

THE VIBRATIONAL SPECTRA, MOLECULAR STRUCTURE AND CONFORMATIONS
OF ORGANIC AZIDES. I. A SURVEY

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ABSTRACT

A number of organic monoazides ($R-N_3$) have been synthesized in which R is: (1) a saturated group, CH_3 , C_2H_5 , $n-C_3H_7$; (2) an olefinic group, allyl, butadiene; (3) an acetylenic group, $N\equiv C-CH_2$, $H-C\equiv C-CH_2$, $CH_3-C\equiv C-CH_2$. Two additional unsaturated diazides ($CH_2=C(N_3)-C(N_3)=CH_2$ and $N_3-CH_2-C\equiv C-CH_2-N_3$) were prepared.

The compounds (most of them very explosive) were studied by IR and Raman spectroscopy in the liquid, in solution and in the solid state, and by matrix isolation technique in IR. The spectra were interpreted in terms of one or in some cases two or more conformers and assigned with the aid of normal coordinate analysis.

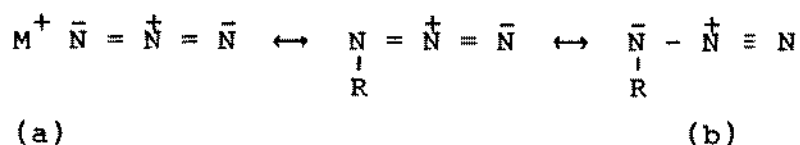
UV photolysis experiments in nitrogen matrices at 12 K were carried out and the reactions monitored by FTIR. The intermediate products could in some cases be identified as imines.

Six of the azides were investigated by gaseous electron diffraction and the molecular structures established. The azide group was situated *gauche* to the hydrocarbon skeleton in $N\equiv C-CH_2N_3$, $H-C\equiv C-CH_2N_3$ and $CH_3-C\equiv C-CH_2N_3$. In the butadienes $CH_2-C(N_3)-CH=CH_2$ and $CH_2=C(N_3)-C(N_3)=CH_2$ the azide group was *syn* to the adjacent C=C bond, while in $H_2C=CH-CH_2N_3$ at least two conformers were detected.

Model calculations on the smaller azides by *ab initio* quantum chemical methods were used to establish trends in the geometry and force fields of the azide group.

INTRODUCTION

The azide group $-NNN$ which is isoelectronic with $-NCO$ has many interesting bond properties. When attached to electropositive metal atoms like the alkali metals an ionic structure $M^+ N_3^-$ is formed in which the azide anion is linear (a) with equivalent N-N bonds of 116 pm each (ref.1). In covalent azides ($R-N_3$), however, formed when R is an organic radical, the azide group has a slightly bent structure with a longer and a shorter N-N distance (b):



Very few covalent azides have hitherto been synthesized and characterized in the vapour phase by physical methods: HN_3 (ref.2), CH_3N_3 (ref.3), $(\text{CH}_3)_3\text{SiN}_3$ (ref.4), ClN_3 (ref.5), CF_3N_3 (ref.6), $\text{CH}_3\text{CO-N}_3$ (ref. 7) and $\text{CH}_3\text{O-CO-N}_3$ (ref. 8). This is particularly true for unsaturated azides, of which only $\text{CH}_2=\text{CHN}_3$ (ref.9), $\text{N}\equiv\text{CN}_3$ (ref.10) and $\text{C}_6\text{H}_5\text{-N}_3$ (ref. 11) have been studied. The reason for this scarcity is obvious, the azides are highly endothermic compounds which can, and do explode violently in the condensed states. It is our experience that the unsaturated azides containing one or more double or triple bonds and the diazides are particularly dangerous. They should be handled with the utmost care and in small quantities, preferably at low temperatures.

A number of organic azides have recently been prepared for the first time in this laboratory and new synthetic routes (ref.12) including two phase reactions using ultrasound (ref.13) have been developed.

