

THE VIBRATIONAL SPECTRA, MOLECULAR STRUCTURE AND CONFORMATION OF ORGANIC AZIDES, PART X. A REVIEW OF THE STRUCTURES OBTAINED FROM VAPOUR PHASE, CRYSTALLOGRAPHIC AND THEORETICAL STUDIES, AND OF THE VIBRATIONAL SPECTRA AND FORCE CONSTANT CALCULATIONS.

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The molecular structures, bonding and conformations of various organic azides, including alkylazides, olefinic azides and acetylenic azides determined by gaseous electron diffraction and microwave spectroscopy are compared with X-ray crystallographic structures of larger azides and with the results obtained by ab initio methods. The number of conformers present are discussed and experimental conformational energy differences are compared with the quantum mechanical results.

IR and Raman spectral results are presented and characteristic localized vibrations for the azide group are tabulated. The spectra are assigned and compared with the results of normal coordinate analyses, based upon a combination of force constants transferred from related molecules and scaled ab initio calculated force constants.

### Introduction

The group of compounds that can formally be derived from hydrazoic acid,  $\text{HN}_3$ , is referred to by the common name azides. The first azide to be prepared, phenylazide, was discovered in 1866 /1/, whereas the acid itself ( $\text{HN}_3$ ) first was prepared in 1890 /2/.

It was first proposed that the azide group had a cyclic structure /3/, and this view was favoured until 1911 when a chain structure, which supposedly could better explain many of the  $\text{HN}_3$  reactions, was presented /4/. The discussions concerning the azide structure in the following years were at times both bitter and personal. They continued even after the X-ray structures of sodium and potassium azide were published in 1925 /5/ showing the azide ion  $\text{N}_3^-$  to be linear and centrosymmetric, supported by Raman spectra /6/. Later, the structures of azidomethane /7/ and cyanuric azide /8/ were determined by gaseous electron diffraction (GED) and by X-ray diffraction, respectively, revealing the azide group to have a chain structure, possibly linear, but with two widely different NN bond distances.

## Structure

The individual azides can be classified according to the structure of the azide group as being either of the ionic type, the coordinative type or the molecular type of which the organic azides form a subgroup. The organic azides can further be divided into two classes, the alkyl and aryl azides, and the acyl azides which contain the group  $-\text{CO}-\text{N}_3$ . When the azide group is connected to electro-positive metal atoms, in which an ionic  $\text{M}^+\text{N}_3^-$  linkage is formed, the azide moiety is linear with two equivalent NN bonds equal to 116 pm, in agreement with the spectral results /9/. In some of the earlier vapour phase studies by GED /10/ or microwave spectroscopy (MW) /11/ it was assumed that the NNN group was linear also in the molecular azides. However, all the recent structure investigations of covalent azides, either as vapours by GED or MW or in the solid state by X-ray crystallography, reveal that the azide group has a slightly bent structure with an NNN angle of ca. 172 deg. Moreover, the NN bond

Table 1. Bond distances (pm) and angles ( $^\circ$ ) of covalent azides  $\text{X}-\text{N}_3$  in the vapour phase.

Compounds	X-N	N=N	N=N	XNN	NNN <sup>a</sup>	Meth. <sup>b</sup>	Ref
$\text{HN}_3$	101.5	124.3	113.4	108.8	171.3	MW	12
$\text{FN}_3$	144.4	125.3	113.2	103.8	170.9	MW	13
$\text{ClN}_3$	174.5	125.2	113.3	108.7	171.9	MW	14
$\text{CH}_3\text{N}_3$	146.8	121.6	113.0	116.8	(180)	GED	10
$\text{CF}_3\text{N}_3$	142.5	125.2	111.8	112.4	169.6	MW	15
$\text{CH}_3-\text{O}-\text{CO}-\text{N}_3$	146.0	124.8	113.1	110.7	(180)	MW	11
$\text{N}=\text{CN}_3$	135.5	126.1	112.1	114.5	169.2	GED	16
$\text{H}=\text{C}-\text{C}-\text{CH}_2\text{N}_3$	146.4	124.9	113.7	114.5	169	GED	17
$\text{N}=\text{C}-\text{CH}_2\text{N}_3$	147.6	124.5	113.5	115.4	173	GED	18
$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_2\text{N}_3$	147.4	124.0	114.2	116.5	174	GED	19
$\text{CH}_2=\text{CH}-\text{CH}_2\text{N}_3$	147.5	123.6	113.8	115.1	174	GED	20
$\text{CH}_2=\text{C}(\text{N}_3)-\text{CH}=\text{CH}_2$	143.4	125.3	114.3	116.8	173	GED	21
$\text{CH}_2=\text{C}(\text{N}_3)-\text{C}(\text{N}_3)=\text{CH}_2$	143.2	124.2	114.1	114.4	166.7	GED	22

<sup>a</sup> paranthesis, assumed value. <sup>b</sup> MW, microwave spectrosc. GED, gaseous electron diffraction.

distances differ by ca. 12 pm making a description as  $\text{N}=\text{N}$  and  $\text{N}=\text{N}$

**TABLE 2.** Structure parameters for the azide group in organic azides, C-N=N=N, [pm, degrees] as determined by X-ray diffraction † 1965 - 1985.

