

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

Part VI[†]. Azidoacetonitrile

P. KLAEBOE, K. KOSA*, C. J. NIELSEN** and H. PRIEBE***

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, 0315 Oslo 3 (Norway)

S. H. SCHEI

Department of Chemistry, University of Trondheim, AVH, N-7055 Dragvoll (Norway)

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ABSTRACT

Azidoacetonitrile (azidoethanenitrile) has been synthesized and the structure determined by electron diffraction from the vapour. IR spectra have been recorded of the vapour, liquid, solutions, solid at ca. 90 K and of the molecule trapped in argon and nitrogen matrices at 15 K. Raman spectra of the cooled liquid and of the amorphous and crystalline solids have also been obtained.

The electron diffraction results show the conformation to be *gauche* around the C-N bond with a dihedral angle of 52°(5) from *syn* and the NNN angle 173°(3) oriented *anti* to the C-N bond.

The following bond distances (r_a) between the heavy atoms were obtained: $r_{C=N} = 115.4(5)$ pm, $r_{C-C} = 146.5(15)$ pm, $r_{C-N} = 147.5(6)$ pm, $r_{N=N} = 124.5(5)$ pm and $r_{N=N} = 113.5(4)$ pm.

Very large changes in both frequency and intensity have been observed in the vibrational spectra upon crystallization which may be due to intermolecular associations formed by the azido group but which can also be explained by a change of the molecular conformation from only *gauche* in the vapour and liquid phases to *anti* in the crystal phase.

INTRODUCTION

The previous papers in this series contain a brief summary of our experimental and theoretical investigations on organic azides [1] and more detailed accounts of the vibrational spectra and the molecular structure of 2-azido-1,3-butadiene [2], 2,3-diazido-1,3-butadiene [3] and 3-azidopropyne [4]. In a recent *ab initio* study we have reported the molecular structure and

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*On leave from Department of Physical Chemistry, Polytechnical University of Budapest, H-1521 Budapest.

**Author to whom correspondence should be addressed.

***Present address: NYCOMED, P.O. Box 4220 Torshov, N-0401 Oslo 4, Norway.

force fields of hydrazoic acid, azidomethane, azidoethane, azidoethene and azidomethanal [5].

The first preparation of azidoacetonitrile ($\text{N}\equiv\text{C}-\text{CH}_2-\text{N}_3$, AZA) took place in 1932 [6] and until 1975 the published chemical and physical properties of the compound could be summarized: Boiling point $53^\circ\text{C}/12\text{ mmHg}$ and "Beim auftropfen auf eine heiße Platte verpufft die Substanz". Since then an IR spectroscopic study of the photoelimination of nitrogen from solid AZA has been published [7] and, more recently, we have reported the preliminary results of a similar investigation of AZA isolated in nitrogen matrices at 15 K [8]. The dipole moment has been measured as 3.05 Debye in C_6H_6 and in CCl_4 solutions [9]. The isoelectronic compound 3-azidopropyne (propargylazide) was recently studied by gas electron diffraction, by IR and Raman spectroscopy and by quantum mechanical *ab initio* methods [4] and was found to exist only in the *gauche* conformation.

EXPERIMENTAL

Preparative

Preparation of AZA has been described elsewhere [6, 10, 11]. The purity, checked by GC, was better than 99%. The sample slowly polymerizes when kept at -30°C but appears otherwise to be considerably more stable than the isoelectronic 3-azidopropyne [4].

Spectral studies

IR spectra of AZA were recorded on a Perkin-Elmer model 225 spectrometer ($5000-200\text{ cm}^{-1}$) and with a Bruker IFS 114C FTIR interferometer ($4000-20\text{ cm}^{-1}$). Spectra were obtained of the vapour phase (1 m pathlength), of the liquid, of C_6C_{12} , C_6H_6 and CCl_4 solutions and of the amorphous and polycrystalline solids at ca. 90 K. We also obtained the IR spectra of AZA isolated in argon and nitrogen matrices at ca. 15 K.

