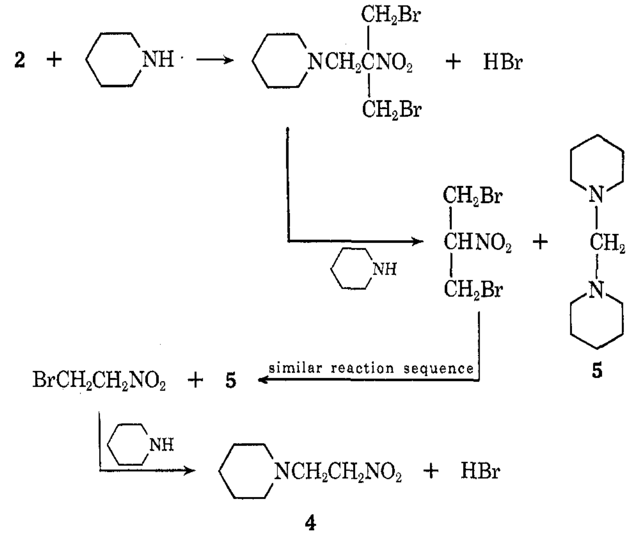
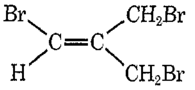
Scheme I



similar reactions of **2** with sodium amalgam[4] and with KOH in alcohol.[5]

The major products of these reactions, **3a** and **3b**, were probably formed in two steps: first the denitration similar to that observed by Kleinfeller, *et al.*, to form **6**, followed by substitution of amine groups for the allylic bromine atoms. The vinyl bromine atom is so unreactive that it is not replaced by the amine group.



**6**

Thus in general the denitration of tertiary nitro alkanes containing vicinal halides can be brought about by amines with a basicity at least as weak as *tert*-butylamine ($K_b$ = 2.8 × $10^{-4}$) as well as by strong bases such as KOH and sodium amalgam as observed previously.[4,5]

### Experimental Section

Boiling points are uncorrected. Nmr spectra were recorded on a Varian A-60 nmr spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating spectrophotometer. Molecular weights were determined by titrating the products with standard HCl, following the titration with a pH meter.

**Reaction of Diethylamine with $(CH_2Br)_3CNO_2$.**—A solution of **2** (25 g, 0.0735 mol) in methanol (300 ml) was placed in a flask fitted with a reflux condenser protected with a drying tube and an addition funnel. The mixture was heated to reflux, and diethylamine (16.2 g, 0.221 mol) was added dropwise. The mixture was refluxed for 1 week and cooled, and then the solvent was evaporated leaving an oily solid, which was mixed with 50 ml of 10% HCl. The resulting mixture was filtered, leaving 21.5 g of the starting bromide. The filtered solution was saturated with $K_2CO_3$ and extracted with ether. The ether extract was dried ($MgSO_4$), concentrated, and distilled, giving 2.3 g (79%) of **4**: bp 68–69° (0.25 mm); ir (film) 3030, 1630 $cm^{-1}$ (CH=C); nmr (neat) $\delta$ 0.93 (t, 12), 2.44 (q, 8), 3.05 (s, 2), 3.17 (s, 2), 6.24 (s, 1). The product decolorized $Br_2$ in $CCl_4$ and gave a positive Beilstein test but did not react with alcoholic $AgNO_3$.

*Anal.* Calcd for $C_{12}H_{25}BrN_2$: C, 51.98; H, 9.09; Br, 28.82; N, 10.11; mol wt, 277.26. Found: C, 51.52; H, 8.96; Br, 29.49; N, 9.77; mol wt (titration), 278.

Similar results were obtained when this reaction was carried out without a solvent.

**Reaction of Piperidine with $(CH_2Br)_3CNO_2$ (2).**—A mixture of **2** (10 g, 0.0294 mol) and piperidine (30 ml) was refluxed for 12 hr, cooled, and diluted with acetone (100 ml). This solution was filtered, yielding 10.8 g of piperidine hydrobromide. The filtered solution was concentrated and distilled into two fractions. The lower boiling fraction [bp 42–44° (0.25 mm)] was shown to be a mixture of **5** and **6** in a ratio of 3:1 by nmr analysis. This fraction weighed 4.0 g; no attempt was made to separate the mixture into its components. The higher boiling fraction, **7**, weighed 9.5 g: bp 104–108° (0.25 mm); ir (film) 3050, 1630 $cm^{-1}$ (CH=C); nmr (neat) $\delta$ 1.42 (m, 12), 2.30 (m, 8), 2.92 (s, 2), 3.06 (s, 2), 6.25 (s, 1). This product decolorized $Br_2$ in $CCl_4$, and gave a positive Beilstein test, but did not react with alcoholic $AgNO_3$.

