

3-Azabicyclo[3,2,2]nonane in the Low-Temperature Crystal Phase

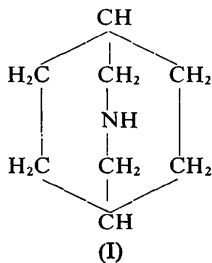
BY L. M. AMZEL,* S. BAGGIO,† R. F. BAGGIO‡ AND L. N. BECKA§

Department of Biophysics, The Johns Hopkins University, School of Medicine, Baltimore, Md. 21205, U.S.A. and Departamento de Química Inorgánica, Analítica y Química-Física, Facultad de Ciencias Exactas y Naturales y Departamento de Físico-Química, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Argentina

(Received 15 November 1973; accepted 14 June 1974)

Abstract. Below 298 K 3-azabicyclo[3,2,2]nonane ($C_8H_{15}N$) is orthorhombic, $a=21.27$ (5), $b=11.31$ (5), $c=6.15$ (3) Å; $D_m=1.12$, $D_x=1.12$ g cm $^{-3}$ (for $Z=8$); $F(000)=608$; $\mu_{Cu}=10.0$, $\mu_{Mo}=1.35$ cm $^{-1}$; space group $Aba2$ from systematic absences and intensity statistics and confirmed by the structure determination. Final $R=0.10$. At 291 K the vibration amplitudes have values within the range normally observed in ordered molecular crystals, the molecular packing can be described as a distorted face-centered cubic arrangement and the symmetry of the molecules is very close to C_s .

Introduction. Of the 13 bicyclic compounds having a plastic phase for which extensive thermodynamic data are available (Westrum, 1967) 3-azabicyclo[3,2,2]nonane (AZBN) (I) has the most suitable characteristics for study with respect to molecular symmetry (C_1 or C_s) and transition temperature (298 K). The crystal and molecular structure of AZBN was determined at 291 K which is only 7° below the transition temperature. This



study shows that at this temperature the molecule does not show anomalous vibrational amplitudes, indicating the absence of marked disorder 7° before the transition. This study also established the molecular symmetry of AZBN and the relation between the packing of the two crystalline phases.

AZBN was obtained from Eastman Chemical Products and was purified by multiple sublimation under

* At first address.

† Present address: Departamento de Físico-Química, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Argentina.

‡ Present address: Departamento de Radiaciones Atómicas y Moleculares, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina.

§ Present address: Departamento de Investigación y Desarrollo, SEGBA, Balcarce 236, Buenos Aires, Argentina.

vacuum with a sample temperature of 70°C and a collecting surface temperature of 15°C. Single crystals were grown by slow sublimation over a period of several weeks in an evacuated container using temperature differences of approximately 1°C between the sample and the collecting surface. Single crystals of sizes up to 10×1×0.1 mm were obtained. Crystals smaller than the maximum size were too thin and fragile to handle. Attempts to cut large crystals to a size suitable for X-ray analysis were unsuccessful because the crystals were easily deformed under very slight stress. For that reason, a crystal of 10×1×0.1 mm was used for the data collection despite the fact that the crystal was larger than the cross section of the X-ray beam. The compound is very hygroscopic, has a high vapor pressure at room temperature and is highly soluble in most organic solvents. Therefore the crystals were glued to glass fibers with dental cement and were sealed under nitrogen inside thin-walled glass capillaries with the longest dimension parallel to the capillary axis. The cell constants and space group for AZBN were obtained from precession photographs with Mo $K\alpha$ radiation and from Weissenberg photographs taken with Cu $K\alpha$ radiation.