The Raman spectra of the pure liquid, cooled to ca. 240 K, and of the amorphous and polycrystalline solids at ca. 90 K were recorded on a DILOR RTI 30 spectrometer (triple monochromator) interfaced to the Aspect 2000 data system of the Bruker FTIR. The 514.5 nm and 488 nm lines of a CRL 52G argon ion laser were used for excitation. The spectrum of the liquid was recorded just above the melting temperature in a capillary surrounded by a Dewar cooled with cold nitrogen gas [12]. For safety the laser power was kept below 40 mW on the cooled liquid sample. We used up to 150 mW on the solid samples without detecting any decomposition.

Electron diffraction

The electron diffraction data were recorded on Kodak Electron Image plates with the Oslo apparatus [13] 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 [14], optical densities were measured with a Joyce—Loebl densitometer and the data were reduced in the usual way [15, 16] yielding two averaged intensity curves (one from each distance) in the form $sI_M(s)$. Four and five plates were selected from the long and short camera distances, respectively.

RESULTS

Vibrational spectra

The IR spectrum of liquid AZA is given in Fig. 1, while Fig. 2 shows a part of the IR spectra ($1000\text{--}400\text{ cm}^{-1}$) of solid AZA at ca. 90 K before and after annealing to ca. 220 K. The IR vapour phase band contours were not always well defined and have consequently been of little help. The Raman spectrum of the cooled liquid was of poor quality and will not be presented here, but for all practical purposes it is identical to that of the amorphous solid in Fig. 3. Finally, the Raman spectrum of the same sample which is now polycrystalline after being annealed to ca. 240 K is shown in Fig. 4. The spectral data are collected in Table 1 and the assigned fundamentals are given in Table 2 together with the results of normal coordinate analysis. As the Raman spectrum of the liquid was of poor quality we have not included intensity specifications for the Raman peaks of the liquid in Table 1.

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. 5. A unit weight matrix was used. The molecular geometry was calculated from the geometry consistent r_α model [17].

Root mean square amplitudes of vibration (l) and perpendicular correction coefficients (K) were constrained to the values calculated from an approximate

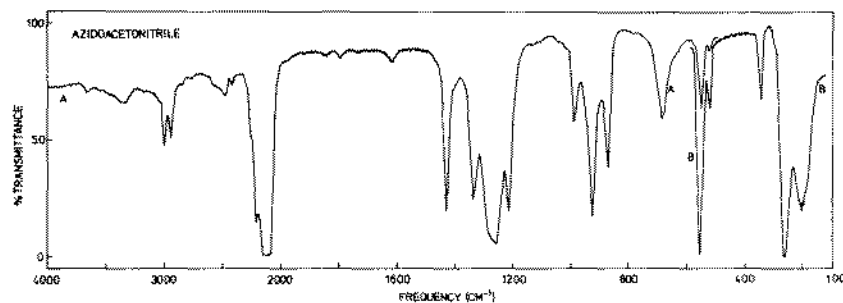


Fig. 1. The mid IR spectrum of liquid azidoacetonitrile. A: 0.012 mm thickness. B: ca. 10% CCl_4 solution, 1 mm thickness.

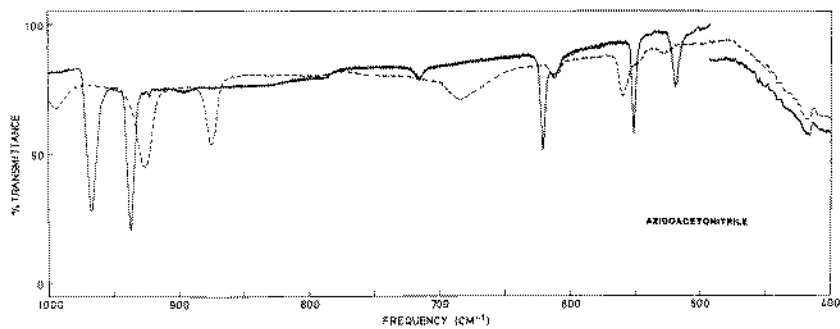


Fig. 2. The mid IR spectrum (1000–400 cm⁻¹) of amorphous (dotted curve) and polycrystalline (solid curve) azidoacetonitrile at ca. 90 K.

