

THE VIBRATIONAL SPECTRA, MOLECULAR STRUCTURE AND CONFORMATION OF ORGANIC AZIDES Part VIII. 3-Azidopropene (allylazide)*

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ABSTRACT

3-Azidopropene ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{N}_3$) has been synthesized and the structure and conformational composition studied by electron diffraction from the vapour. IR spectra have been recorded of the vapour, of the liquid and of the amorphous solid at ca. 90 K. Raman spectra of the cooled liquid and of the amorphous and crystalline solids at 90 K have also been obtained.

Analysis of the electron diffraction data reveals a multiplicity of indistinguishable solutions to the conformational composition consisting of variable amounts of the three conformers *SG*, *GG* and *GG'*, the letters referring to the conformation around the C-C and C-N bonds, respectively. As extremes, the electron diffraction data could be interpreted by either a mixture of only two conformers, 73(15)% *GG* and 27% *SG*, or a mixture consisting of equal amounts of *GG* and *GG'*, 87(20)% in total, and 13% *SG*. Assuming only the *GG* and *SG* conformers to be present in the vapour, a transoid arrangement of the azide chain, $r_{\text{C-C}}=150.8$ pm, $\angle_{\text{C-C-H}}=120.8^\circ$ and torsional angles $\tau_{\text{C-C}}=0, 120^\circ$ the following structural parameters (r_{a} , \angle_{α}) are derived for the *GG* form: $r_{\text{N=N}}=113.8(4)$ pm, $r_{\text{N=N}}=123.6(5)$ pm, $r_{\text{C-N}}=147.5(15)$ pm, $r_{\text{C-C}}=133.1(7)$ pm, $\angle_{\text{NNN}}=174(5)^\circ$, $\angle_{\text{CNN}}=115.1(14)^\circ$, $\angle_{\text{NCC}}=111.8(34)^\circ$, $\angle_{\text{CCC}}=121.6(30)^\circ$ and $\tau_{\text{C-N}}=60(10)^\circ$.

The vibrational spectra are interpreted in terms of two conformers, *GG* and *SG*, present in the vapour and the liquid and, based upon normal coordinate calculations, of the *SG* conformer in the crystalline solid. The normal modes of vibration for the five distinct conformations of 3-azidopropene are calculated using transferred scaled quantum mechanical force fields for propene and azidoethane.

* Part VII of this series is given as ref. 1.

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INTRODUCTION

3-Azidopropene ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{N}_3$, allylazide, ALAZ) was synthesized for the first time as early as in 1908 [2]. We note without comment a description from that early paper of a property of the compound, "The vapour, when inhaled, produces the characteristic throbbing sensation at the base of the forehead". The compound is relatively stable and easy to prepare. However, it has not aroused general interest among chemists and the published physical properties of the compound are scant. Actually, the compound was not studied again by physical methods until 1950 when good quality Raman data and a low resolution IR spectrum of the 4000–1000 wavenumber region were published [3]. Later the dipole moment was measured as 1.92 D in benzene solution [4] and the position and intensities of the stretching frequencies of the azide group were investigated as part of a general study of the IR spectra of organic azides [5]. More recently, the gas phase pyrolysis of ALAZ has been studied by photoelectron spectroscopy [6], the UV, ^{13}C NMR and ^1H NMR data published [7] and a preliminary report containing some of the spectroscopic and structural properties of ALAZ has been published together with a brief survey of our studies on organic azides [8].

It is well established from microwave, electron diffraction, NMR and vibrational studies that 1-butene [9–12], the 3-halopropenes (F, Cl, Br and I) [13–18] and the 3-pseudohalo-propenes ($-\text{NCO}$, $-\text{NCS}$ and $-\text{CN}$) [19–21] exist as mixtures of *syn* and *gauche* conformations in the vapour and liquid

