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## Infrared and Ultraviolet Absorption Spectra of Alpha-Azido Ethers and Amines<sup>†</sup>

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#### Abstract

The ultraviolet absorption spectra of a series of alpha- azido ethers, alpha- azido thioethers, and alpha- azido amines exhibited extinction coefficient maxima in the region 264-300 m $\mu$  A shift to the lower wavelength was found to occur in the order S>O>N when these atoms are substituted alpha to an azido- group.

Infrared absorption spectra were recorded in the 2 to 15 micron region, and assignments made for the asymmetric and symmetric  $N_3$ stretching vibrations. The  $N_3$  asymmetric vibration occurred in the range 2141-2090 cm<sup>-1</sup> for the azides examined. The  $N_3$  symmetric vibration was more variable. Tentative assignments were made for this absorption occurring for alpha- azido ethers and alpha- azido thioethers. However, no assignment was made for this vibration for the alphaazido amines due to the complicated spectra in this region. The  $N_3$ asymmetric vibration for azidomethyl methyl ether, azidomethyl methyl sulfide and N-azidomethyl phthalimide exhibited a doublet while other azides exhibited a single absorption for this mode.

#### Introduction

The linear structure of the azido-group, as in covalent and ionic azides, coupled with its facility of forming five membered azoles of structure I:



where A is carbon and B may be carbon, nitrogen or sulfur, respectively, has led to questions concerning the nature of the intermediate state. The basic question to be answered involves the process whereby three sequentially linked nitrogen atoms changes from the linear structure to the bent structure. The present investigation is part of a program which attempts to study this problem.

The use of absorption spectroscopy to the solution of structural problems in the thiatriazole ring system has been reported by Lieber and students (1-4). It was demonstrated that reactions which should lead to thiocarbamyl azides are in reality derivatives of the thiatriazole ring system. Infrared spectral evidence confirmed thus (1-7). On the other hand, spectroscopic evidence just as clearly demonstrates the existence of the carbamyl azide structure rather than the oxytriazole ring system. Scott (8) reported a broad clean asymmetric N<sub>3</sub> absorption band in the infrared for a number of phosphoryl azides and concluded that a ring structure does not exist.

Azides are reported (9) to be readily recognized by the strong N<sub>3</sub> asymmetric stretching absorption, which occurs with constancy near 2130 cm<sup>-1</sup>. The corresponding symmetric stretching occurs at a considerably lower frequency (about 1300 cm<sup>-1</sup>) but is much more variable in frequency and intensity. Contributions to the infrared absorption spectroscopy of azides have been made by Eyster (10), Sheinker (11), Boyer (12,13) Lucien (14) and Lieber (15,16). More recently, Lieber (17) has discovered that aromatic acid azides exhibit a doublet for the N3 asymmetric stretching absorption. An extension of this work (23) demonstrated that the  $N_3$  asymmetric doublet was due to the proximity of the conjugative aromatic unsaturation (benzene ring) and that the band again appeared as a singlet when the aromatic ring was reduced, as in cyclohexyl carboxylic acid azide. It was with the objective of studying such alpha interactions (which the authors now term perturbation effects) that the investigation of the absorption spectroscopy of alpha-azido ethers and amines was initiated. These compounds can be generalized by the structure:  $R-X-CH_2-N_3$ , where X may be oxygen, sulfur, or nitrogen and R is an alkyl or aryl group, respectively. The similarity of these compounds to thiocarbamyl azides, carbamyl azides, and carbonyl azides may be ob-

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served by rewriting the structure in the following form given by:



where X = O, S, or N, in which the *perturbating effect* is limited to the oxygen, sulfur or nitrogen atoms, respectively. A systematic study of the ultraviolet and infrared absorption spectra of alpha azide ethers has not been previously reported.

#### **Experimental\***

#### Alpha-Azido Ethers and Amines

In general, these compounds were prepared by the action of sodium azide upon the corresponding alpha-haloether as described by Bohme for alpha-azido-ethers (18), alpha-azido thio ethers (19) and N-azido-methylamines  $(\hat{2}0)$ . The compounds prepared for spectroscopic study are summarized in Table I. In most cases satisfactory elemental analyses for carbon and hydrogen were obtained. Unlike that reported by Bohme (18) the methyl- and ethyl- alphaazido ethers proved to be too explosive for carbon and hydrogen combustion. In the case of the alpha-azido thioethers satisfactory elemental sulfur analyses were obtained in all cases. Bis-azido-methyl sulfide, a new compound, proved to be too explosive for carbon-hydrogen analysis. All of the compounds reported in Table I are liquids, except that of N-azidomethylphthalimide, a new compound, which comprised colorless plates, melting at 72-73° (uncorrected). All of the liquids had boiling points which agreed with the values previously reported (18-20). Alphaazido ethers and amines are dangerous compounds. Repetitions of these synthesis should observe proper safety equipment including spark-proof stirring motors.