The following azides were prepared: saturated, ethylazide (I), n-propylazide (II); one or two double bonds, 3-azidopropene $\text{CH}_2=\text{CH-CH}_2\text{N}_3$ (III), 2-azido-1,3-butadiene $\text{CH}_2=\text{C(N}_3\text{)-CH=CH}_2$ (IV); one triple bond, azidoacetonitrile $\text{N}\equiv\text{C-CH}_2\text{N}_3$ (V), 3-azido-propyne $\text{HC}\equiv\text{C-CH}_2\text{N}_3$ (VI), 3-azidopropyne-1d, $\text{DC}\equiv\text{C-CH}_2\text{N}_3$ (VIa), 1-azido-2-butyne $\text{CH}_3\text{-C}\equiv\text{C-CH}_2\text{N}_3$ (VII). In addition, two unsaturated diazides were synthesized: 2,3-diazido-1,3-butadiene $\text{CH}_2=\text{C(N}_3\text{)-C(N}_3\text{)=CH}_2$ (VIII) and 1,4-diazido-2-butyne $\text{N}_3\text{CH}_2\text{-C}\equiv\text{C-CH}_2\text{N}_3$ (IX).

These azides have all been studied by IR and Raman spectroscopy including matrix isolation technique, and the detailed interpretation of these spectra supported by normal coordinate analyses are in progress. Six of the unsaturated azides, compounds III, IV, V, VI, VII and VIII were investigated by gaseous electron diffraction (ED) and the molecular structures were determined.

Quantum mechanical ab initio calculations were carried out on the following azides: hydrazoic acid (X), methylazide (XI), on I, etheneazide (XII) and on VI. The experimental structures were compared with the optimized ab initio structure. Quadratic force constants derived from the calculations were compared with those

obtained from normal coordinate analyses based upon the observed vibrational spectra.

Finally, the photolytic reactions of organic azides were investigated in inert gas matrices. The IR matrix spectra were observed at intervals after irradiation with UV light from a Hg source. Some preliminary results for azides XI and VI have been reported (ref.14).

A survey of the spectral, structural, quantum mechanical and photolytic results for the azides I-XII will be presented. The detailed results which have involved a number of coworkers in this laboratory will be presented in forthcoming papers.

EXPERIMENTAL

Chemicals

The organic azides were prepared by different synthetic routes. Detailed procedures were developed for the preparation and purification of unsaturated azides (refs.12,13). The physical and spectroscopic properties necessary for characterisation of the new compounds have been reported (refs.12,13).

Electron diffraction

The electron diffraction data were recorded at 293 K either on a Balzer Eldigraph KDG-2 (compound VI) or on the Oslo apparatus (ref.15) (compounds III-VIII). Data sets from two nozzle-to-plate distances were recorded for compounds III-VII, but for VIII only the recordings made at the long distance (50 cm) were successful. Averaged (all camera distances and all plates) intensity curves in the form $\underline{S} I_m(s)$ were obtained and least squares analysis carried out using unit weight matrix. Molecular geometries were calculated from geometry consistent parameters. The detailed calculations involving the root mean square amplitudes of vibration (\underline{l}) and the perpendicular correction coefficients (\underline{K}) will be described in the forthcoming papers.

Spectroscopy

The IR spectra were recorded with Perkin-Elmer model 225 and Bruker model 114C spectrometers. Conventional sealed cells with windows of CsI and polyethylene were used for the liquids, solutions and vapours. Spectra of the pure liquids were also recorded in sealed cells with CsI windows, which were cooled with acetone-

dry ice baths to temperatures just above freezing. Cryostats cooled with liquid nitrogen served for obtaining amorphous and crystalline materials. Matrix isolated azides in 1:1000 ratio in argon and nitrogen were deposited on a CsI window in a Displex unit and later photolyzed through a quartz window with an medium pressure Hg lamp.

Raman spectra were recorded with a Dilor RT-30 spectrometer interfaced with the Aspect 2000 of the Bruker spectrometer. Argon ion (CRL model 52G) and helium-neon (Spectra-Physics model 125A) lasers were used for excitation. Laser power below 50 mW was employed. The liquids were invariably recorded in a capillary tube of 2 mm inner diameter cooled with cold nitrogen gas (ref.16). Amorphous and crystalline samples were deposited on a copper finger, cooled with liquid nitrogen.

Quantum chemical calculations

Ab initio Hartree-Fock calculations were performed in order to investigate the molecular structures and preferred conformations of a series of organic azides. All calculations were carried out with a gradient version of the program MOLECULE (refs.17,18). A basis set of double zeta quality was employed, contracted from 7s3p primitive sets for C and N (ref.19) and from a 3s set for H (ref.20). The relaxation of the geometries was continued until all Cartesian forces on the atomic coordinates were less than 0.001 hartree/bohr.