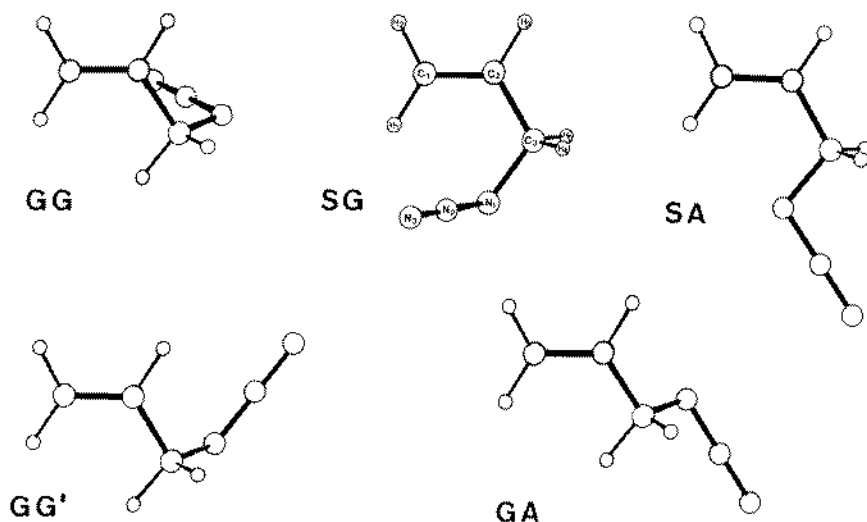


Fig. 1. The five possible conformations of 3-azidopropene: (SA) $\tau_{\text{C-C}}=0^\circ$, $\tau_{\text{C-N}}=180^\circ$; (SG) $\tau_{\text{C-C}}=0^\circ$, $\tau_{\text{C-N}}\approx 60^\circ$; (GA) $\tau_{\text{C-C}}=120^\circ$, $\tau_{\text{C-N}}=180^\circ$; (GG) $\tau_{\text{C-C}}=120^\circ$, $\tau_{\text{C-N}}\approx 60^\circ$; (GG') $\tau_{\text{C-C}}=120^\circ$, $\tau_{\text{C-N}}\approx -60^\circ$.

phases (see also older references quoted in refs. 9–21). In 3-azidopropene there are in addition to the conformational possibilities around the C–C bond (*syn* and *gauche*) also the same possibilities around the C–N bond (*anti* and *gauche*). As shown in Fig. 1 there are five distinct conformations of ALAZ with the obvious designations *SA*, *SG*, *GA*, *GG* and *GG'*, respectively. As to the preferred conformation of the azido group in a $-\text{CH}_2-\text{N}_3$ arrangement only four vapour phase studies have so far been reported: 3-azidopropyne [22], azidoacetonitrile [23], azido-2-butyne [1] and 3,3-bisazidomethyloxetane [24]. All these molecules exist only in the *gauche* conformation with $\tau_{\text{C-N}} = 37, 52, 37$ and 70° from the *syn* position, respectively. On the other hand, both ab initio calculations [25] and the results from a vibrational spectroscopic study of azidoethane [26] show a very small energy difference between the *gauche* and *anti* conformations in this molecule.

EXPERIMENTAL

Sample preparation

The sample of ALAZ was prepared by an ultrasound synthesis from 3-bromopropene and sodium azide dissolved in water as previously described [7]. $\text{B.p.}_{760} = 76.5^\circ\text{C}$ [2].

Spectra

IR spectra of ALAZ 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 and 20 cm pathlengths equipped with windows of CsI and polyethylene, respectively. Spectra were also obtained of a CCl_4 solution at room temperature and of the solid at ca. 90 K before and after annealing using cryostats cooled with liquid nitrogen. However, in spite of persistent annealing experiments we never succeeded in obtaining a crystalline sample.

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. The tube was inserted in a transparent Dewar [27] and cooled to ca. 220 K. Raman spectra of the solid formed by further cooling to ca. 90 K were also obtained. It was very difficult to obtain a crystalline sample and we succeeded only once, in an experiment where the sample was annealed overnight in a capillary at ca. 150 K.

Electron diffraction

The electron diffraction data were recorded on Kodak Electron Image plates with the Oslo apparatus [28] at a nozzle temperature of 293 K and nozzle-to-plate distances of 48.5 and 20.5 cm; five plates for each distance were selected for the analysis. The electron wavelength was calibrated against benzene [29], optical densities were measured with a Joyce Loebel densitometer and the data were reduced in the usual way [30,31] yielding two averaged intensity curves (one from each distance) in the form $sI_m(s)$.

RESULTS AND DISCUSSION

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. 2. A unit weight matrix was used. The molecular geometry was calculated from the geometry consistent r_α model [32] and the root mean square amplitudes of vibration (l) and perpendicular correction coefficients (K) were constrained to the values calculated from approximate force fields.

As previously mentioned ALAZ can exist in five distinct conformations (Fig. 1). The RD curves for each of these five conformers are shown for comparison with the experimental curve in Fig. 3. It is immediately clear from a visual

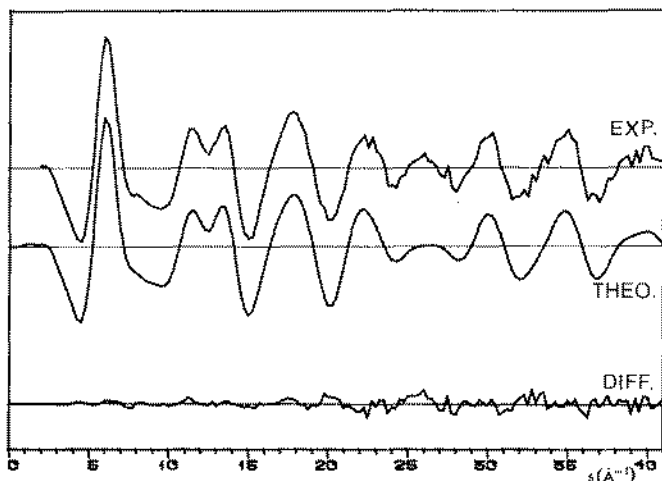


Fig. 2. Experimental and theoretical intensity curves in the form $sI_m(s)$ for 3-azidopropene. Experimental curve is the composite of all plates and camera distances. Theoretical curve was calculated from the parameters in Tables 1 and 2. All curves are on the same scale. $\Delta s = 0.25 \text{ \AA}^{-1}$.