Molecule	$r_{\text{C-N}}$	$r_{\text{N=N}}$	$r_{\text{N=N}}$	$\alpha_{\text{C-N=N}}$	$\alpha_{\text{N=N=N}}$	$\tau_{\text{N=N}}$	$N_{\text{Ref}}$	R	Ref.
<i>p</i> -Nitrophenyl azide	141.7(17) <sup>‡</sup>	127.0(16)	112.7(17)	115.0(10)	173.4(13)	-178.	586	8.7	25
3-Azidotropone	142.6(9) <sup>‡</sup>	124.8(9)	112.2(9)	116.	172.		841	6.5	26
$\Delta^6$ -6-Azidobetametasone-21-acetate	144.4(6) <sup>‡</sup>	124.5(7)	111.5(7)	114.9(4)	174.2(5)	-175.	1662	4.6	27
6-Deoxy-6-azido-dihydroisomorphine	148.3(6)	121.0(5)	114.7(6)	115.8(4)	173.0(4)	179.	1218	4.4	28
4-Phenyl-3(5)-azidopyrazole	140.7(5) <sup>‡</sup>	124.4(5)	114.0(5)	114.2(3)	171.9(4)	174.	427	5.0	29
Tri- <i>O</i> -acetyl- $\alpha$ -D-arabino-pyranosylazid	144.9(5)	124.5(5)	113.6(6)	113.3(4)	172.6(5)	-177.	1394	4.4	30
7-Azido-8-deoxy-1,2,3,4-di- <i>O</i> -isopropylidene-6,7- <i>S</i> , <i>S</i> -trimethylene-6,7-dithio- $\alpha$ -D-erythro-D-galacto-octapyranose	148.6(6)	123.7(6)	113.0(6)	114.9(4)	173.0(5)	-178.	1929	4.6	31
Tri- <i>O</i> -acetyl- $\beta$ -D-xylo-pyranosylazid	144.4(7) <sup>#</sup>	121.2(9)	113.1(11)	115.5(5)	171.5(6)	178.	2644	6.0	32
	144.6(9)	121.0(12)	112.0(16)	112.8(6)	171.4(8)	-174.			
2,4-Diazido-5-iodopyrimidine	141.1(1) <sup>‡</sup>	124.1(1)	113.1(1)	114.1(1)	172.1(1)	-176.	1170	4.6	33
	140.1(1) <sup>‡</sup>	128.1(1)	111.1(1)	113.1(1)	174.1(1)	-179.			
1-Azido-1-benzoyl-2-phenylethylene	141.1(1) <sup>‡</sup>	123.1(1)	112.1(1)	121.0(5)	168.1(5)	174.	959	5.5	34
5-Azido-5-deoxy-1,2- <i>O</i> -isopropylidene-3- <i>O</i> -mesyl- $\beta$ -L-iduronic acid diethylamide	145.1(1) <sup>#</sup>	124.1(1)	118.1(1)	114.4(5)	171.5(7)	-177.	3821	5.0	35
	151.1(2)	122.1(1)	114.1(1)	116.6(7)	172.3(7)	157.			
2,4-Diazido-2,4-dideoxy-1,6-anhydro- $\beta$ -D-glycopyranose	148.6(7) <sup>#</sup>	122.5(7)	112.9(7)	119.0(4)	169.0(5)	-179.	1831	4.3	36
	148.6(6)	123.3(6)	112.7(7)	115.0(4)	172.6(5)	176.			
	148.1(6)	122.9(6)	112.9(6)	118.2(4)	170.7(5)	179.			
	147.7(6)	123.7(6)	112.1(6)	114.6(4)	172.9(5)	167.			
6- <i>O</i> -Acetyl-2-azido-3,4-di- <i>O</i> -benzyl-2-deoxy- $\alpha$ -D-glucopyranosyl 2,3,4,6-tetra- <i>O</i> -acetyl- $\alpha$ -D-mannopyranoside	145.8(9)	121.0(7)	112.5(8)	118.	170.4(8)	-170.	3802	6.5	37
5-(Azido- <i>t</i> -butyl-phenylmethyl)-4- <i>t</i> -butyl-2-tosyl-1,2,3-triazole	151.9(3)	122.0(4)	114.3(5)	115.8(2)	173.7(3)	-170.	2980	4.5	38
<i>t</i> -Butyl-2-azido-2-deoxy- $\beta$ -D-galactopyranoside	147.9(5)	122.9(6)	112.8(7)	114.7(4)	173.9(6)	-177.	1299	5.3	39
Isopropyl-2-azido-2-deoxy- $\beta$ -D-galactopyranoside	148.5(5)	121.4(5)	113.0(5)	115.7(3)	172.8(5)	180.	942	3.6	40
3- <i>O</i> -(6- <i>O</i> -Acetyl-2,4-diazido-3- <i>O</i> -benzyl-2,4-dideoxy- $\alpha$ -D-glucopyranosyl)-1,6-anhydro-2,4-diazido-2,4-dideoxy- $\beta$ -D-glucopyranose	148.7(8)	119.2(9)	114.1(1)	116.3(4)	174.3(7)	177.	2102	6.3	41
	148.1(1)	122.1(1)	110.1(1)	116.7(7)	170.4(9)	-172.			
	147.1(1)	114.5(9)	111.1(1)	117.1(7)	170.1(1)				
	147.9(6)	117.	111.2(2)	122.6(2)	172.8(6)	127.			
11b-Azido-5,6,7a,11b-tetrahydro-benzocyclobuten(1,2- <i>f</i> )-7H-benzocycloheptene	149.8(6)	122.9(6)	112.0(6)	113.9(5)	174.3(6)	-174.(4)	1147	3.1	42
1-(Azidomethyl)-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane	151.3(5) <sup>#</sup>	120.2(5)	110.1(5)	113.5	173.5	155.	1856	3.7	43
	151.6(5)	117.5(5)	109.5(5)	114.5	173.6	172.			
Methyl-2-azido-deoxy-2- $\beta$ -D-galactopyranoside	147.2(4)	122.8(4)	112.8(5)	115.5(3)	173.2(4)	176.7(5)	1002	3.8	44
Ethyl-2-azido-deoxy-2- $\beta$ -D-galactopyranoside	148.2(10)	118.6(14)	111.3(14)	117.7(4)	170.0(5)	180.0(7)	699	4.6	44
6-Azidotetrazolo [5,1- $\alpha$ ]phthalazine	139.6(3) <sup>‡</sup>	126.2(3)	111.3(4)	114.4(2)	171.2(3)	172.	892	3.5	45
	141.4(15) <sup>‡</sup>	125.2(17)	112.2(10)	115.3(25)	172.1(19)	175.4(24)			
Average	148.1(21)	121.3(25)	112.6(18)	115.9(21)	172.2(15)	172.(12)			