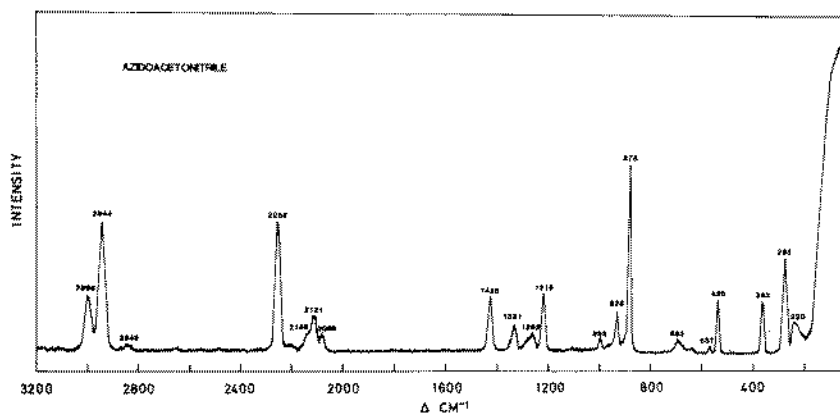


Fig. 3. Raman spectrum of azidoacetonitrile as an amorphous solid at ca. 90 K.

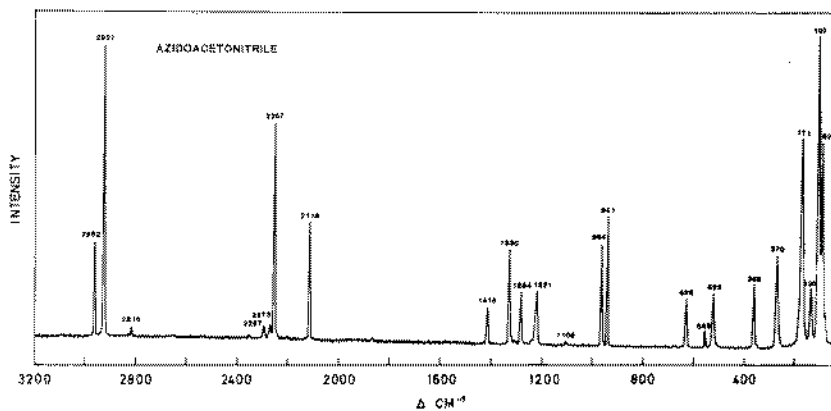


Fig. 4. Raman spectrum of polycrystalline azidoacetonitrile at ca. 90 K.

TABLE 1

Vibrational spectral data^a for azidoacetonitrile (AZA)

Infrared ^b					Raman ^b			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	
2947 w	~3000 vw ~2930 w ~2870 vw	2996 m 2939 m 2852 vw	3000 m 2945 m 2850 vw	2962 m 2929 s		2998 m 2944 s 2846 w	2963 m 2927 s 2816 vw 2297 vw	ν_1 ν_2 $2\nu_3$
2254 w	~2245 w	~2300 vw, sh 2250 m, sh	~2255 m, br	2257 m 2247 m	2254	2258 s	2257 s	ν_3
2218 m	~2200 m, br	2209 s	2213 m	2227 m, br		2210 w		
2185 m		~2180 s, sh	2180 m, sh	2178 m				
2151 s	~2160 s, sh			2166 w				
2137 s	~2145 vs, sh	~2150 vs, sh	2146 s	2135 s, sh		2145 w		
2113 vs	~2120 vs	2115 vs	2116 vs	2115 vs, br 2093 s		2120 w	2118 m	ν_6
2086 s	~2085 s, sh	~2080 vs, sh	2086 s	2076 s		2086 w		
1444 m	~1440 w	1430 s	1426 s	1424 s	1428	1427 m	1415 m	ν_5
1332 w	1348 1335 } w, B	1335 s	1335 m	1333 s		1333 w	1330 m	ν_6
1287 w	~1300 w, sh	~1285 s, sh	~1285 s, sh	1311 w				
1260 vs	1263 1256 Q } s, AB 1251 1231	1260 s	1263 s	1287 s		1262 w	1284 m	ν_7
1227 m	1222 Q } m, C 1214	1217 m	1217 s	1243 m	1219	1216 m	1221 m	ν_8
		~1135 vw ~1110 vw					1106 w	
983 m	1000 } w, B 986	990 m	994 m	968 s		995 w		ν_9
		~950 m, sh						
927 s	940 } m, B 928	928 s	926 s	937 s	927	926 m	964 m	ν_{10}
873 m	886 877 Q } w, C 869	875 m	875 s		873	875 s	941 m	ν_{11}
		~700 w, sh		716 w				HCN?
682 m	697 } w, B 685	687 m, br	684 m, br	621 m		683 w	627 m	ν_{12}
		~640 w, sh				~640 vw		
560 m	~560 vw	555 m	560 m	552 m		557 vw	558 w	ν_{13}
		525 w	528 w	519 m	528	526 m	522 m	ν_{14}
		347 w ^c	352 w	355 m		353 m	362 m	ν_{15}
		260 m ^c	266 m	274 m		265 s	270 s	ν_{16}
		204 m, br ^c	225 m, br	170 m	221	225 w	171 s	ν_{17}
				129 m			136 m	
				111 m			107 s	
		~80 w, br ^c	~110 m, br	89 m			92 s	ν_{18}