Intensity data were obtained from layers $hk0$ to $hk4$ recorded on integrated equi-inclination Weissenberg photographs taken with Ni-filtered Cu $K\alpha$ radiation and layers $h0l$ to $h2l$ recorded on integrated precession photographs with Zr-filtered Mo $K\alpha$ radiation. The intensities were measured on a manual microdensitometer. The 572 reflections measured with $l \leq 4$ and $2 \sin \theta/\lambda \leq 1.3$ Å $^{-1}$ represent approximately 80% of the total number of reflections fulfilling this condition. The resolution in the c direction corresponds to $2 \sin \theta/\lambda = 0.65$ Å $^{-1}$. Corrections for absorption and for the change in the volume of the crystal bathed by the X-ray beam were applied to the measured intensities. The values of these corrections varied between 1.0 and 1.67. The intensities were also corrected for polarization and Lorentz factors, and values obtained from different layers were scaled using the method of Hamilton, Rollett & Sparks (1965). The average discrepancy between the $|F|$ values of equivalent reflections measured in precession and Weissenberg photographs was 8%.

The statistics of E values for AZBN correspond more closely to that of a non-centric distribution and

Table 1. Positional and thermal parameters ($\times 10^4$) for the non-hydrogen atoms of AZBN with standard deviations ($\times 10^4$) in parentheses

The temperature factor is of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1793 (3)	809 (6)	3165 (24)	19 (2)	80 (9)	172 (78)	-2 (4)	13 (10)	-11 (33)
C(2)	1146 (3)	711 (6)	2076 (22)	18 (2)	38 (6)	27 (85)	0 (4)	16 (10)	30 (21)
C(3)	616 (3)	1337 (7)	3264 (24)	21 (2)	94 (12)	270 (79)	-4 (5)	0 (11)	-23 (25)
C(4)	662 (3)	2670 (7)	3052 (22)	22 (2)	69 (8)	50 (66)	-4 (5)	11 (10)	56 (21)
C(5)	1201 (3)	3083 (5)	1718 (23)	13 (2)	44 (6)	204 (81)	6 (4)	20 (10)	-48 (20)
C(6)	1837 (3)	2973 (6)	2927 (24)	21 (2)	83 (9)	418 (85)	-5 (4)	-18 (11)	-32 (23)
C(7)	1171 (4)	1104 (7)	-262 (21)	28 (3)	65 (10)	358 (117)	10 (5)	-6 (13)	-87 (30)
C(8)	1199 (3)	2455 (6)	-500	21 (2)	86 (9)	191 (84)	-4 (5)	2 (10)	-27 (26)
N	2166 (2)	1841 (5)	2626 (22)	16 (2)	82 (7)	217 (54)	-7 (4)	-1 (8)	35 (20)

therefore the space group *Aba2* was used for the structure determination. The structure was solved with the program *MULTAN* (Germain, Main & Woolfson, 1970). The set of phases with best internal consistency was used to calculate an *E* map which showed the position of the non-hydrogen atoms of the molecule. A structure-factor calculation using these positions gave a conventional *R* value ($\sum|F_o - F_c|/\sum|F_o|$) of 0.233. Five cycles of full-matrix least-squares refinement minimizing $W\Delta^2$ ($\Delta = F_o - F_c$) and using isotropic temperature factors lowered the *R* index to 0.135. The H atoms bound to the C atoms were then included with coordinates predicted from the geometry of the molecule. The positional parameters and anisotropic temperature factors for the non-hydrogen atoms were refined using a weighting scheme with $W = \{1.02 - \exp[-2.5(\sin\theta/\lambda)^2]\}/\{0.35|F_o|[1 - 1.35(\sin\theta/\lambda)^2]\}$ in order to keep $w\Delta^2$ approximately constant in ranges of $|F_o|$ and of $\sin^2\theta/\lambda^2$. After four cycles the refinement converged with residuals $R = 0.126$ and $R' (\sum W\Delta^2/\sum WF_o^2) = 0.164$. Eight reflections affected by secondary extinction were left out of the calculations and refinement was continued giving a final *R* index of 0.101. The atomic scattering factors used were taken from

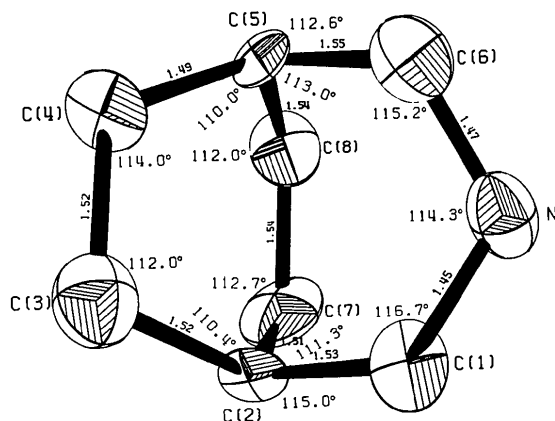


Fig. 1. View of the AZBN molecule along the *c* axis. Values for the bond distances and bond angles are indicated.