† Uncertainties in parentheses as given by the authors; R-factor in %. ‡  $sp^2$ -hybridized carbon atom.

# Two symmetry independent molecules in the crystal.

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bonds feasible.<sup>#</sup> We have collected the known vapour phase structures of organic azides in Table 1 where we also have included the structures of  $\text{NH}_3$ ,  $\text{FN}_3$  and  $\text{ClN}_3$ .

A much larger collection of organic azide structures have been determined by X-ray diffraction technique on single crystals. Most of these (ca. 40 X-ray studies) have been published after the earlier reviews on the structure of azides /23,24/. For the sake of brevity we only present the more well determined structures in Table 2. It is characteristic that in most of these investigations the azide structure has not been an essential part of the study. The NNN bonding is therefore seldom discussed in detail and it is even more seldom that the CNNN torsional angle is mentioned at all. We have included this dihedral angle in Table 2, whenever it could be calculated from the published coordinates, as well as the number of reflections used in the least squares refinement and the R-factor (%).

In addition to the azide structures determined experimentally in the vapour (Table 1) and in the crystalline state (Table 2), certain simple azides such as hydrazoic acid, azidomethane, azidoethane, azidoethene as well as 3-azidopropyne and 3-azidopropene have been studied by ab initio quantum mechanical calculations at the Hartree Fock SCF level. Fully optimized geometries were obtained for these molecules and the results have been reported /17,46,48/, the relevant structural parameters are listed in Table 3.

Various conclusions can be drawn from a comparison between the structural parameters of different azides within each table and by comparing the data from vapour, crystalline state and quantum mechanics in Tables 1-3.