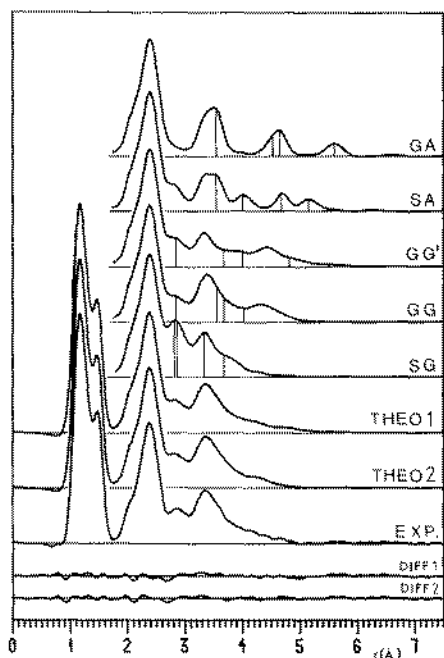


Fig. 3. Theoretical radial distribution curves for the 5 possible conformations of 3-azidopropene (*GA*, *SA*, *GG'*, *GG* and *SG*), for the conformational compositions *SG*+*GG* (Theory 1) and *SG*+*GG*+*GG'* (Theory 2) and the experimental curve calculated from the intensity curve in Fig. 2 after 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.

inspection that:

(i) the conformations *GA* and *SA* can only be present in very small amounts, probably less than 5%;

(ii) more than one of the three conformations *GG'*, *GG* and *SG* are present.

A closer inspection of the RD-curves and a simple conformational composition analysis reveals that:

(iii) the amount of the *SG* conformer present is less than the combined amounts of the *GG'* and *GG* conformations;

(iv) the amount of the *GG* conformer is larger than that of the *GG'* conformer. Hence, we analysed the electron diffraction data using two limiting models; the simpler, model 1, taking only the *SG* and the *GG* conformations into account, and a more elaborate, model 2, also including the *GG'* conformation in an amount equal to that of the *GG* form.

Some constraints had to be imposed upon the molecular models. The bonded distances are in all likelihood almost identical for the *GG*, *GG'* and *SG* conformers. However, some of the skeletal angles may vary by a few degrees from conformer to conformer as has been demonstrated by the microwave study of 3-fluoropropene [13] and indicated by the electron diffraction studies on other

TABLE 1

3-Azidopropene: geometrical parameters for the *GG* conformer from a least squares refinement of the electron diffraction data at 293 K; the final model has two conformers, *GG* and *SG*

No.	Parameter ^a	Values ^b	No.	Parameter ^a	Values ^b
1	$r_{N_1-N_2}$	123.6(5)	10	$\angle C-C=C$	121.6(30) ^e
2	$r_{N_2-N_3}$	113.8(4)	11	$\left. \begin{array}{l} \langle \angle C-C-H \rangle \\ \langle \angle N-C-H \rangle \end{array} \right\}$	109 ^d
3	r_{C-N}	147.5(15) ^c			
4	$r_{C_1-C_2}$	133.1(7)	12	$\langle \angle C=C-H \rangle$	120.8 ^d
5	$r_{C_2-C_3}$	150.8 ^d	13	$\tau_{C_2-C_3}$	120 ^{d,f}
6	$\langle r_{C-H} \rangle$	109.4(15)	14	τ_{C-N}	60(10) ^e
7	$\angle N-N-N$	174(5)	15	α_{GG}	73(15)
8	$\angle C-N-N$	115.1(14)		R_{lc}/R_{sc} ^g	5.9/17.7
9	$\angle N-C-C$	111.8(34) ^e			

Correlation coefficients > 0.4

$$C_{12} = 0.41 \quad C_{14} = 0.65 \quad C_{26} = -0.35$$

$$C_{78} = 0.67 \quad C_{710} = 0.42 \quad C_{810} = 0.41$$

$$C_{910} = -0.88$$

^aAtomic numbering as shown in Fig. 1. ^b r_a values in pm and \angle_α values in degrees. ^cValue found by systematic variation, uncertainty estimated. ^dValue constrained, chosen from related molecule.

^eThe corresponding value for the *SG* conformer was constrained to be 1.5° larger. ^fNNN fragment eclipsing the C=C bond in the *SG* conformation. ^g R -factors in % for long camera (lc) and short camera (sc) distances.