Molecular force fields, including anharmonic terms, were obtained by a least squares fitting of a potential energy expansion to the ab initio calculated gradients in a number of points on the potential energy surface. For this purpose the gradient was also calculated for a number of distorted structures. The bond lengths were typically displaced ± 2.5 pm and the angles ± 2 degrees from their equilibrium values.

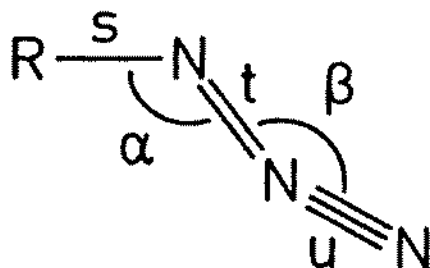
RESULTS AND DISCUSSION

Structure

The molecular parameters for the azide group determined for six of the present unsaturated azides are listed in Table 1. These results are compared with reported structural data for HN_3 (ref.2), CH_3N_3 (ref.3), CF_3N_3 (ref.6), ClN_3 (ref.5), $\text{N}\equiv\text{CN}_3$ (ref.10), $\text{CH}_3\text{O}-\text{CO}-\text{N}_3$ (ref. 8) and $\text{C}_6\text{H}_5-\text{N}_3$ (ref. 11) determined

TABLE 1

Structures of azides determined in the vapour phase.



Compounds	s	t	u	α	β	Meth. ^a	Ref.
HN ₃	101.5	124.3	113.4	108.8	171.3	MW	2
CH ₃ N ₃	140.8	124.	116.8	(120)	(180) ^b	ED	3
CF ₃ N ₃	142.7	125.0	111.7	111.8	175.3	ED, MW	6
ClN ₃	174.5	125.2	113.3	108.7	171.9	MW	5
CH ₃ -CO-N ₃	146.0	124.8	113.1	110.7	(180) ^b	MW	8
N≡CN ₃	135.5	126.1	112.1	114.5	169.2	ED	10
H-C≡C-CH ₂ N ₃	146.4	124.9	113.7	114.5	169	ED	24
N≡C-CH ₂ N ₃	147.6	124.5	113.5	115.4	173	ED	23
CH ₃ -C≡C-CH ₂ N ₃	147.4	124.0	114.2	116.5	174	ED	25
CH ₂ =CH-CH ₂ N ₃	147.5	123.6	113.8	115.1	174	ED	21
CH ₂ =C(N ₃)-CH=CH ₂	143.4	125.3	114.3	116.8	173	ED	22
CH ₂ =C(N ₃)-C(N ₃)=CH ₂	143.2	124.2	114.1	114.4	166.7	ED	26
C ₆ H ₅ N ₃		123.0	114.3		174.4	MW	11 ^b

^aMW, microwave; ED, electron diffraction, ^bassumed value.

partly by electron diffraction (ED) and partly by microwave (MW) spectroscopy. The detailed structural parameters for the series of molecules numbered III (ref.21), IV (ref.22), V (ref.23), VI (ref.24), VII (ref.25) and VIII (ref.26) will be published in separate papers. It appears from Table 1 that the distances t (N-N(R)) and u (N-N(N)) are remarkably constant for all the azides studied.

The significant difference between t and u suggests that the bonds should be described as N=N and N≡N, respectively. Slightly larger variations were encountered for the angles α (RNN) and β (NNN), although the standard deviations for the angles are considerable. It is highly significant that the NNN angle β is not 180°, but deviates 5-11° from linearity in the covalent azides, and that it is always situated anti with respect to the RNN angle (α). A bent NNN skeleton is also in agreement with the results from the ab initio calculations (see below).

The RNN angle α is constant within the experimental error in the molecules III-VIII. The smaller α value reported for ClN_3 (refs.5,27) and HN_3 (ref.2) may be due to decreased repulsion between the small substituents and the azide group.

A main purpose of the present structural and spectroscopic studies is concerned with the conformations present in the azides. What is the torsional angle around the C-N bond? Are there more than one pronounced minimum on the potential curve giving rise to additional conformers?

In 2-azido-1,3-butadiene (IV) the butadiene skeleton is obviously anti like in butadiene (ref.28) and in 2-halogenated butadienes (ref.29). The azide group is lying in the symmetry plane eclipsing the adjacent C=C bond. No additional conformers were detected neither by ED nor by spectroscopy.