1. The  $\text{N}=\text{N}$  and  $\text{N}\equiv\text{N}$  distances and the XNN and NNN angles are reasonably constant in the vapour (Table 1) except for the NNN angles in the non-organic molecules  $\text{NH}_3$ ,  $\text{FN}_3$  and  $\text{ClN}_3$  (and for  $\text{CH}_3\text{N}_3$  assuming  $180^\circ$  for NNN).
2. The individual structure parameters vary slightly more in the crystalline state (Table 2). This is expected considering the lattice effects and the fact that the azides in Table 2 are quite different chemically.

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<sup>#</sup> The authors apologize for neglecting the octet rule in the lexicographical description of the organic azides,  $\text{R}-\text{N}=\text{N}=\text{N}$ .

Table 3. Bond distances (pm) and angles ( $^{\circ}$ ) of covalent azides X-N<sub>3</sub> determined by quantum chemical calculations /17,46,48/.

Compounds	Basis <sup>a</sup>	X-N	N=N	N≡N	XNN	NNN
HN <sub>3</sub>	DZ	101.8	126.8	110.9	108.5	172.1
	HF	100.5	123.6	108.9	108.1	173.8
CH <sub>3</sub> N <sub>3</sub>	DZ	150.3	125.6	111.2	112.6	174.0
CH <sub>3</sub> CH <sub>2</sub> N <sub>3</sub>	anti	151.0	125.3	111.3	114.1	173.6
	gauche	150.8	125.5	111.3	113.8	173.4
HC≡C-CH <sub>2</sub> N <sub>3</sub>	gauche	151.2	125.7	111.1	114.8	172.6
CH <sub>2</sub> =CHN <sub>3</sub>	syn	143.2	126.5	110.8	115.8	173.1
	anti	143.6	125.6	111.1	115.3	172.6
HCON <sub>3</sub>	syn	140.4	130.1	109.6	112.9	172.7
CH=CH-CH <sub>2</sub> N <sub>3</sub>	GG	151.5	125.8	111.1	113.1	173.6

<sup>a</sup> DZ, double zeta basis; HF, Hartree-Fock limit, see ref. /46/.

Whereas the XNNN atoms are considered co-planar in all the vapour structures, the N=N torsional angles deviate from 180 $^{\circ}$  in many of the crystal structures, apparently as a result of crystal forces. However, the averaged structure parameters from the X-ray crystallographic studies agree well with the corresponding vapour phase values. It is especially noteworthy that there are significant differences between the C-N and N=N bond distances in the alkyl and aryl azides, obviously due to conjugation, whereas the other structure parameters are identical.

3. Unlike the isoelectronic NCO (isocyanate) group which is believed to be linear, the NNN angle in the azides is bent and is close to 172 $^{\circ}$  in the vapours as well as in the crystals. The size and the electronegativity of the substituent X seem to play a minor role for the NNN angle.

4. The two N-N distances in the covalent azides are significantly different in all the compounds listed (the difference being ca. 12 pm). This difference in bond distance and in bond energy between the two N-N bonds is also apparent from a large difference in force constants (see below).

5. As discussed previously /46/ the N=N distances are systematically longer, the N≡N distances shorter in the quantum chemical calculations (Table 3) compared to the experimental values. It should be noticed, however, that the XNN and the NNN angles are quite well predicted in the calculations.

### Conformations

In the simple azides  $\text{HN}_3$ ,  $\text{FN}_3$ ,  $\text{ClN}_3$  and  $\text{N}=\text{CN}_3$  of Table 1, the molecules are planar and the NNN group is oriented anti to the substituents. In the larger azides as well, the NNN group is invariably oriented anti to the substituent X. When the substituent X deviates from cylindrical symmetry around the X-N bond, restricted rotation around this bond will clearly result in conformational alternatives. Certain conclusions about conformer stabilities can be drawn from the (1) vapour phase structures, (2) the ab initio conformational energies and (3) the vibrational spectra in particular.

When the azide is attached to a  $\text{C}\equiv\text{C}-\text{CH}_2$  /17/,  $\text{N}=\text{C}-\text{CH}_2$  /18/ or  $\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2$  /19/ fragment, the spectroscopic data revealed that only one conformer was present in significant amount in the vapour, in the liquid as well as in the crystal. From GED this conformer was found to be oriented gauche around the C-N bond with a dihedral angle of  $37^\circ$  from syn both in azido-2-butyne /19/ and in 3-azidopropyne /17/. In the related azidoacetonitrile /18/ the dihedral angle was found equal to  $52^\circ$ . The large frequency shifts in the IR and Raman spectra observed upon crystallization for this compound, suggest that the anti conformer is present in the crystal. The experimental results for 3-azidopropyne are in good agreement with the quantum chemical calculations, where the C-N torsional potential was calculated to have a minimum in the gauche position,  $38^\circ$  from syn, and maxima at the syn and anti positions,  $6.6$  and  $8.6 \text{ kJ mol}^{-1}$  higher, respectively.