TABLE I. ALPHA-AZIDO ETHERS AND AMINES R-X-CH2-N3

R			Nitrogen, %	
	<u>X</u>	Formula	Calcd.	Found
CH₃	0	C <sub>2</sub> H <sub>5</sub> N <sub>3</sub> O <sup>a</sup>	48.26	48.26
$C_2H_5$	0	C <sub>3</sub> H <sub>7</sub> N <sub>3</sub> O <sup>a</sup>	41.56	41.20
CH <sub>3</sub>	S	C <sub>2</sub> H <sub>5</sub> N <sub>3</sub> S	40.74	40.03
$C_2H_5$	S	$C_3H_7N_3S$	35 86	35.80
$n-C_3H_7$	S	C₄H₃N₃S <sup>b</sup>	32.03	32.35
$C_6H_5$	S	C7H7N3S	25.43	25.43
$C_6H_5CH_2$	S	C <sub>8</sub> H <sub>9</sub> N <sub>3</sub> S	23.44	23.75
$N_3CH_2$	S	C <sub>2</sub> H/N <sub>6</sub> S <sup>a, b</sup>	58 30	58.50
(CH <sub>3</sub> ) <sub>2</sub>	$N^{e}$	$C_3H_8N_4$	55.97	55.65
C <sub>5</sub> H <sub>10</sub>	Ne	$C_6H_{12}N_4$	39.97	40.30
$C_6H_2C_2O_2$	N <sup>d</sup>	$C_9H_6O_2N_4^{b}$	27.71	27 65

<sup>a</sup>Three independent analytical laboratories were unable to analyze for carbon and hydrogen due to the very explosive thermal degradations of the compounds when heated.

<sup>b</sup>New compounds

'Piperidino-group

<sup>d</sup>Ortho-phthalimido-group

"Bohme (20) was unable to obtain a satisfactory analysis for this compound.

RX	$\lambda_{max}, m\mu$	Emaa
CH <sub>3</sub> O	274	39.9
CH <sup>1</sup> CH <sup>-</sup> O	276	331
CH <sub>3</sub> S	284	28.0
CH₃CH₂S	284	284
CH₁CH₂CH₂S	284	298
N <sub>3</sub> -CH <sub>2</sub> -S	284	54.9
C <sub>6</sub> H <sub>5</sub> S	a,	а
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> S	A.	в
(CH <sub>3</sub> ) 2N	264 <sup>b</sup>	326
C <sub>5</sub> H <sub>10</sub> N	264 <sup>b</sup>	37.7
$C_6H C_2O_2N$	4	a

<sup>a</sup>Azide absorption in the 260-290 m $\mu$  region matked by strong aromatic absorption.

 ${}^{b}\lambda_{max}$  taken as the inflection point.



Bis-azido-methyl sulfide

N-Azidomethylphthalimide

#### Ultraviolet Absorption Spectra

Spectra were obtained on a Beckman Model DU quartz spectrophotometer with 1 cm matched quartz cells over the range of 240-300 m $\mu$  and curves plotted for log  $\epsilon$ versus wave length. All samples were dissolved in anhydrous spectroscopic methanol, and absorbance readings using a methanol blank were taken. Anhydrous conditions were rigidly maintained. The data obtained are summarized in Table II. Figure 1 shows a typical plot for each of the three different types of azido-ether.