TABLE 2

3-Azidopropene (ALAZ), interatomic distances (r_a) and calculated^a root mean square amplitudes of vibration (l) in pm for the *GG* and *SG* conformers

Distance ^b	r_a	l	Distance ^b	r_a	l
	<i>GG/SG</i>	<i>GG/SG</i>		<i>GG/SG</i>	<i>GG/SG</i>
C-H	109	7.8	$N_1 \cdots H_3$	284/346	18.0/10.9
N_2-N_3	114	3.4	$N_2 \cdots H_3$	284/287	16.5/14.7
N_1-N_2	124	3.9	$N_2 \cdots H_3$	324/388	31.4/18.8
C_1-C_2	133	4.1	$N_3 \cdots C_3$	330	9.1
C-N	148	4.8	$C_1 \cdots H_5$	314	14.7
C_2-C_3	151	4.8	$N_3 \cdots H_1$	340/342	22.9/21.4
$N_1 \cdots H_5$	208	10.5	$N_1 \cdots C_1$	348/281	13.2/12.7
$C_1 \cdots H_3$	211	9.9	$N_2 \cdots C_1$	353/282	24.8/25.4
$C_3 \cdots H_3$	222	10.5	$N_2 \cdots C_2$	361/365	23.4/20.3
$N_1 \cdots N_3$	237	4.6	$N_2 \cdots H_1$	370/220	38.0/39.8
$N_1 \cdots C_2$	248	7.9	$N_1 \cdots H_1$	374/246	22.5/20.8
$C_1 \cdots C_3$	249	6.4	$N_3 \cdots H_5$	397/462	42.2/25.9
$C_3 \cdots H_1$	273	14.3	$N_3 \cdots C_1$	404/332	34.0/37.1
$C_3 \cdots H_2$	348	10.0	$N_3 \cdots H_1$	412/255	49.6/55.8
$C_2 \cdots H_4$	212	10.7	$N_3 \cdots H_4$	425	11.0
$N_2 \cdots C_3$	228	7.6	$N_2 \cdots H_2$	434/382	27.3/27.0
$C_1 \cdots H_4$	254/315	14.2/14.7	$N_1 \cdots H_2$	437/389	15.6/14.6
$N_2 \cdots H_4$	255	17.7	$N_3 \cdots H$	470/415	39.6/41.5

^aThe l -values shown in the table correspond to torsional force constants of 0.06 and 0.10 mdyne Å rad⁻² for torsion around the C-C and C-N bonds, respectively.

^bAtomic numbering shown in Fig. 1.

TABLE 3

Comparison of some geometrical parameters (bond lengths in pm, angles in degrees) of 3-azidopropene with related molecules

Molecule	r_{C-C}	r_{C-C}	$\angle CCC$	r_{C-N}	$r_{N=N}$	$r_{N=N}$	$\angle CCN$	$\angle CNN$	$\angle NNN$	Ref.
$CH_2=CH-CH_3$	133.6(4)	150.1(4)	124.3(3)							43
$CH_2=CH-CH_2-F$	133.3(10)	148.8(15)	121.6(10) ^a 124.6(10) ^b							13
$CH_2=CH-CH_2-Cl$	134.4(5)	150.6(6)	122.7(11)							15
$CH_2=CH-CH_2-Br$	133.5(7)	148.5(8)	126.0(26)							16
$CH_2=CH-CH_2-CN$	132.6(7)	150.8(5)	125.0(18)							20
$CH_2=CH-CH_2-N=N=N$	133.1(7)	150.8 ^d	121.6(30) ^c	147.5(15)	123.6(5)	113.8(4)	111.8(34) ^c	115.1(4)	174(5)	This work
$N=C-CH_2-N=N=N$		146.5(15)		147.6(6)	124.5(5)	113.5(4)	113.4(10)	115.4(11)	173(3)	23
$HC\equiv C-CH_2-N=N=N$		148.1(13)		146.4(13)	124.9(7)	113.7(6)	114.6(12)	114.5(15)	169.2(41)	22
$CH_3C\equiv C-CH_2-N=N=N$		146.8(5)		147.4(15)	124.0(6)	114.2(5)	113.8(16)	116.5(14)	174(5)	1
$H-N=N=N$					124.3(5)	113.4(2)			171.3(50)	38
$CH_3-N=N=N$				146.8(5)	121.6(4)	113.0(5)		116.8(3)	180 ^d	43
$CF_3-N=N=N$				142.7(5)	125.0(7)	111.7(4)		111.8(11)	175.3(43)	37
$N\equiv C-N=N=N$				135.5(2)	126.1(1)	112.7(2)		114.5(2)	169.2(16)	36
$CH_2-O-CH_2-C-(CH_2N_3)_2$				147.0(9)	124.0 ^e	114.2	111.4(12)	119.2(10)	180 ^d	24

^aAngle in *gauche* conformation. ^bAngle in *syn* conformation. ^cThe corresponding angle in the *SG* conformer was constrained to be 1.5° larger.^dAssumed. ^eGiven as $NN_{av.} = 1.191(2)$ and $NN_{diff.} = 0.098(2)$ pm.