^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. ^c CCl_4 solution.

TABLE 2

Observed and calculated fundamental modes of vibration for azidoacetonitrile (AZA)

No.	Observed		Calculated LSFF ^a			Description
	Liquid	Cryst.	Gauche	Anti	Syn	
ν_1	2996	2962	3024	2944	2943	CH ₂ antisym str
ν_2	2939	2929	2919	2902	2902	CH ₂ sym str
ν_3	2258	2257	2256	2256	2255	C≡N str
ν_4	2115	2118	2103	2106	2113	N=N str
ν_5	1430	1424	1438	1416	1435	CH ₂ bend
ν_6	1335	1330	1333	1310	1365	N=N str
ν_7	1265	1288	1254	1274	1232	CH ₂ wag
ν_8	1217	1221	1223	1226	1218	CH ₂ twist
ν_9	990		1000	1015	1012	C—C/C—N antisym str
ν_{10}	925	968	941	947	955	CH ₂ rock
ν_{11}	875	937	858	923	843	C—C/C—N sym str
ν_{12}	685	621	694	629	703	NNN bend
ν_{13}	555	552	557	549	546	NNN bop
ν_{14}	525	518	505	516	517	C—C—N bend
ν_{15}	347	354	357	346	346	C—C≡N bend
ν_{16}	260	272	277	266	275	C—C≡N bend
ν_{17}	221	171	173	150	117	C—N=N bend
ν_{18}	80		52	50	81	C—N tors

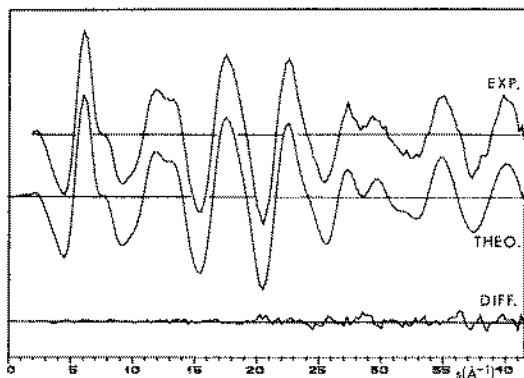
^aLocal symmetry force field, see text.

Fig. 5. Azidoacetonitrile, intensity curves in the form $sI_m(s)$. 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. $\Delta s = 0.25 \text{ \AA}^{-1}$.

force field. The set of I - and K -values was adjusted corresponding to the resulting torsional angle and torsional force constant as the analysis progressed.

A few constraints had to be introduced among the geometrical parameters. The CH₂ group was positioned so that the four CCH and NCH angles were

equal. The C—C=N fragment was found to be linear (refined to $179 \pm 6^\circ$) and kept linear in the final refinements. There was no detectable deviation from the calculated shrinkage. By systematic testing, the bent bond of the NNN fragment was found to be *anti* relative to the CNN angle.