In 2-azido-1,3-butadiene /21/ and 2,3-diazido-1,3-butadiene /22/ the azide group(s) is (are) lying in the molecular plane, apparently as a result of conjugation. In both molecules the NNN group was oriented syn to the adjacent C=C double bond, and the NNN moiety was always oriented anti to the C-N bond. The CNN angles were  $117$  and  $114.5^\circ$  in the two molecules, respectively. For comparison, the crystal structures of the aryl azides in Table 2 reveal small dihedral angles, less than  $20^\circ$ , between the  $\text{N}=\text{N}=\text{N}-\text{C}$  and the  $\text{N}-\text{C}=\text{C}$  planes; the deviation apparently being caused by lattice effects.

(7)

The preferred conformation in azidomethane appears from the calculations /46/ to be staggered rather than eclipsed, with an energy difference equal to  $3.75 \text{ kJmol}^{-1}$ . In azidoethane (which is also calculated to be staggered /46/) the gauche conformer was found to be more stable than anti by  $0.57$  and  $1.15 \text{ kJmol}^{-1}$  in the vapour and liquid, respectively, from IR matrix isolation and Raman spectral data recorded at different temperatures /47/. In comparison, the ab initio calculations indicated a negligible energy difference of  $0.26 \text{ kJmol}^{-1}$  with anti being the more stable /47/. As expected the gauche conformer was present in the crystal. Interesting annealing experiments with azidoethane in nitrogen and argon matrices revealed a barrier height of  $9.0 \text{ kJmol}^{-1}$  in the former and less than  $6 \text{ kJmol}^{-1}$  in the latter matrix /47/. The spectroscopic data for azidopropane have not yet been analyzed, but certain results of the quantum mechanical calculations are shown in Fig. 1. As is apparent, the GA and the GG conformers seem to be the more stable with AG and AA the next while the GG' has an energy of  $5.6 \text{ kJmol}^{-1}$  above GA. Taking the different statistical weights for G and A into account, the conformational equilibria for azidopropane are probably quite complex as is apparent from our matrix isolation IR spectra.

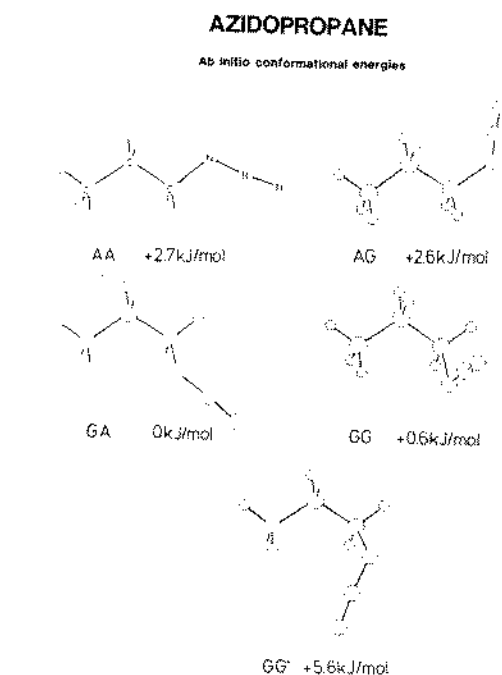


Fig. 1. Quantum chemical conformational energies of azidopropane.

In 3-azidopropene ( $\text{CH}_2=\text{CH}-\text{CH}_2\text{N}_3$ ) there are again five possible conformers due to restricted rotation around the C-C bond (syn and gauche) and two around the C-N bond (anti and gauche) leading to the conformers GG, SG, SA, GG' and GA (see Fig. 1, Ref. /20/). Our results from GED were not conclusive, but suggested ca. 20% SG, 40-80% GG and 40-0% GG' /20/. Recent results /48/ have shown that at least three conformers, probably GG, SG and GG' are present in the argon matrices (Fig. 2, curves B and C) but only the G was trapped in nitrogen matrices at 14 K (curve A). The dotted curves denote the spectra after annealing to 35 K (curve B) and 27 K (curve C) revealing a low barrier around the C-N bond and a higher barrier

around the C-C bond /48/. Quantum chemical calculations have given the values: 0, 2.1, 5.3, 6.4 and 6.5  $\text{kJmol}^{-1}$  for the conformational energies of GG, SG, SA, GG' and GA, respectively, again emphasizing the tendency of the azide group to adopt the gauche conformation around the C-N bonds. The gauche conformers in 3-azidopropene (GG, SG and GG') /20,48/ as well as in 3-azidopropyne /17/, azidoacetonitrile /18/ and azido-2-butyne /19/ involve a closer distance between the  $\text{N}_3$  group and the  $\text{C}\equiv\text{C}$  /17,19/ or the  $\text{C}=\text{C}$  bonds /20,48/ than the anti conformers, probably favoured by  $\pi$ -electron interactions between these bonds.