3-substituted propenes [15, 16, 20] and on 4-substituted butenes [33]. Such variations were likewise introduced as constraints to the models. We have further treated the five C-H distances as identical, constrained the three C=C-H angles to 120.8° , the four $\text{CCH}_2/\text{NCH}_2$ angles to 109° and assumed a transoid arrangement of the azide group in accordance with previous results for covalently bonded azides [1, 22, 23, 34-38]. These constraints had virtually no influence on the other structural parameters or on the conformational composition. Finally, the C-C distance turned out to be strongly correlated to the C-N distance and was consequently constrained to 150.8 pm in the final refinements.

The torsional angles, $\tau_{\text{C-C}}$ and $\tau_{\text{C-N}}$, were varied systematically for all conformers in the regions near the expected potential energy minima. However, the data allowed no precise determination of these angles and only the extremes could be fixed.

The theoretical RD curves for models 1 and 2 have been included in Fig. 3. As can be seen it is difficult, if not impossible, to favour either model over the other based on a purely statistical analysis. According to model 1 the conformational composition was 27(15)% and 83% of the *SG* and the *GG* conformations, respectively, and in the other extreme (model 2) the conformational composition was 87(20)% of *GG* and *GG'* (in equal amounts) and consequently 13% of the *SG* form.

In conclusion, the electron diffraction data indicate that at room temperature 3-azidopropene exists as a mixture of two or three conformers: approximately 20% of the *SG* form, somewhere between 40-80% of the *GG* form and accordingly 40-0% of the *GG'* form.

A series of ab initio calculations is currently being performed on the five conformations of ALAZ [39] and only preliminary results are available for the present investigation. However, the calculations indicate that the most stable conformer is indeed the *GG* form, followed by the *SG* form (ca. 2 kJ mol^{-1} higher) while the *GG'*, *GA* and *SA* forms are a further ca. 4 kJ mol^{-1} higher in energy. This suggests then that the two-conformer model (model 1) is quite adequate for the analysis of the electron diffraction data at 293 K but not at higher temperatures.

The geometrical parameters as obtained from the electron diffraction experiment using the two-conformer model (model 1) are listed in Table 1, whereas the internuclear distances and the corresponding *l*-values are given in Table 2. The similar results using the three-conformer model (model 2) are, within the uncertainties, identical to those given in Table 1. Finally, in Table 3 the structural parameters are compared with the results for related molecules verifying that the structural parameters are reasonable and thus lending some support to the validity of the conformational composition analysis.

The bonding properties and the charge distribution in covalent bonded azides are usually discussed in terms of two resonance structures:



Gross atomic charge calculations at the Hartree-Fock SCF-level with large basis sets on HN_3 [25, 40] and ClN_3 [41] show that the charge distribution of the azide group is best described by structure (a). The conformational preference in ALAZ, *GG* and *SG*, may be rationalized in terms of Coulombic attraction/repulsion between the π -electron system of the $\text{C}=\text{C}$ double bond and that of the azide group by analogy to our proposals for the all *gauche* series $\text{H}-\text{C}=\text{C}-\text{CH}_2-\text{N}_3$, $\text{N}=\text{C}-\text{CH}_2-\text{N}_3$ and $\text{CH}_3-\text{C}=\text{C}-\text{CH}_2-\text{N}_3$ [1]. As can be seen from Fig. 1, only the *GG* and *SG* conformations would have an attractive term in the potential energy.

Vibrational spectra

The IR spectrum of ALAZ as a vapour is given in Fig. 4 while the Raman spectra of the cooled liquid and of the crystalline solid at ca. 100 K are given in Figs. 5 and 6, respectively. The 25 year old Raman data [3] are very impressive and only two weak bands reported at 504 and 1115 cm^{-1} have not been observed in any of our spectra. On the other hand, our spectra are much more detailed and several new (weak) bands have been observed. The spectral data are collected in Table 4 and the assigned fundamentals are compared with the results of normal coordinate calculations (see later) for each of the five possible conformations of ALAZ in Table 5.

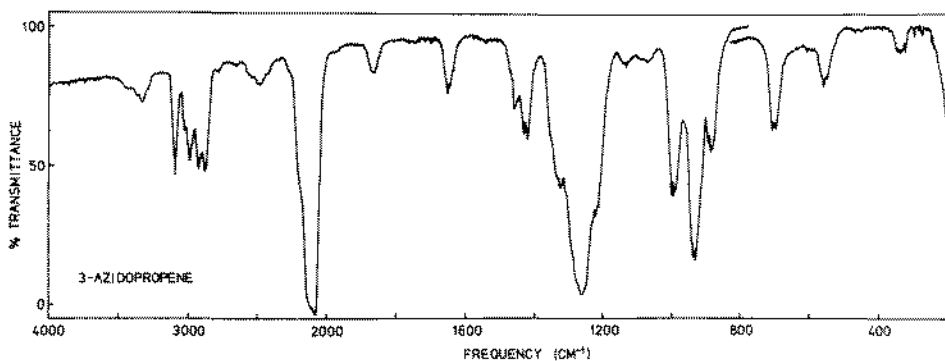


Fig. 4. Mid-IR vapour phase spectrum of 3-azidopropene. Pathlength 10 cm, pressure 40 Torr.