In Fig. 6 the radial distribution curves for the possible conformations of AZA (*anti*: $\tau = 180^\circ$, *skew*: $\tau = 120^\circ$, *gauche*: $\tau = 52^\circ$ and *syn*: $\tau = 0^\circ$) show that it is possible to discriminate quite well among them. However, the torsional angle could not be determined precisely, because the molecule exhibits a large amplitude motion, as indicated by the root mean square torsional amplitude. Further, the ED data could not give an indication of whether the torsional potential is symmetric or not around the torsional angle minimum, τ_0 . Therefore, the ED analysis was based upon a gaussian distribution of six pseudo conformers in the *gauche* conformational position. This led to a minimum at a dihedral angle $\tau_0 = 52(5)^\circ$ from *syn*. Further, the root mean square torsional amplitude was found to be $((\tau - \tau_0)^2)^{1/2} = 22(4)^\circ$, which in the harmonic approximation [18] is associated with a torsional force constant $F_\tau = 0.03 \text{ mdyn } \text{\AA} \text{ rad}^{-2}$, giving a torsional frequency of 42 cm^{-1} .

The calculated root mean square amplitudes of vibration (l) corresponding to $\tau_0 = 52^\circ$ are listed in Table 3. We have included two sets of l -values in this

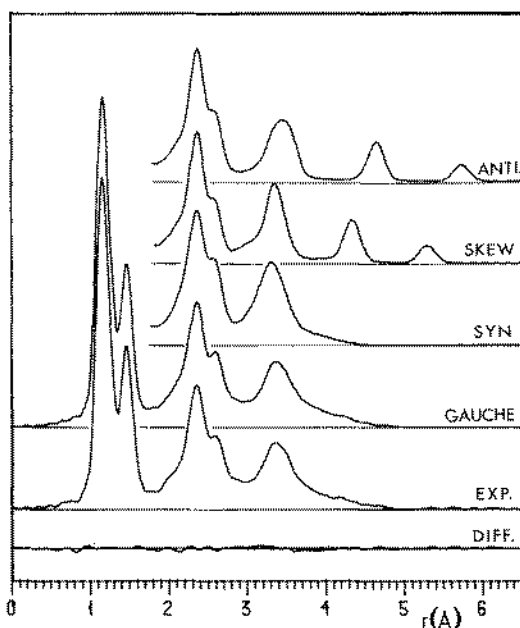


Fig. 6. Azidoacetonitrile, comparison between the theoretical radial distribution curves for the *anti*, *skew*, *syn* and *gauche* conformations and the experimental radial distribution curve calculated from the intensity curves in Fig. 5 after multiplication by $(f'_N(s) * f'_C(s))^{-1}$, using theoretical data for unobserved area $s < 2.0 \text{ \AA}^{-1}$ and a damping factor $B = 0.02 \text{ \AA}^2$. All curves are on the same scale.

TABLE 3

Azidoacetonitrile (AZA), interatomic distances (r)^a and calculated root mean square amplitudes of vibration (l) in pm. Atomic numbering: $N_1-N_2-N_3-C_1(H_1H_2)-C_2-N_4$

Distance	r_a	l^b	
		A	B
C_1-H	111	78	
N_1-N_2	114	34	
C_2-N_4	115	36	
N_2-N_3	125	40	
C_1-C_2	147	46	
C_1-N_3	148	51	
$H \cdots H$	184	132	
$C_2 \cdots H$	210	106	
$N_3 \cdots H$	211	102	
$N_2 \cdots C_2$	228	71	
$N_1 \cdots N_3$	237	46	
$N_3 \cdots C_2$	244	82	
$N_4 \cdots C_2$	261	50	
$N_2 \cdots H_1$	263	238	155
$N_2 \cdots C_2$	280	225	89
$N_4 \cdots H$	314	123	
$N_2 \cdots H_2$	317	101	101
$N_3 \cdots C_1$	331	89	
$N_3 \cdots N_4$	344	106	
$N_1 \cdots H_1$	350	343	198
$N_2 \cdots N_4$	357	311	107
$N_1 \cdots C_2$	356	319	102
$N_1 \cdots N_3$	413	490	109
$N_1 \cdots H_2$	424	109	104

