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 Kα 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.

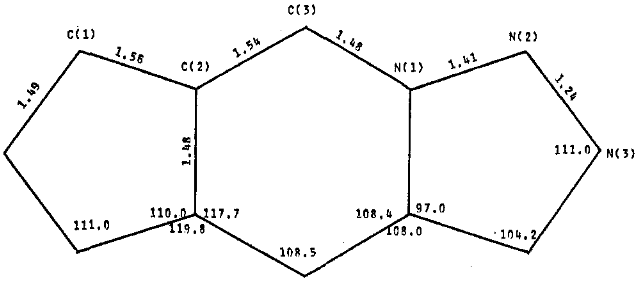

Figure 1.—Bond distances and angles.

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.

(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).

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

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

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

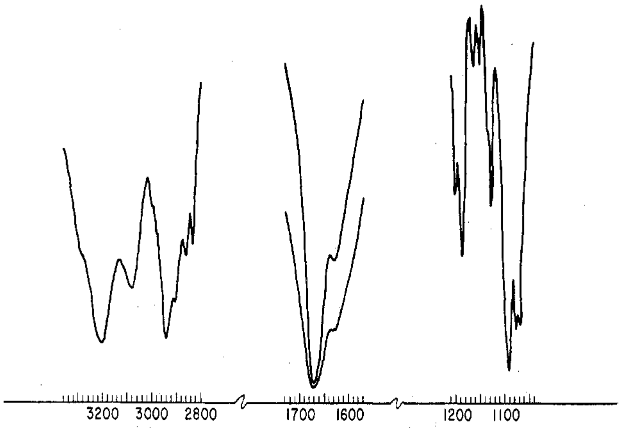


Figure 1.—Infrared spectrum of β-methoxy-ε-caprolactam.

appear to be well founded in light of results obtained in studies on caprolactam derivatives carried out in our laboratory. Although it had been shown that substituted caprolactams can be obtained from α-bromocaprolactam by nucleophilic substitution,[2,3] the reaction between the latter and a strong base such as sodium alkoxide was found to be governed by a quite different mechanism. Nevertheless, to verify the available information, α-bromocaprolactam and sodium methoxide were allowed to react according to both the procedure given in ref 1 and a modified one which gave the same reaction product but in a higher yield (60%). The modified procedure resembled one reported earlier[4] and differed from that given in ref 1 mainly by eliminating the vacuum distillation of the reaction product. Purification was achieved by crystallization from a chloroform–petroleum ether (bp 30–50°) system. An analytically pure sample, mp 62°, was obtained in either case by recrystallization from petroleum ether. A melting point of 54–55° was reported in ref 1. *Anal.* Calcd for $C_7H_{13}NO_2$: C, 58.68; H, 9.15; N, 9.78. Found: C, 58.68; H, 9.43; N, 9.89.

Considering the results of previous studies[4] on similar compounds, the reaction product was identified by spectroscopic analyses to be not the α-methoxy- but the β-methoxy-ε-caprolactam. The significant bands of the infrared spectrum (KBr, Beckman IR9) are shown in Figure 1. They are 3205, 3080 (NH stretching); 2860, 2830 (methoxy, CH stretching); 1670 (amide I); 1072, 1080, 1090 [C–O asymmetrical stretching, this triplet seems to be characteristic for the isopropyl ether moiety $>(CH_2)_2CHOCH_3$].

The 100-MHz nmr spectrum is shown in Figure 2; it consists of four major groups, the integral of which correspond to the proportional relation of 1:6:2:4.

The most significant signal is the triplet centered at about 2.75 ppm which has been attributed to the protons of the methylene group located between a carbonyl group and a carbon linked to an ether oxygen.[4]

The formation of the β derivative may be explained by a mechanism that entails elimination of HBr, followed by nucleophilic addition of the methoxide anion to the formed unsaturated lactam. It was shown earlier[4] that treating α-bromocaprolactam with a strong base can yield both 1,5,6,7- and 1,3,6,7-tetrahydro-2*H*-azepin-2-one (**1** and **2**, respectively). This can be rationalized by a mechanism such as shown below.

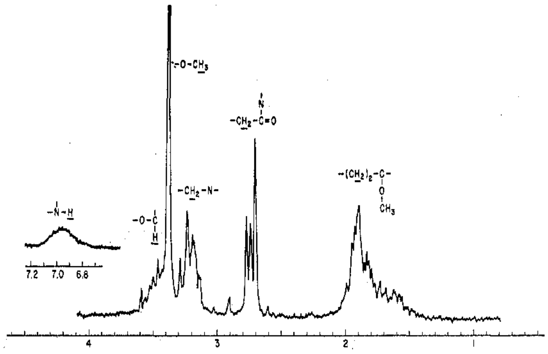
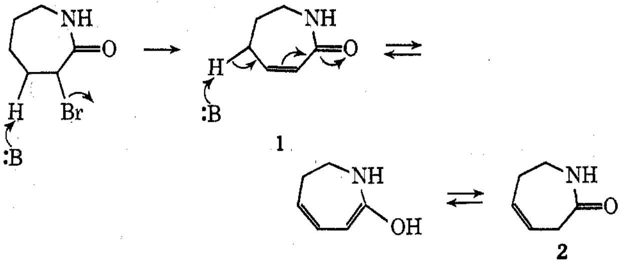


Figure 2.—Nmr spectrum of β-methoxy-ε-caprolactam.



Isomerization of the β,γ-unsaturated lactam **2** into the α,β-unsaturated **1** can easily be visualized for the reaction conditions employed.

Typical 1,4 addition involving **1** yields then as the principal reaction product, the β-methoxy-ε-caprolactam.

There is no disagreement with the phenomenological aspects of the paper by Kondeliková, *et al.;* however, any conclusions regarding the behavior of the lactam as a function of the position of the methoxy group may need revision.

Registry No.—α-Bromo-ε-caprolactam, 3457-66-7; sodium methoxide, 124-41-4; β-methoxy-ε-caprolactam, 36982-61-3.

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Conformational Properties of 2,2'-Disubstituted Diphenyl Ethers and Sulfides by Dipole Moments. A Reexamination

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The conformational properties of diphenyl ethers (DPO) and diphenyl sulfides (DPS) in solution have received continued attention up to recently, and several workers have resorted to dipole moment (DM)

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[2] H. K. Reimschuessel, *J. Heterocycl. Chem.*, **1**, 193 (1964).

[3] T. G. Bassiri and H. K. Reimschuessel, U. S. Patent 3,331,835 (1967).

[4] H. K. Reimschuessel, J. P. Sibilia, and J. V. Pascale, *J. Org. Chem.*, **34**, 959 (1969).