TABLE 4

Vibrational spectral data^a for 3-azidopropene (allylazide)

Infrared			Raman			Interpretation	
Vapour	Solution 300 K	Amorph. solid 90 K	Liquid 250 K	Amorph. solid 90 K	Cryst. solid 90 K	SG confor- mation	GG confor- mation
3103	Q } m	3090 s	3090 m	3088 m	3090 m	ν_2	
3096							
3088							
~3080	w	3075 m			3071 w		
3033	Q } w	3020 m	3020 vs	3018 vs	3018 s	ν_2	
3026							
3018							
2990	} m	2989 s	2989 s	2984 s	2991 w	ν_3	
2975							
		~2970 m, sh			2960 m	ν_4	
2931	} m	2925 s	2932 m	2936 m	2926 m	ν_5	
2924							
		~2910 m, sh	2917 m	2915 w	2915 w		
2892	Q } m	2875 m	2880 w	2880 w	2866 w		
2884							
2875							
		~2860 m, sh	2860 vw, sh				
			2832 vw, sh	2840 vw, sh			
2210	m, sh		2210 w, sh				
~2190	m, sh		2185 m				
			~2150 s, sh				
2146	w, sh		2125 vs, sh	~2125 vw, sh			
2108	vs	2105 vs	2108 vs	2104 w	2105 w	2097 m	ν_6
2078	w, sh	2080 s, sh	2075 vs	2076 w	2073 w	2067 w	
1657	} w	1649 m	1648 w	1644 vs	1641 vs	1648 m	ν_7
1649							
1643							
		1642 m, sh	1640 m	1620 vw	~1616 vw		
			1635 w, sh				
			1458 w, sh				
~1455	w	1452 m	1453 m	1455 w	1454 w	—	ν_8
~1440	w	1440 m	1439 w	1443 w	1441 vw	1442 m	ν_8
1431	Q } m	1418 s	1420 w, sh	1420 m	1417 m	1414 m	ν_9
1423							
1416							
		1408 m, sh	1405 w, sh	1410 w, sh			
		1371 m				1377 vw	
1356	m, sh	1345 s	1347 m				
1335	} m	1325 s	1338 m	1339 w	1341 w	1342 m	ν_{10}
1322							
			~1330 m, sh	~1325 w, sh			ν_{10}
1305	} m	1290 s, sh	1297 m, sh	1291 s	1289 s	1288 s	ν_{11}
1289							
		1275 s, sh	1280 s			1280 m	ν_{12}
1260	} s	1250 vs	1252 s	1251 w	1249 m	—	ν_{12}
1245							

Infrared		Raman					Interpretation						
Vapour	Solution 300 K	Amorph. solid 90 K	Liquid 250 K	Amorph. solid 90 K	Cryst. solid 90 K	SG confor- mation	GG confor- mation						
1227	} m	1215 s	1221 m, sh	1221 m	1221 m	1217 m	ν_{12}						
1220			1212 s		1212 m			—	ν_{13}				
1210													
1133 w	1133 w	1131 w 1126 vw, sh	1134 vw	1130 vw	—		ν_{14}						
1094 vw			1110 vw ~1080 vw, sh	1083 vw									
		1045 w	1065 w	1066 vw	1066 w	1066 m	ν_{14}						
1000	} ms	991 vs	998 vs	995 vw	1000 vw	1009 w	ν_{15}						
994 Q								966 m	969 m	968 vw	970 vw	~988 vw?	ν_{16}
988													
938	} Q	933 vs	940 s	940 w	946 w	935 w	ν_{17}						
934													
928								925 s, sh	921 s	~925 vw, sh	920 w	918 w	ν_{18}
921													
892	} m	875 s	~900 vw	~900 vw, sh	902 vw								
886			856 w 786 w	~860 w, sh	857 w	856 m	ν_{19}						
709	} m	706 s	709 s	~706 w	708 w	—	ν_{20}						
698			~695 m, sh	~685 vw, sh	~690 vw, sh	688 w	ν_{20}						
619	} vw	603 m	609 m	608 m	610 m	—	ν_{21}						
612													
569	} w	558 s ~555 m, sh	563 s	561 w	565 w	565 w	ν_{21}						
562			557 m, sh	~540 vw	~540 vw	543 w	ν_{22}						
553			423 m	420 m	422 m	—	ν_{23}						
347	} w	344 m	359 m	346 w	~360 w	—							
344			283 w	294 w	291 w	~295 vw	294 m	ν_{24}					
329			278 w	280 w	277 w	~280 vw	—						
227	} w	224 m	229 m	224 m	230 w	261 m	ν_{25}						
218													
212													
									~160 w	~170 w	175 m	ν_{28}	
				123 m	$\nu_{28} ?$								
				96 s									
				76 vs									

*Weak bands in the regions 4000–3100, 2800–2200 and 2000–1700 cm^{-1} have been omitted. *Abbreviations: s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder; — denotes bands vanishing in the crystal.