^aDistances correspond to a torsional angle of 52° . ^bA: torsional force constant $0.03 \text{ mdyn } \text{A rad}^{-2}$, B: contribution from torsional motion excluded.

table: corresponding to the single conformer model ($\tau_0 = 52^\circ$, $F_\tau = 0.03 \text{ mdyn } \text{A rad}^{-2}$) and one corresponding to the average torsional position, but with the contribution from the torsional motion excluded. (In the actual refinement each of the six quasi-conformers were refined with l -values corresponding to their torsional angle.)

The nearly equal bond distances r_{C-C} and r_{C-N} were difficult to determine simultaneously. Consequently, one of the distances had to be varied systematically. The final results are given in Table 4.

There are a few large correlation coefficients among the geometry parameters. Those larger than 0.5 have been included in Table 4.

TABLE 4

Azidoacetonitrile (AZA), final results from the least squares refinements* of the electron diffraction data at 293 K

No.	Parameter	$r_a/\angle\alpha$
1	$r(\text{C}\equiv\text{N})$	115.4(5)
2	$r(\text{C}-\text{C})$	146.5(15) ^a
3	$r(\text{C}-\text{N})$	147.5(6)
4	$r(\text{N}=\text{N})$	124.5(5)
5	$r(\text{N}\equiv\text{N})$	113.5(4)
6	$r(\text{C}-\text{H})$	111(5)
7	$\angle\text{C}-\text{C}\equiv\text{N}$	180 ^b
8	$\angle\text{C}-\text{C}-\text{N}$	113.4(10)
9	$\angle\text{C}-\text{N}=\text{N}$	115.4(11)
10	$\angle\text{N}=\text{N}\equiv\text{N}^c$	173(3)
11	$\langle\angle\text{C}-\text{C}-\text{H}\rangle$ $\langle\angle\text{N}-\text{C}-\text{H}\rangle$	108(3)
12	τ_0	52(5) ^e
13	$\langle(\tau - \tau_0)^2\rangle^{1/2}$ R^d	22(4) ^e 4.4/9.2

^aValue found by systematic variation, uncertainty estimated. ^bKept constant, see text. ^cThe NNN linkage is bent *trans* to the C-N bond. ^d R -factors for long and short camera data, respectively. ^eThe electron diffraction results are based on a gaussian distribution for the torsional motion. *Correlation coefficients >0.5 : $C_{1,2} = -0.57$; $C_{1,3} = 0.51$; $C_{1,4} = 0.62$; $C_{1,5} = -0.67$; $C_{2,3} = -0.88$; $C_{2,9} = 0.65$; $C_{3,9} = -0.65$; $C_{4,9} = -0.60$; $C_{5,9} = 0.65$; $C_{6,9} = 0.55$; $C_{8,12} = -0.61$; $C_{8,13} = 0.53$; $C_{9,10} = 0.64$; $C_{9,12} = -0.54$; $C_{12,13} = 0.58$.

DISCUSSION

Structure

It is natural to discuss the structure of AZA in relation to that of the isoelectronic compound 3-azidopropyne [4]. In 3-azidopropyne the potential to rotation around the C-N bond was calculated by ab initio methods [4] to be of the single minimum type with ca. 6.5 and 8.5 kJ mol⁻¹ barriers in the *syn* and *anti* positions, respectively. Although the polarity of these isoelectronic molecules is quite different, this has very little effect on the molecular conformation; the dihedral angle is 37° from the *syn* position in 3-azidopropyne and 52° in AZA. Because the dipole moment of the azide group invariably is directed along the C-N bond (ref. 5 and older references therein) one would only expect small variations in the molecular dipole moment of AZA with the torsional angle. (In ref. 9 the dipole moment of AZA, calculated by vectorial addition of bond moments, shows a variation with the torsional angle from 1.4 D to 5.1 D, apparently caused by a calculational error.) Hence the torsional potential in AZA is expected to be of the same single minimum type and with roughly the same barriers in the *syn* and *anti* positions.

