^eFrom ref. 7.

TABLE 5

Observed and calculated vibrational fundamentals of 2,3-diazido-1,3-butadiene (DAZBUT) (cm^{-1})

	IR liquid	Raman liquid	Calculated		Description
			Quantum chemistry	LSFF ^b	
a_g ν_1		3120	3100	3143	asym CH_2 stretch
ν_2		3018	3017	3040	sym CH_2 stretch
ν_3		2118	2112	2112	$\text{N}=\text{N}$ stretch
ν_4		1627	1654	1655	sym $\text{C}=\text{C}$ stretch
ν_5		1415	1409	1433	sym CH_2 scissor
ν_6		1340	1261	1338	$\text{C}-\text{C}/\text{C}-\text{N}$ stretch
ν_7		1238	1216	1232	$\text{N}=\text{N}$ stretch
ν_8		938	911	924	CH_2 rock
ν_9		840	805	843	$\text{C}-\text{N}$ stretch
ν_{10}			630	629	NNN bend
ν_{11}			438	526	CCC bend
ν_{12}			259	303	CCN bend
ν_{13}		185	162	177	CNN bend
b_g ν_{14}		855		853	CH_2 wag
ν_{15}				698	CH_2 twist
ν_{16}				550	CNNN torsion
ν_{17}				438	$\text{C}-\text{N}$ b.o.p.
ν_{18}				90	$\text{C}-\text{N}$ torsion
a_u ν_{19}	856			853	CH_2 wag
ν_{20}	680			701	CH_2 twist
ν_{21}	537			544	CNNN torsion
ν_{22}	377 ^a			370	$\text{C}-\text{N}$ b.o.p.
ν_{23}	97 ^a			96	$\text{C}-\text{N}$ torsion
ν_{24}				39	$\text{C}-\text{C}$ torsion
b_u ν_{25}	3122		3100	3112	asym CH_2 stretch
ν_{26}	3020		3018	3040	sym CH_2 stretch
ν_{27}	2098		2110	2110	$\text{N}=\text{N}$ stretch
ν_{28}	1574		1563	1609	asym $\text{C}=\text{C}$ stretch
ν_{29}	1375		1376	1380	asym CH_2 scissor
ν_{30}	1272		1314	1270	$\text{N}=\text{N}$ stretch
ν_{31}	1109		1126	1089	CH_2 rock
ν_{32}	904		873	885	$\text{C}-\text{N}$ stretch
ν_{33}	700		743	721	NNN bend
ν_{34}	492		500	483	CCN bend
ν_{35}	292 ^a		234	285	CCC bend
ν_{36}	125 ^a		80	109	CNN bend

^aWavenumbers from spectrum of the amorphous solid. ^bLSFF, local symmetry force field.

several combinations are plausible. The intensity enhancement of these bands is obviously caused by Fermi resonance with the fundamentals.

Force constant calculations

We have adopted three sets of force constants common for AZBUT and DAZBUT for calculating the normal modes of vibration and other vibrational quantities: (1) a standard valence force field for butadiene extended with force constants transferred from methylazide [14]; (2) a symmetry force field constructed from scaled force constants from quantum chemical calculations on 1,3-butadiene [15] and on azidoethene [16]; and (3) a symmetry force field constructed by adding the abovementioned constants for azidoethane to a slightly adjusted local-symmetry force field (LSFF) for 1,3-butadiene [17]. The results of the last two calculations are listed in Table 5. It must be emphasized that the "theoretical" force constants have not been adjusted to the wavenumbers of AZBUT and DAZBUT.

For the sake of brevity we only give the azide part of the force field in Table 6 as obtained from Hartree-Fock level calculations using a gradient version of the program MOLECULE [18, 19]. A $7s3p$ (C, N) [20] and a $4s$ (H) [21] primitive basis set was employed. The primitive sets were contracted to double zeta quality ($7s3p \rightarrow 4s2p$; $4s \rightarrow 2s$), the orbital exponent on hydrogen being scaled by a factor of 1.2 [22].

Together with the computed harmonic force constants, F_{ij} , the scaled

TABLE 6

Force field for the in-plane deformations of the azide group attached to a vinylic fragment as calculated by quantum chemical methods

	C=C	C-N	N=N	N≡N	CCN	CNN	NNN
C=C	12.13 ^{a,b} 8.89 ^c	0.65	-0.16	0.16	0.42	0.01	-0.02
C-N	0.5	5.40 ^b 4.75 ^c	0.60	-0.37	0.17	0.81	-0.03
N=N	-0.1	0.5	7.22 ^b 8.85 ^c	2.29	-0.62	1.17	0.34
N≡N	0.1	-0.3	2.2	22.57 ^b 18.00 ^c	0.15	-0.20	-0.11
CCN	0.3	0.1	-0.6	0.1	2.07 ^b 1.65 ^c	-0.03	0.00
CNN	0	0.6	1.1	-0.1	0	1.44 ^b 1.30 ^c	0.15
NNN	0	0	0.3	-0.1	0	0.1	0.77 ^b 0.63 ^c

^aUnits: mdyne Å⁻¹ (stretch), mdyne Å rad⁻¹ (bend), mdyne rad⁻¹ (stretch/bend). ^bComputed harmonic force constants above diagonal (see text). ^cScaled harmonic force constants below diagonal (see text).

values, $F'_{ij} = (x_i x_j)^{1/2} F_{ij}$, are listed where the scale factors, x_i and x_j , for the coordinates i and j , respectively, have been transferred from theoretical studies of other azides [16, 23]. Further details regarding the force fields are available from the authors upon request.

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