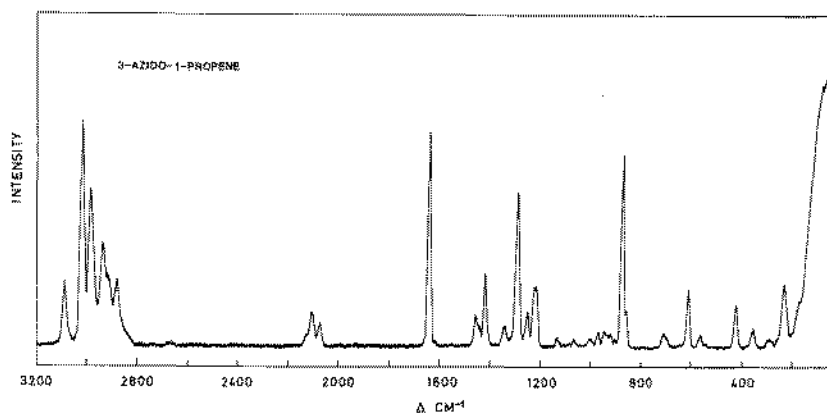


Fig. 5. Raman spectrum of 3-azidopropene as a liquid at 100 K.

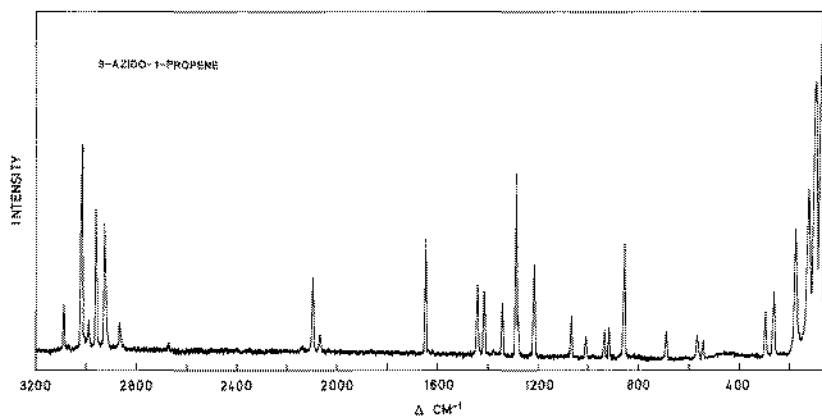


Fig. 6. Raman spectrum of 3-azidopropene as a crystalline solid at 100 K.

Crystal phase

As can be seen from Table 4 a number of Raman bands, present in the spectra of the liquid and amorphous solid and with IR counterparts in the vapour phase as well, vanish in the spectrum of the crystalline solid. They have been marked with asterisks in Table 4 and attributed to conformers present in the vapour and liquid but absent in the crystal. Moreover, it appears from Table 4 that there is no significant change in the conformational abundance between the vapour phase and the liquid.

The electron diffraction investigation indicates, as previously mentioned, the *GG* form to be the most stable conformation of ALAZ in the vapour phase. However, judging from the results of the normal coordinate calculations shown in Table 5, the spectral data are best explained by the *SG* form being the most stable form in the crystal. The majority of the bands that disappear upon crys-

TABLE 5

Observed and calculated vibrational frequencies for the five possible conformations of 3-azidopropene

No.	Observed ^a	Calculated					Approximate description
		SG	GG	GG'	SA ^b	GA	
ν_1	3090	3105	3105	3105	3105	3105	asym =CH ₂ str
ν_2	3020	3031	3031	3031	3031	3031	sym =CH ₂ str
ν_3	2989	3017	3017	3016	3017	3017	=CH str
ν_4	2970	3024	3023	3024	2943 <i>a</i> "	2943	asym > CH ₂ str
ν_5	2925	2920	2920	2920	2903	2903	sym > CH ₂ str
ν_6	2105	2103	2103	2103	2106	2106	N=N str
ν_7	1642	1644	1638	1639	1643	1641	C=C str
ν_8	1440 (1452)	1419	1417	1420	1396	1404	> CH ₂ def
ν_9	1418	1402	1402	1399	1403	1395	=CH ₂ def
ν_{10}	1325	1337	1341	1343	1258	1312	> CH ₂ wag
ν_{11}	1290	1299	1299	1293	1291	1298	=CH bend
ν_{12}	1275 (1250)	1275	1267	1270	1313	1253	N=N str
ν_{13}	1221 (1215)	1214	1208	1208	1223 <i>a</i> "	1212	> CH ₂ twist
ν_{14}	1066 (1133)	1096	1111	1118	1116	1118	=CH ₂ rock
ν_{15}	991	1009	1008	1003	1008 <i>a</i> "	1003	CH ₂ =CH <i>trans</i> wag
ν_{16}	966	959	975	974	967	994	C-C str
ν_{17}	933	929	917	920	932 <i>a</i> "	925	> CH ₂ rock
ν_{18}	925	909	901	904	909 <i>a</i> "	910	=CH ₂ wag
ν_{19}	860 (875)	860	872	872	903	903	C-N str
ν_{20}	685	708	693	710	625	652	NNN bend (NNN bip)
ν_{21}	558 (603)	560	587	590	568 <i>a</i> "	593	CH ₂ =CH <i>cis</i> wag
ν_{22}	555	546	520	543	554 <i>a</i> "	503	N=N tors (NNN bop)
ν_{23}	(420)	489	403	400	540	400	N-C-C bend
ν_{24}	283 (278,344)	267	389	387	260	393	C=C-C bend
ν_{25}	160	223	218	217	153	176	C-N=N bend
ν_{26}		107	70	94	131 <i>a</i> "	101	C-C tors
ν_{27}		35	57	39	53 <i>a</i> "	49	C-N tors