The three compounds with triple bonds, V, VI and VII all had the azide group situated gauche to the hydrocarbon skeleton. No additional anti conformer was detected either from ED or from

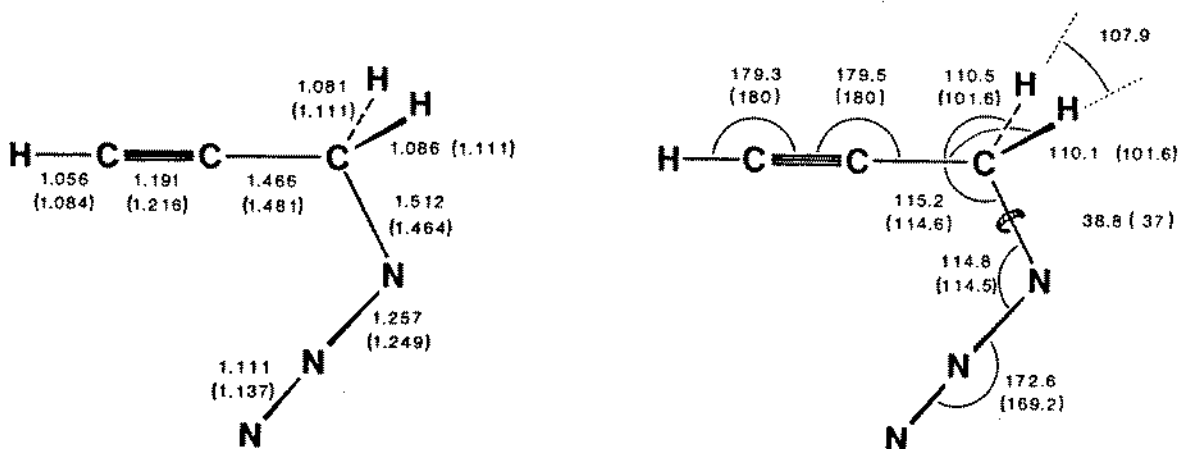


Fig. 1. Bond lengths (in Å units) and angles for 3-azidopropyne (compound VI) derived from quantum chemical calculations and from electron diffraction (parentheses).

spectroscopy (see below) for these compounds, and this was supported by the quantum chemical calculations for VI (see Fig. 1).

Quantum chemical calculations

The molecular structures and preferred conformations were computed on selected azides by the double zeta basis Hartree-Fock calculations using the gradient method. Preliminary results (ref.30) reveal that: (1) the azido group is non-linear with an

NNN angle of $172-174^\circ$ and (2) the NNN group is situated anti to the C-N bond. Both these conclusions are in agreement with the results from ED (refs.6,21-26) and MW (refs.2,6). The experimental structural parameters for 3-azidopropyne (ref.24) show a very satisfactory agreement with the calculated values as seen in Fig. 1. Excellent agreement between the experimental (ref.2) and calculated (ref.30) structural parameters was also obtained for HN_3 .

For methylazide (XI) the staggered conformer was calculated to be the more stable and the methyl group was tilted away from the azido group by 4.2° (ref.30), similar to the experimental results for CF_3N_3 (ref.6). The present calculations also include structure optimization for I, XII and for HCON_3 . Ab initio calculated force fields were also compiled in order to compare the observed spectral trends in the vibrational modes of the azide group.

Spectral interpretations

The detailed IR and Raman spectra of the azides investigated will be presented in the forthcoming papers. Due to the chemical instability and the danger of explosions some of the spectra were not of a very good quality. This is particularly true for the diazides VIII and IX which both decomposed in the laser beam and

TABLE 2
Vibrational group frequencies of the azide group R-N=N=N .