*Anal.* Calcd for $C_{14}H_{25}BrN_2$: C, 55.81; H, 8.36; Br, 26.53; N, 9.30; mol wt, 301.28. Found: C, 56.01; H, 8.49; Br, 26.34; N, 9.18; mol wt (titration), 297.

Similar results were obtained when methanol was used as a solvent.

**Registry No.**—**2**, 36809-38-8; **3a**, 36809-39-9; **3b**, 36809-40-2.

## The Crystal and Molecular Structure of Dimeric Allyl Azide[1]

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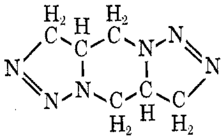
*Received February 28, 1972*

The dimer of allyl azide was first synthesized by Forster and Fierz[2] from the spontaneous dimerization of the monomer, $C_3H_5N_3$. The resulting prismatic crystals melted with decomposition at 150° but were found to be stable at room temperature. The conclusion that a dimer was present was based on boiling point elevation measurements of chloroform solutions of the compound. Forster and Fierz[2] considered several possible molecular structures and, a number of years later, Boyer and Canter[3] proposed the following as being more consistent with the known chemistry of olefinic azides.



The subsequent X-ray diffraction analysis of the compound shows this molecular structure to be the correct one.

### Experimental Section

Preliminary diffraction photographs showed the crystals to be orthorhombic with systematic absences uniquely determining the space group as *Pbca*. The cell parameters were determined from calibrated photographs to be *a* = 7.803, *b* = 10.821, and *c* = 8.819 Å with standard deviations of 0.006 Å. The density measured by the flotation method was 1.45 g $cm^{-3}$; the density calculated on the basis of four dimer units per unit cell is 1.44 g $cm^{-3}$.

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(4) H. Kleinfeller, A. Kirsch, and F. Eckert, *Ber.*, **62B**, 1582 (1929).

(5) H. Kleinfeller and H. Stahmer, *ibid.*, **66B**, 1127 (1933).

(1) Based on a thesis submitted by J. C. Pezzullo in Feb 1969 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93**, 1178 (1908).

(3) J. H. Boyer and F. C. Canter, *Chem. Rev.*, **54**, 1 (1954).

Equi-inclination Weissenberg photographs (multiple-film technique) were taken of the *h0l* and *hkh* zones, and layer lines *hkl* with $k = 1$–4, using Cu K$\alpha$ radiation. The intensities were estimated visually with the use of a standard scale. A total of 354 independent reflections was obtained. The dimensions of the crystals employed were approximately 0.5 mm, but, owing to the low linear absorption coefficient of the compound, no correction for absorption was made.

## Structure Determination and Refinement

Since there are four dimer units in the unit cell and *Pbca* is centrosymmetric with an eightfold general position, the dimer must possess a center of symmetry. The problem is therefore reduced to one of determining the positions of the three carbon and three nitrogen atoms in the asymmetric unit. The sign determination technique developed by Sayre[4] and Zachariasen[5] was employed to accomplish this. A three-dimensional electron density map was calculated and a trial structure was developed based on the positions of the largest peaks. A calculation of interatomic distances indicated a bonding arrangement which corresponded to the molecular model proposed by Boyer and Canter.[3] The three positions to which the nitrogen atoms were assigned were chosen so as to be in agreement with the model. It was observed that several reflections with low Bragg angle values had calculated structure factors substantially exceeding the observed values. This was attributed to secondary extinction and the calculated structure factors were corrected according to the relation of Darwin.[6] A full-matrix least-squares program was written specifically for this compound so that the secondary extinction coefficient might be included as an adjustable parameter. Hydrogen positions were also incorporated into the least squares refinement (fixed positions, no temperature factors). The value of *R*, the reliability index, in the final structure was 0.133. The atomic coordinates (fractions of cell edges) and temperature factors, *B*, are given in Table I; the estimated standard errors (hydrogens excluded) are 0.01 Å for the positional coordinates and 0.2 Å$^2$ for the temperature factors.