^aVibrational frequencies from solution or liquid phase. Wavenumbers in parentheses corresponds to bands that disappear upon crystallization.

^bWavenumbers corresponding to vibrations of *a*" symmetry have been duly marked.

tallization have medium to strong intensities in the IR spectra and in the Raman spectrum of the liquid as well. Hence, although care should be taken in inferring conformational abundance from IR and Raman band intensities, the relative band intensities do not seem to be in conflict with this possible switch of conformational stability from the vapour/liquid to the crystalline solid. Further, a comparison with the vibrational spectra of the 3-halopropenes [18], of 3-cyanopropene [21] and of 3-isocyano- and 3-isothiocyanopropene [19], which crystallize in the *syn* conformation (fluoro, cyano, isocyano and iso-

thiocyano) and in the *gauche* conformation (chloro, bromo and iodo), also seems to favour the *SG* conformation as being the more stable in the crystal.

Vibrational assignment

The assignment and interpretation of the vibrational spectra of ALAZ is based on analogies with the 3-halopropenes [18], with 3-cyanopropene [21], with 3-isocyano- and 3-isothiocyanopropene [19] and with our previous results for organic azides [1, 22, 23, 34, 35].

More than half of the 27 fundamental modes of vibration in ALAZ can be characterized as typical group frequencies. A few of these modes show a marked dependence upon the C–C torsional angle but according to the normal coordinate calculations only minor differences are expected between the vibrations of the *GG* and the *GG'* conformations. Hence, we have no reliable way of distinguishing between bands from these conformers and therefore rely on the preliminary results from the *ab initio* calculations [39] that indicate the *GG'* form to be ca. 6 kJ mol⁻¹ higher in energy than the *GG* conformer.

The C–H stretching and bending modes hardly need any comment as they are found at nearly the same wavenumbers as in the isoelectronic compound 3-isocyanopropene [19]. Only one of these, the =CH₂ rocking mode, is strongly dependent upon the conformation: 1066 and 1133 cm⁻¹ for the *SG* and the *GG* conformations, respectively. Further, both the C–C and the C–N stretching modes are found in the expected regions, the former at 966 cm⁻¹, the latter at ca. 860 cm⁻¹ for the *SG* form and 875 cm⁻¹ for the *GG* form.

Taking the liberty of neglecting the octet rule, we prefer to describe the azide stretching vibrations in accordance with the normal coordinate calculations as N=N and N=N rather than by the antisymmetric and symmetric NNN. The former of these is as usual found around 2100 cm⁻¹ and the latter, showing a conformational dependence, at 1275 cm⁻¹ (*SG*) and 1250 cm⁻¹ (*GG*). The azide deformation modes, the NNN bending and the N=N torsional mode (or the NNN *bop*) are both, as observed for other azides [1, 22, 23, 26], of medium intensity in the IR but weak in the Raman effect. The NNN bending is found at 706 cm⁻¹ for the *GG* form with the corresponding mode for the *SG* form as a shoulder at ca. 685 cm⁻¹. Finally, the N=N torsional mode, which is expected to be overlapping for the *SG* and the *GG* conformations, is located at ca. 540 cm⁻¹.

Force constant calculations

The normal modes of vibration for ALAZ were calculated from an approximate, local symmetry force field (LSFF) constructed from scaled quantum mechanical (SQM) force fields for the *anti* and *gauche* conformations of azidoethane [25] and for propene [42]. The vibrational frequencies for the dif-

ferent conformations of ALAZ were calculated assuming torsional angles $\tau_{C-C}=0^\circ$ and 120° for the *S* and *G* conformations and $\tau_{C-N}=60^\circ$ and 180° for the *G* and *A* conformations, respectively. Further details of the calculations are available from the authors upon request.

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