#### Infrared Absorption Spectra

The spectra were recorded on a Perkin-Elmer Model 21 double beam spectrophotometer with a sodium chloride prism (calibrated against a polystyrene film) over the range of 2-15 microns using an automatic slit drive with a program of 927 and a scanning rate of twenty min. The spectra of liquids were recorded in a demountable cell containing a 0.025 mm silver spacer. Solids were mulled in a drop or two of white oil (Nujol). Spectra over selected ranges were recorded from solution by nulling out the solvent spectra in the reference beam. Exact N3 asymmetric absorption frequencies were recorded from carbon tetrachloride solution in 0.20 mm matched cells with a program of 960, adjusting the concentration so as to absorb 70-80% of the energy input at the absorption maximum. Because of the complicated vibrations appearing in the N<sub>3</sub> symmetric stretching region, this portion of the spectrum was also recorded in carbon tetrachloride. Spectra of the halomethyl intermediate were also recorded from solution and super imposed on the azido spectra in order to locate the N3 symmetric stretching absorption. The infrared assignments for the N3 asymmetric and symmetric vibration are summarzied in Table III. A typical full scale spectrum is shown by Figure 2 for azidomethyl methyl sulfide. The more precise study in the asymmetric region for the same compound is shown in Figure 3, which shows the asymmetric doublet. The complexity of the symmetric region is illustrated by bis-(azido methyl) sulfide in Figure 4.

<sup>&#</sup>x27;Elemental micro-analyses were carried out by Dr. C. Weiler and Dr F. B. Strauss, Oxford, England.



FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA OF (1) Azidomethyl methyl sulfide, (2) N-azidomethyl dimethylamine, and (3) Azidomethyl methyl ether.

WAVELENGTH, (mµ)

#### Discussion

#### Ultraviolet Absorption Spectra

Gilliam and Stern (21) report that aliphatic azides such as ethyl azide or azidoacetic acid show a characteristic low intensity band near 285 m $\mu$  (E = 20-50) and a band of high intensity near 222 m $\mu$  (E ca. 150) and that this band differs from that of azide ion, e.g., sodium azide. Lieber (22) has reported a weak absorption band between 282 and 288 m $\mu$  for a number of alphatic and aromatic azides. The intensity of this band was very weak, and an increase in chain length did not effect the intensity of this band. The absorption was stronger in the phenyl and substituted phenyl azides, although not as strong as the primary band of benzene. Bohme (18,19) reported the presence of a weak band for azido-methyl ethers and azidomethyl thioethers in the 275-290 m $\mu$  region.

As seen in Table II, spectra of azidomethyl ethers, -thioethers, and -amines exhibited absorptions of weak intensity in the 264-284 m $\mu$  region. A shift toward the lower wavelength is seen to occur in the order S>O>N (Figure 1), when these atoms are substituted alpha to an azido group. An increase in chain length had little effect upon the intensity of this absorption. However, the introduction of a second azido group into a molecule increased the intensity of this absorption nearly two fold. Spectra of aromatic azides were not plotted, since the primary aromatic bands overshadowed the weaker azide absorption. As in the past, absortpions in this region are assigned to the nitrogen -nitrogen multiple linkages of covalently bound azides. However, the effect of the substituent alpha to the azido group is seen by a shift of the azide absorption. Although limited in scope, this appears to be the first systematic study of the effect of an alpha substituent on the ultraviolet azido frequency.



Fig. 2. Infrared Absorption Spectra of Liquid Azidomethyl Methyl Sulfide in 0.025 MM Cell:





#### Infrared Absorption Spectra

The infrared absorption spectra of azidomethyl ethers, -thio-ethers, and -amines were studied with particular emphasis upon the  $N_3$  asymmetric and symmetric vibrations. The spectra of azidomethyl ethers, -thioethers, and -amines were recorded and compared to the spectra of the corresponding halomethyl compounds. A strong broad band exhibiting 100% absorption was observed in the  $N_3$  asymmetric stretching region for all azide spectra with but a single exception. N-azidomethyl phthalimide exhibited a doublet in this region as well as in the carbonyl region. Alpha-halo methyl compounds have no significant absorptions in the  $N_3$  asymmetric stretching region. The  $N_3$ symmetric stretching region was complicated by the presence of other absorptions. However, tentative assignments were made when possible.

The spectra of azidomethyl ethers -thioethers and -amines were recorded in carbon tetrachloride solution across the  $N_3$  asymmetric stretching region (Figure 3). Assignments for the  $N_3$  asymmetric stretching absorption are summarized in Table III. This absorption occurred in the range 2141-2090 cm<sup>-1</sup> for the azides examined, with all but one falling in the range 2121-2091 cm<sup>-1</sup>; thus confirming the constancy of the  $N_3$  asymmetric stretching band regardless of environmental groups as reported by previous workers (15,17).