Table I
Coordinates and Isotropic Temperature Factors for the Final Structure

| Atom | *x* | *y* | *z* | *B* |
|---|---|---|---|---|
| C-1 | 0.2088 | 0.3526 | 0.5205 | 2.8 |
| C-2 | 0.3193 | 0.4718 | 0.5357 | 1.9 |
| C-3 | 0.4621 | 0.4460 | 0.6516 | 2.2 |
| N-1 | 0.6077 | 0.5298 | 0.6193 | 1.8 |
| N-2 | 0.6060 | 0.6514 | 0.6758 | 2.8 |
| N-3 | 0.7078 | 0.7176 | 0.6054 | 3.3 |
| H-1[a] | 0.075 | 0.380 | 0.500 | |
| H-2[a] | 0.215 | 0.300 | 0.625 | |
| H-3[b] | 0.250 | 0.550 | 0.575 | |
| H-4[c] | 0.400 | 0.475 | 0.750 | |
| H-5[c] | 0.535 | 0.370 | 0.625 | |

[a] Attached to C-1. [b] Attached to C-2. [c] Attached to C-3.

## Discussion

Bond distances and angles are shown in Figure 1. All bond distances agree well with those previously reported for similar bond types. Calculation of intermolecular distances indicates that the nearest-neighbor contacts are of the van der Waals type. The individual five-membered rings are not planar; atom C-2 is 0.42 Å out of the least-squares plane of the other four atoms. The two least squares planes of these rings are stepped with an interplanar distance of 1.90 Å.

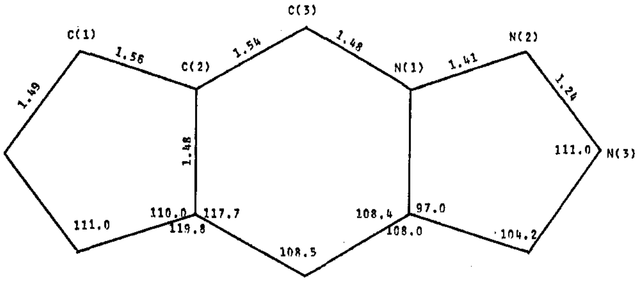

Figure 1.—Bond distances and angles.

The stability of the crystal, as evidenced by the high melting point and somewhat low temperature factors, warrants interest in the conformational aspects of this molecule. Dreiding stereomodels were constructed and manipulation of these models indicated that the conformation was strongly influenced by the nitrogen atom, N-1, at the junction of the five- and six-membered rings. With a tetrahedral atom (sp$^3$) at this position, the model closest to the observed structure corresponds to a cis–cis attachment of the five-membered rings to the six-membered ring having the $CH_2$ groups equatorial (C-1–C-2 bonds) and the N═N groups axial (N-1–N-2 bonds). This model, however, is not stable with respect to a noncentrosymmetric conformation in which the six-membered ring is a boat and both five-membered rings are planar. The introduction of a trigonal atom (sp$^2$) at the N-1 position produces a stable centrosymmetric model, but with planar five-membered rings which are stepped with an interplanar distance of only 1.2 Å. In the actual case, the bridgehead nitrogen is found to be 0.30 Å out of the plane of the atoms to which it is bonded, whereas a value of 0.48 Å would correspond to sp$^3$ hybridization. Consequently, neither extreme satisfactorily describes the hybridization.

**Registry No.**—Dimeric allyl azide, 36895-17-7.

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[4] D. Sayre, *Acta Crystallogr.*, **5**, 60 (1952).

[5] W. H. Zachariasen, *ibid.*, **5**, 68 (1952).

[6] C. G. Darwin, *Phil. Mag.*, **43**, 800 (1922).

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## On the Reaction of α-Bromo-ε-caprolactam with Methoxide

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In a recent paper, Kondeliková, Králiček, and Křivinkova asserted that they were successful in preparing $\alpha$-methoxy-$\epsilon$-caprolactam by a nucleophilic substitution reaction entailing sodium methoxide and $\alpha$-bromo-$\epsilon$-caprolactam.[1] This assertion, however, did not

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[1] J. Kondeliková, J. Králiček, and D. Křivinková, *Collect. Czech. Chem. Commun.*, **36**, 3391 (1971).