In Table 5 the structural parameter of AZA are listed together with the results from related molecules. Apart from different torsional angles the structural parameters of AZA, 3-azidopropyne [4] and azido-2-butyne [19] are identical within the experimental uncertainty. Moreover, a comparison with other related molecules is favorable.

The azide chain in AZA deviates from linearity by being "bent away" from the substituent by a few degrees. This "transoid" arrangement of the azide group was unambiguously revealed by the experimental data and agrees with the experimental results for other azides [2, 3, 4, 19–22] and with the results from ab initio calculations [5].

Spectral interpretation

The interpretation of the vibrational spectra of AZA is obviously closely connected with those of 3-azidopropyne [4] and azido-2-butyne [19]. Since the vibrational spectra of 3-azidopropyne were discussed in detail in the previous paper in this series [4] and since there is essentially a one-to-one correspondence between the vibrational modes of the $\equiv\text{C}-\text{CH}_2-\text{N}_3$ fragment in these molecules, most comments would be superfluous in the present context.

Among the low frequency modes only the $\text{C}-\text{C}\equiv\text{N}$ bop (with respect to the $\text{N}\equiv\text{C}-\text{C}-\text{N}$ plane) is a typical group frequency. The interpretation of the rest of the low frequency bending modes relies upon the normal coordinate calculations. We have assigned the weak, broad band observed in the FIR spectra of CCl_4 and C_6H_{12} solutions around 80 cm^{-1} to the $\text{C}-\text{N}$ torsional mode. Not unexpectedly the frequency of this mode is strongly dependent upon the surroundings.

The spectra of the crystalline solids are, however, very different from those of the liquid (and of the amorphous solid) as can be seen from Figs. 2–4 and from Tables 1 and 2. Very large frequency shifts and intensity changes have been observed for some of the bands, and normally such dramatic spectral changes are connected with either molecular associations or with a conformational change.

The very polar cyano group can easily be imagined to be the origin of intermolecular associations. However, neither the $\text{C}\equiv\text{N}$ stretching mode nor the $\text{C}-\text{C}\equiv\text{N}$ bending modes seem to change significantly upon crystallisation. Instead, it is the $\text{N}=\text{N}$, $\text{C}-\text{C}$ and $\text{C}-\text{N}$ stretchings, the CH_2 rocking and the NNN bending modes that change the most. This can be then interpreted as due to intermolecular associations formed by the azido group, but such associations have not been observed in the spectra of 3-azidopropyne [4] and have not been reported for any other organic azides.

Alternatively, the spectral changes upon crystallisation might be explained as a conformational change. As mentioned, the barriers to rotation around the $\text{C}-\text{N}$ bond are probably around $6-8\text{ kJ mol}^{-1}$ in the *syn* and *anti* positions, i.e. rather low barriers. For comparison, two dipoles of 1 D placed

TABLE 5

Comparison of some of the geometrical parameters [pm, degrees] of azidoacetonitrile with related molecules