In azidocyclohexane the equatorial azide is more stable than the axial azide by 1.8  $\text{kJmol}^{-1}$  in the vapour and by 2.0  $\text{kJmol}^{-1}$  in the liquid according to IR and Raman spectral measurements at different temperatures /49/. IR spectra of azidocyclohexane in a high pressure diamond anvil cell revealed that the equatorial azide was present in the high pressure as well as in the low temperature crystals. The isoelectronic isocyanatocyclohexane, on the other hand, contained equatorial substituents in the low temperature and axial substituents in the high pressure crystals /50/. Due to rotations around the C-N bonds both the equatorial and the axial azide can adopt two different orientations compared to the ring, giving rise to molecules with total symmetries  $\text{C}_s$  (symmetry plane) and  $\text{C}_1$  (no symmetry). Preliminary results obtained by matrix isolation spectroscopy /49/ give a barrier of ca. 8  $\text{kJmol}^{-1}$  between the  $\text{C}_s$  and the  $\text{C}_1$  conformers in the axially substituted molecules. These data /49/ also suggest that the  $\text{C}_s$  and  $\text{C}_1$  conformers are stabilized to a different extent in the nitrogen and the argon matrices, as recently observed for certain polyhalogenated cyclobutanes /51/.

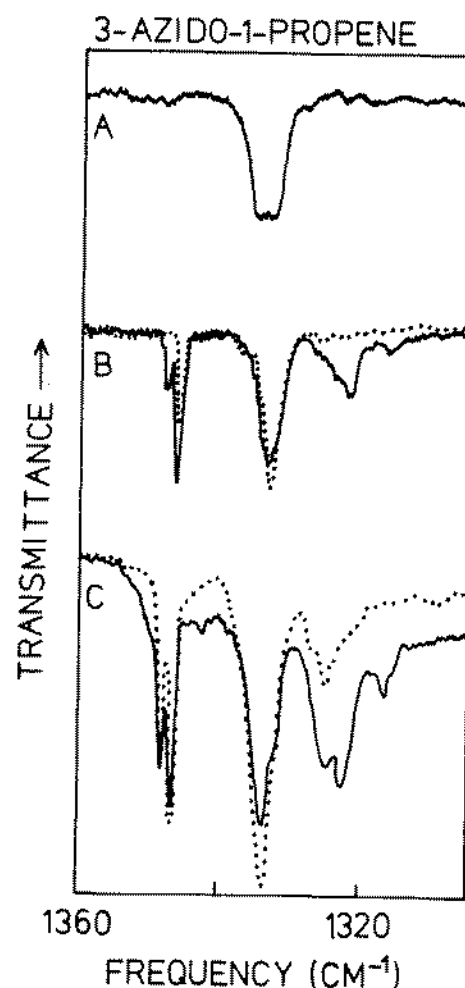


Fig. 2. IR matrix spectra of 3-azidopropene in  $\text{N}_2$  (curve A, 313 K deposit) and Ar (curve B, 313 K; curve C, 450 K deposition temp.). Dotted lines after annealing to 35 K (B) and 27 K (C).



The series of organic azides studied in our laboratory were all investigated quite thoroughly by IR and Raman spectroscopy in various states of aggregation and if possible at different temperatures. All the unsaturated azides investigated as well as the saturated azides with a high nitrogen/carbon ratio are very explosive, and led to some violent explosions in our laboratory. Therefore, they were not studied at ambient (and definitely not by elevated) temperatures in the condensed states. The exceptions were azidopropane and azidocyclohexane which were studied at ambient temperature even when irradiated by laser light. As the only member of the series azidocyclohexane was studied at high pressure at ambient temperature without any explosions occurring /49/.

Table 4. Characteristic fundamentals of the azides, X-N=N=N.