Azides	No.	N \equiv N str	N=N str	NNN bip	NNN bop	Ref.
HN_3	X	2140	1274	522	637	3
DN_3		2141	1183	498	630	3
CH_3N_3	XI	2106	1272	666	560	3
CD_3N_3		2118	1285	640	560	3
$\text{C}_2\text{H}_5\text{N}_3$	I	2110	1241	659	563	TW
$n\text{-C}_3\text{H}_7\text{N}_3$	II	2096	1261	679	558	TW
$\text{C}_6\text{H}_5\text{N}_3$		2120	1278	669	531	11a
CH_3CON_3		2137	1211	620	580	7
$\text{N}\equiv\text{C}-\text{CH}_2\text{N}_3$	V	2115	1265	685	555	23
$\text{H}-\text{C}\equiv\text{C}-\text{CH}_2\text{N}_3$	VI	2123	1247	670	559	24
$\text{D}-\text{C}\equiv\text{C}-\text{CH}_2\text{N}_3$	VIa	2121	1248	694	558	24
$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_2\text{N}_3$	VII	2133	1248	690	556	25
$\text{CH}_2=\text{CH}-\text{CH}_2\text{N}_3$	III	2100	1250	625	563	21
$\text{CH}_2=\text{C}(\text{N}_3)-\text{CH}=\text{CH}_2$	IV	2111	1224	617	577	22
Diazides						
$\text{N}_3\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2\text{N}_3$	IX	2120	1245	699	553	TW
		2109	1216	665	-	
$\text{CH}_2=\text{C}(\text{N}_3)-\text{C}(\text{N}_3)=\text{CH}_2$	VIII	2124	1272	700	537	26
		2098	1238	600	523	

TW, this work; bip, bending in-plane; bop, bending out-of-plane.

were considered the most highly explosive of the series (VIII exploded during a Raman recording and damaged the collection optics).

The localized azido group frequencies of the present azides studied for the first time are compared with those reported earlier (Table 2) including $C_6H_5N_3$ (ref.11a) and CH_3CON_3 (ref.7). The two azide stretches which conveniently can be interpreted as $N\equiv N$ and $N=N$ stretch rather than NNN asymmetric and symmetric stretch, are easily identified since they are frequently the two most intense bands in the entire spectrum both in IR and in Raman. As is apparent from Table 2 the two stretching modes are quite constant in frequency for all the azides. Although the $C\equiv C$ stretch is situated close to the $N\equiv N$ stretch in VI, VIa and VII the azide