Molecule	$r_{\text{N}=\text{C}}$	$r_{\text{C}-\text{C}}$	$\angle \text{CCX}$	$r_{\text{C}-\text{N}}$	$r_{\text{N}=\text{N}}$	$r_{\text{N}=\text{N}}$	$\angle \text{CNN}$	$\angle \text{NNN}$	Ref.
$\text{N} \equiv \text{C}-\text{CH}_3$	115.4(2)	146.4(2)							23
$\text{N} \equiv \text{C}-\text{CH}_2-\text{Cl}$	115.8 ^a	145.8 ^a	111.5(10)						24
$\text{N} \equiv \text{C}-\text{CH}_2-\text{NH}_2$	115.9(20)	145.1(20)	114.5(15)						25
$\text{N} \equiv \text{C}-\text{CH}_2-\text{CH}_3$	115.7(7)	147.4(10)	110.5(5)						26
$\text{N} \equiv \text{C}-\text{CH}_2-\text{CH}=\text{CH}_2$	116.2(7)	146.0(7)							27
$\text{N} \equiv \text{C}-\text{CH}_2-\text{N}=\text{N} \equiv \text{N}$		146.5(15)	113.4(10)	147.6(6)	124.5(5)	113.5(4)	115.4(11)	173(3)	this work
$\text{HC} \equiv \text{C}-\text{CH}_2-\text{N}=\text{N} \equiv \text{N}$		148.1(13)	114.6(12)	146.4(13)	124.9(7)	113.7(6)	114.5(15)	169.2(41)	4
$\text{CH}_3\text{C} \equiv \text{C}-\text{CH}_2-\text{N}=\text{N} \equiv \text{N}$		146.8(5)	113.8(16)	147.4(15)	124.0(6)	114.2(5)	116.5(14)	174(5)	19
$\text{H}-\text{N}=\text{N} \equiv \text{N}$					124.3(5)	113.4(2)		171.3(50)	20
$\text{CH}_3-\text{N}=\text{N} \equiv \text{N}$				146.8(5)	121.6(4)	113.0(5)	116.8(3)	180 ^a	28
$\text{CF}_3-\text{N}=\text{N} \equiv \text{N}$				142.7(5)	125.0(7)	111.7(4)	111.8(11)	175.3(43)	21
$\text{N} \equiv \text{C}-\text{N}=\text{N} \equiv \text{N}$				135.5(2)	126.1(1)	112.7(2)	114.5(2)	169.2(16)	22
$\text{CH}_2-\text{O}-\text{CH}_2-\text{C}-(\text{CH}_2\text{N}_3)_2$			111.4(12)	147.0(9)	124.0 ^b	114.2	119.2(10)	180 ^a	29

^a Assumed. ^b Given as $\text{NN}_{\text{avg.}} = 1.191(2)$ and $\text{NN}_{\text{diff.}} = 0.098(2)$.

antiparallel 300 pm apart lower the energy by ca. 2 kJ mol⁻¹ compared to the situation where they are placed perpendicular to each other. Hence, orientational and packing effects may easily change the torsional potential for AZA beyond recognition and conformational changes upon crystallisation cannot be ruled out.

A comparison between the observed and the calculated vibrational frequencies of AZA in the *gauche* and in the hypothetical *syn* and *anti* conformations (Table 2) shows that the unexpected frequency shifts from the liquid to the crystal phase can be accounted for quite well by assuming a change in conformation from *gauche* (vapour, liquid) to *anti* (crystal). With the sole exception of ν_6 , the other large frequency shifts on crystallisation (ν_7 , ν_{10} , ν_{11} , and ν_{12}) are much better explained as a change of conformation than of association. If the suggested conformational behaviour is correct (and not just wishful thinking by the authors), it constitutes a unique example of large intermolecular interactions bringing about a change in a well-defined, single minimum intramolecular potential with resulting drastic conformational changes. However, further spectroscopic studies of AZA and isotopically substituted AZA would have to be carried out before any firm conclusions could be drawn.

Force constant calculations

The normal modes of vibration for AZA 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 [5] and from a LSFF for the halonitriles as previously described [4]. The results are given in Table 2.

We have also calculated the normal modes for a possible *syn* or *anti* conformation of AZA. The force field for these conformations was constructed by adopting the SQM force field for the *anti* conformation of ethylazide [5]. The results for the possible *syn* or *anti* conformations of AZA are also included in Table 2. It must be emphasized that the only force constants in the transferred force field that have been modified are the diagonal CH₂ wag and twist force constants and the N=N torsional force constant. Obviously, these must be different from their values in the halonitriles and in azidoethane. Further, the diagonal CH₂ bending force constants have been assumed to be equal for the *gauche* and the hypothetical *syn* and *anti* conformations of AZA.

The definition of the internal coordinates and the force field can be obtained from Table 10 in ref. 4 by deleting the C≡C—H bending coordinates and by replacing C≡C—C with N≡C—C. The only different force constants are: $F_{C=N} = 17.98$ mdyn Å⁻¹ and $H_{C-C=N} = 0.297$ mdyn Å rad⁻².

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