Compounds	N=N	N=N	NNN	NNN	Ref.
	str	str	bip	bop	
CH <sub>3</sub> N <sub>3</sub>	2106	1272	666	560	see 52
CD <sub>3</sub> N <sub>3</sub>	2118	1285	640	560	see 52
C <sub>2</sub> H <sub>5</sub> N <sub>3</sub>					
anti	2114	1279	630	562	47
gauche	2114	1261	679	558	47
C <sub>3</sub> H <sub>7</sub> N <sub>3</sub>	2096	1261	679	558	TW
C <sub>6</sub> H <sub>5</sub> N <sub>3</sub>	2120	1278	669	531	53
CH <sub>3</sub> CON <sub>3</sub>	2137	1211	620	580	54
C <sub>6</sub> H <sub>11</sub> N <sub>3</sub>					
equatorial	2103	1255	669	561	TW
N≡C-CH <sub>2</sub> N <sub>3</sub>	2115	1335	685	555	18
H-C≡C-CH <sub>2</sub> N <sub>3</sub>	2130	1340	692	558	17
D-C≡C-CH <sub>2</sub> N <sub>3</sub>	2129	1338	692	558	17
CH <sub>3</sub> -C≡C-CH <sub>2</sub> N <sub>3</sub>	2104	1336	678	556	19
CH <sub>2</sub> =CH-CH <sub>2</sub> N <sub>3</sub>					
GG	2112	1251	712	565	48
SG	2112	1277	689	570	48
GG'	2112	1270	717	555	48
CH <sub>2</sub> =C(N <sub>3</sub> )-CH <sub>2</sub> =CH <sub>2</sub>	2121	1227	620	548	21
CH <sub>2</sub> =C(N <sub>3</sub> )-C(N <sub>3</sub> )=CH <sub>2</sub>	2118	1238		537	22
	2098	1272	700		

Wavenumbers in cm<sup>-1</sup>; bip, bending in plane; bop, bending out of plane; TW, this work; GG, SG and GG' see text.

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The azide group  $N=N=N$  gives rise to characteristic localized vibrations connected with  $N=N$  stretch,  $N\equiv N$  stretch and  $NNN$  in plane (bip) and out of plane (bop) bending. The wave numbers as well as the intensities of these bands in IR and in Raman seemed fairly constant for all the azides studied and they should therefore be suitable as a diagnostic tool. These group frequencies are listed in Table 4 and represent a revised and extended version of a preliminary table in Ref. /55/. With a few exceptions the four fundamentals remain remarkably constant among the organic azides studied.

It must be noted that in the acetylenic azides included in Table 4, the  $N=N$  stretching mode is strongly mixed with the  $CH_2$  wagging mode at ca.  $1250\text{ cm}^{-1}$ . The two  $NN$  stretching modes are invariably very strong in IR and medium in Raman. The bip is generally medium to weak in IR and in Raman, whereas the bop is medium to weak in IR and very weak or absent in Raman. A reasonably good agreement between the experimental IR spectra of azidomethane and azidoethane in the vapour phase, and spectra calculated by quantum chemical methods, taking frequencies, intensities and vapour phase band contours into account, has been achieved /46/.

The wave numbers listed in Table 4 are partly obtained from IR vapour or liquid, partly from Raman liquid, whereas the GG, SG and GG' conformer values for 3-azidopropene are from IR matrix spectra. Only the equatorial conformer bands of azidocyclohexane have been analyzed so far. It was hoped that the positions of the azide bands might give a clue to which conformers were present.

Among the azides investigated, azidoethane /47/, 3-azidopropene /20,48/ and azidocyclohexane /49/ were recorded in Raman as liquids at various temperatures /56/ and by matrix technique employing a hot nozzle before the mixture was trapped on the window at 14 K /57/. From these data, the energy difference between the conformers were evaluated.

In all the azides studied the IR as well as the Raman spectra were obtained, if at all possible, both in the liquid, amorphous and crystalline states. This procedure was essential to establish the existence of one or more conformers. In 3-azidopropene the crystallization was extremely difficult to achieve and required cooling to an exact, but previously unknown temperature, for several hours. Raman spectra of the amorphous and crystalline solids have been published before /20,55/, but an improved spectrum of the low frequency region is presented in Fig. 3. Although the GG conformer is most abundant,

we believe that the SG conformer is present in the crystal /20/. In spite of numerous attempts no crystal spectrum was ever obtained in the IR cryostats.