It is interesting to note the band splitting of the  $N_3$  asymmetric stretching absorption for azidomethyl methyl ether and azidomethyl methyl sulfide (Figure 3), when





these azides are present in a concentration low enough to keep the absorption on scale. Higher homologues of these azides failed to show this band splitting, but exhibited a single  $N_3$  asymmetric stretching absorption (Table III). The corresponding N-azido-methyl amines exhibited a single absorption, with the exception of N-azido-methyl phthalimide whose doublet was also evident from a Nujol mull as described earlier.

Hydrazoic acid, in the gaseous state exhibited a doublet for the  $N_3$  asymmetric stretching mode (23), a solution of hydrazoic acid in carbon tetrachloride was prepared,

Azıde	Asymmetric N₃ Stretchingª	Symmetric N3 Stretching <sup>a</sup> (tentative)
CH <sub>1</sub> OCH <sub>2</sub> N <sub>3</sub>	2121vs, 2098vs	12325
CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> N <sub>3</sub>	2119vs	1227s
CH <sub>3</sub> SCH <sub>2</sub> N <sub>3</sub>	2113vs, 2091vs	1304-1294m
CH <sub>3</sub> CH <sub>2</sub> SCH <sub>2</sub> N <sub>3</sub>	2098vs	1302m
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> SCH <sub>2</sub> N <sub>3</sub>	2105 vs	1299m
$C_6H_5SCH_2N_3$	2101vs	1304-1295m
C <sub>6</sub> H <sub>7</sub> CH <sub>2</sub> SCH <sub>2</sub> N <sub>3</sub>	2107 vs	1309-1295m
$N_3CH_2SCH_2N_3$	2112vs	1304-1292s
(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>2</sub> N <sub>3</sub>	2094vs	b
$C_5H_{10}NCH_2N_3$	2094vs	Ъ
$C_{b}H_{5}C_{2}O_{2}NCH_{2}N_{3}$	2140s, 2104s	Ъ

Table III. Infrared Assignments for  $N_3$  Asymmetric and Symmetric Stretching Vibrations

<sup>a</sup>In cm<sup>-1</sup>; vs, very strong, etc.

<sup>b</sup>Spectrum is complicated by the presence of other absorptions and no assignment can be made.

and the spectrum recorded with a single  $N_3$  asymmetric stretching absorption observed for this spectrum.

The spectra of these azides and the corresponding halo compounds were recorded from carbon tetrachloride solution across the  $N_3$  symmetric stretching region (Figure 4). While this band is complicated by the presence of other absorptions in the region, tentative assignments are made for this mode and appear in Table III.

The spectra of azidomethyl methyl sulfide and azidomethyl ethyl sulfide were recorded as solutions of methanol and acetonitrile as well as carbon tetrachloride with no noticeable changes in the  $N_3$  asymmetric stretching absorptions.

The reason for the absence of band splitting for other members of the series of compounds studied is not clearly understood. A theoretical study of the above systems from a quantum mechanical point of view is underway which will be reported upon in a separate communication.

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### Notes

# Infrared Spectra of Diethylenetriamine and 2-(2-Aminoethylamino)ethanol

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The formation of a coordination compound between diethylenetriamine (DETA) and cellulose has been reported by Segal and Loeb (4), and studies have been planned for elucidating the structure and mode of bonding of the complex. X-ray diffraction studies (4) indicate that the DETA-cellulose complex, and the complex formed between ethylenediamine (EDA) and cellulose have very similar crystalline interplanar dimensions. Segal and Loeb concluded that the DETA molecule was bonded to the cellulose chain molecules in a manner similar to that accepted for the EDA molecule, this being possible because of a similarity in amine structures. To further pursue the structure study on the complex, another combound, 2-(2-aminoethylamino)ethanol (AEAE), was selected for its structural relationship to DETA and EDA. Infrared spectroscopy was considered to be the best way of obtaining the data needed for elucidating the manner of bonding. However, the study was hampered by lack of information on the infrared spectra of the above amine compounds. In this note the infrared spectra of the amine compounds are presented, and assignments of the observed bands to structural units in the molecule are made.

The DETA was obtained as a commercial product. It was purified by digestion over stick sodium hydroxide, drying with a sodium-lead alloy, and finally distillation. The cut was taken in the boiling range  $205-207^{\circ}$  C (b.p. (1), 207.1° C). The AEAE was a water-white, high-purity product and was used without further purification. The carbon tetrachloride solutions of the amines

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