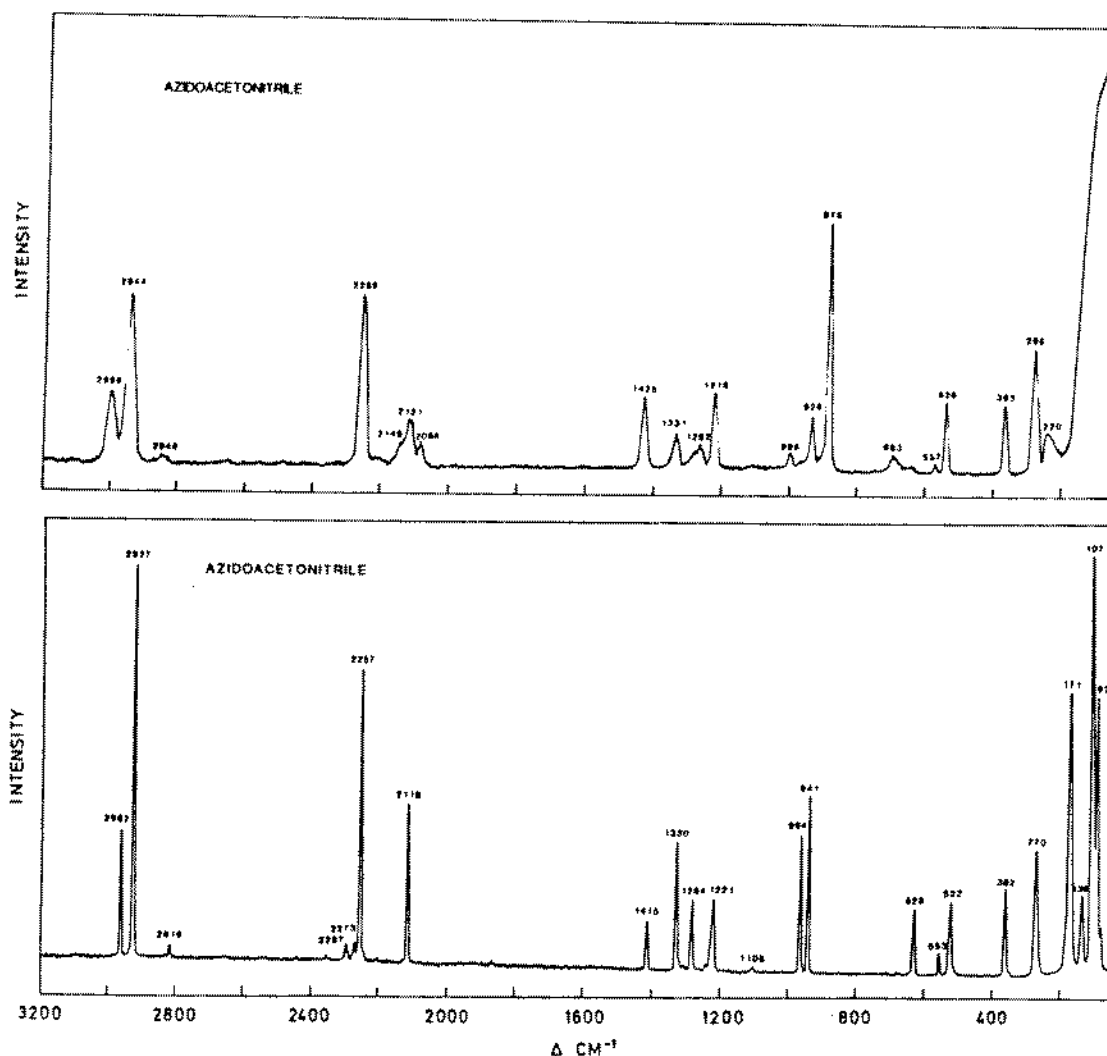


Fig. 2. Raman spectra of azidoacetonitrile (V) at 90 K as an amorphous solid (top) and as an annealed crystal (bottom), revealing large frequency shifts on crystallization.

mode is only slightly perturbed. For IV and VIII the conjugation between C=C and the azide has negligible effect on the frequencies.

There are two NNN bending modes of which the bip (bending-in-plane) is at a higher wave number than bop (bending out-of-plane, which is really a torsion) for all the azides investigated, except for HN_3 . Both are much weaker than the stretching modes, and the bop is usually very weak or completely absent in Raman.

It was a main purpose of the spectral investigations to determine if one or more conformers of the azides were present. For this purpose the IR and Raman spectra were investigated in the liquid state and as amorphous and crystalline solids at 90 K. These studies gave the following results:

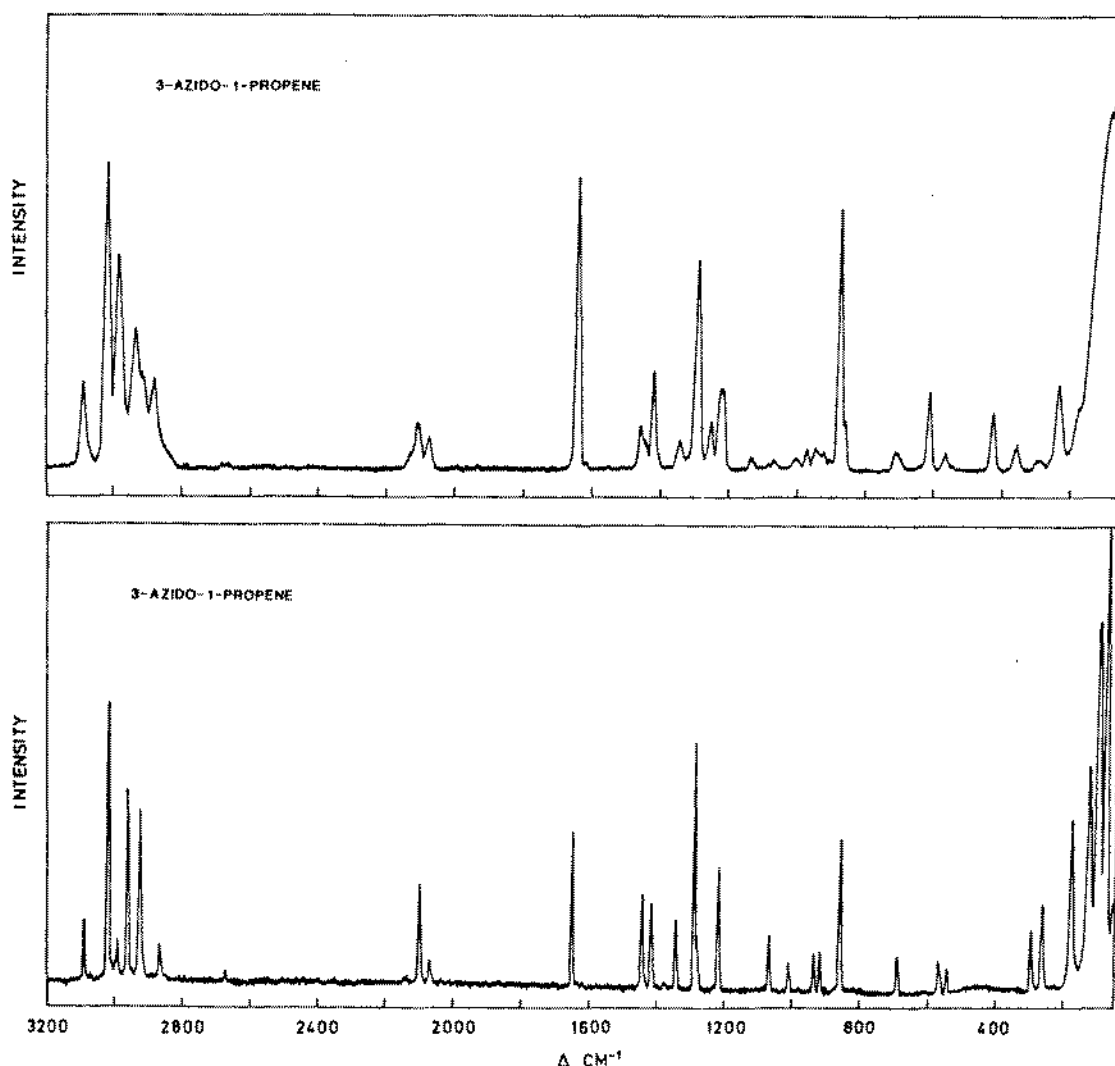


Fig. 3 Raman spectra of 3-azido-propene (III) at 90 K as an amorphous solid (top) and as an annealed crystal (bottom), indicating the existence of two or more conformers in the amorphous solid.

The two compounds VI and VII as well as the two butadienes IV and VIII had no IR or Raman bands which vanished in the crystalline state in agreement with the ED data revealing one conformer only. For azidoacetonitrile (V) the frequency shifts between the amorphous and crystalline state were exceptionally large as seen from the Raman spectra of Fig. 2. We believe that the shifts are due to a strong interaction between the $C\equiv N$ and the $-N=N\equiv N$ dipoles in the crystal lattice, but the spectra are not yet analyzed in detail (ref.23).

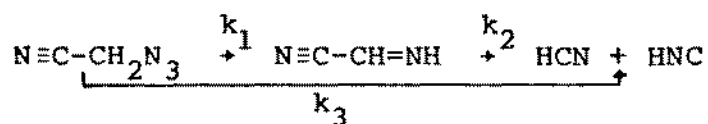
In I there are spectral indications suggesting two conformers, and for II there are definitely various conformers present. For 3-azidopropene (III) large efforts were made to study this compound in the amorphous and crystalline states (ref.19). In spite of numerous attempts, III never did crystallize by annealing an amorphous solid formed by condensing the vapour on a CsI window (IR) or a copper block (Raman) at 90 K. It was also extremely difficult to crystallize III by cooling a liquid. When a capillary filled with III was left in the vapour over a Dewar filled with liquid nitrogen over night crystallization was achieved (ref.21). The Raman spectrum of the amorphous and crystalline solids recorded at 90 K are shown in Fig. 3. It is clearly seen that various weaker bands vanish in the crystal, and we believe that the gauche-gauche conformer is present in the crystal (ref.21).

Photolysis

Photolytic studies of organic azides isolated in inert gas matrices have been reported for methylazide (refs.31,14), ethylazide (ref.32), t-butylazide (ref.33) and 3-azido-1-propyne (ref.14). The photodecomposition of azides may involve a discrete nitrene intermediate or alternatively a concerted group migration and subsequent loss of nitrogen.

We have recorded the IR spectra at certain time intervals during the UV irradiation. By analyzing the relative band intensities as a function of time it was possible to deduce a kinetic model for the photodecomposition.

In methylazide the decomposition to methylenimine and $HCN + HNC$ follows a scheme with two consecutive first order reactions (ref.14). For 2-azido-1-propyne (ref.14) and azidoacetonitrile (ref.34) the decomposition is more complex:



and the rate constants k_2 and k_3 are of the same magnitude.

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