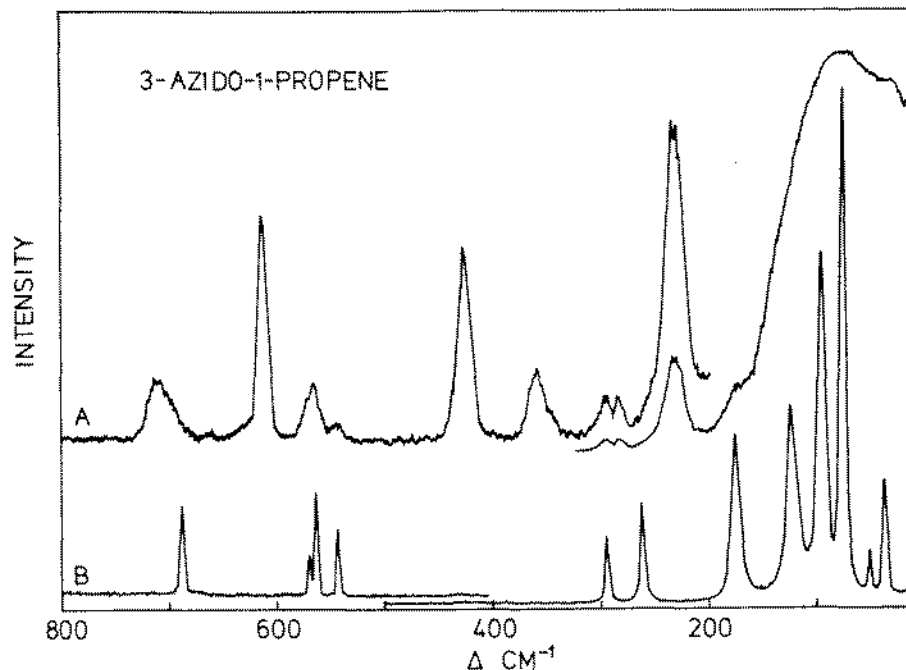


Fig. 3. Raman spectra of 3-azidopropene as an amorphous (curve A) and crystalline (curve B) solid at 85 K from /48/.

#### Force constant calculations

Attempts have been made to derive force fields for the azide groups in hydrazoic acid /52,58/ and in azidomethane /52/. In spite of the extensive isotopic data for hydrazoic acid /58/, it was not possible to construct a complete harmonic force field for this molecule.

In order to facilitate the spectral assignments, to interpret the spectra of coinciding conformer bands, and to correlate the spectra with the structural parameters, we decided to derive force fields by quantum mechanical methods for some of the smaller azides investigated. The ab initio calculated force fields were scaled in order to reproduce the observed frequencies of hydrazoic acid, azidomethane and azidoethane /46/. The scaled force field for the azide part of the anti conformer of azidoethane is given in Table 5. As is apparent from Table 5 (see also Tables 1-3) the large difference between the two NN stretching force constants justify the primitive description of the two NN bond distances as an N=N and an N≡N bond.

TABLE 5. Valence force constants for the azido group in azidoethane (anti) obtained from ab initio calculations.<sup>#</sup>

	N≡N	N=N	N-C	N≡N=N	N=N-C
N≡N	17.073				
N=N	1.805	9.666			
N-C	-0.150	0.177	4.231		
N≡N=N	-0.070	0.228	-0.017	0.629	
N=N-C	-0.107	0.725	0.516	0.100	0.873

<sup>#</sup>Scaled values, see Ref./46/. Units: m dyn·Å<sup>-1</sup>, m dyn·Å·rad<sup>-1</sup> and m dyn·Å<sup>-2</sup>.

The scaled force field for the azido group was subsequently transferred to the other azides studied. Thus, in the three acetylenic azides: 3-azidopropyne /17/, azidoacetonitrile /18/ and azido-2-butyne /19/ the force fields were derived from scaled quantum mechanical force fields from the gauche conformer of azidoethane /46,47/ concerning the N<sub>3</sub> group. This was combined with a local symmetry force field (LSSF) for the 3-halopropynes, haloacetonitriles and halo-2-butyne by the overlay technique, using dimensionless coordinates Δ r/r<sub>e</sub> as employed for trans-1,4-dihalocyclohexanes /59/ and halogenated neopentanes /60/. These force fields gave very satisfactory agreement with the observed spectra in the three molecules /17-19/.

In 3-azidopropene /20/ a force field was constructed for each of the five possible conformers from an LSSF and a scaled quantum mechanical force field for anti and gauche conformations of azidoethane /46,47/ and for propene /61/. The calculated wavenumbers supported the conclusion that this molecule crystallizes in the SG conformer rather than in the more stable GG /20/.

In azidopropane and in azidocyclohexane the different conformer fundamentals are presently being calculated in a corresponding way from the scaled quantum mechanical force constants for the azido group based upon the gauche conformer of azidoethane /46/ and transferred force constants for the propane and cyclohexane /59/.

A slightly different procedure was employed for the azidobutadienes /21,22/. The ab initio calculated force constants for azidoethene /46/ were modified using the same scaling factors found for

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azidoethane /46/. This force field was subsequently combined with a scaled quantum mechanical force field for 1,3-butadiene /62/ and with an LSSF for the same molecule /63/.

In our opinion the procedure used: namely combining quantum mechanical ab initio and "experimental" force fields to the various types of azides have been of considerable help in the spectral assignments. The overall agreement between the observed and calculated vibrational frequencies /17-22, 46-48/ is generally quite satisfactory and support this approach.

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