Table 1 (cont.)

Fractional coordinates ($\times 10^4$) of the positions used for the hydrogen atoms. The carbon atoms to which they are bound are indicated.

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)C(1)	2057	44	2766
H(2)C(1)	1718	820	4887
H(3)C(2)	1038	-216	2155
H(4)C(3)	175	1046	2616
H(5)C(3)	637	1101	4954
H(6)C(4)	240	2995	2329
H(7)C(4)	709	3048	4336
H(8)C(5)	1165	4012	1393
H(9)C(6)	2140	3666	2351
H(10)C(6)	1757	3101	4613
H(11)C(7)	1583	728	-1402
H(12)C(7)	766	772	-1011
H(13)C(8)	1612	2696	-1374
H(14)C(8)	793	2744	-1402

International Tables for X-ray Crystallography (1962). The final atomic parameters for one AZBN molecule are given in Table 1.*

Discussion. The bond distances (Fig. 1) do not differ significantly from the values expected for C-C and C-N bonds while most bond angles have values larger than tetrahedral values. This deformation is a consequence of the bicyclic skeleton. The dihedral angles between the planes defined by C(2), C(5), C(3) (plane I) and C(2), C(5), C(4) (plane II); C(2), C(5), C(1) (plane III) and C(2), C(5), C(6) (plane IV); and C(2), C(5), C(7) (plane V) and C(2), C(5), C(8) (plane VI) are a direct measure of the 'twisting' of the molecule around the axis C(2)-C(5). The observed values for these angles I-II 2°; III-IV 3°; and V-VI 0° indicate that the molecule is essentially not 'twisted' and, therefore, the molecular symmetry is very close to *C_s*. The vibration amplitudes for the atoms in the AZBN

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30529 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

molecule do not seem to present any marked anisotropy, within the accuracy of the data. Furthermore, no anomalously high values of vibration amplitude were observed; all of the mean square amplitudes being less than 0.293 \AA^2 .

At temperatures higher than T_i , the crystals of AZBN are 'close packed' f.c.c. crystals with $a=9.47 \text{ \AA}$ as determined by powder diagrams at 323 K (Amzel, Cucarella & Becka, 1971). This phase can be 'supercooled' below T_i by a fast drop in the temperature (Amzel, 1967). At 293 K the crystals of the supercooled high-temperature phase gave diagrams compatible with an f.c.c. crystal with $a=9.41 \text{ \AA}$ (Amzel, Cucarella & Becka, 1971). A similar packing can be observed in this orthorhombic crystal of AZBN. The distances from the center of one AZBN molecule in the orthorhombic crystals to its 18 nearest neighbors suggest the presence of 12 nearest neighbors and 6 second nearest neighbors in an arrangement similar to that of a 'close packed' f.c.c. crystal (Fig. 2). The average distance from one molecule to the nearest neighbors is 6.46 \AA and to the second nearest neighbors is 9.02 \AA . In the f.c.c. phase supercooled at 293 K the equivalent distances are 6.64 and 9.41 \AA . Furthermore, the transformation $a'=c$, $b'=0.75a$ and $c'=0.5b-0.5c$ gives the following cell dimensions: $a'=6.15$, $b'=15.97$, $c'=6.43 \text{ \AA}$ and $\beta'=118.6^\circ$, which resemble those of a hexagonal lattice with three molecules per unit cell. This hexagonal lattice corresponds to the primitive rhombohedral cell with $a=6.4 \text{ \AA}$ and $\alpha=59^\circ$ which in turn can be transformed to an f.c.c. lattice with $a=9.02 \text{ \AA}$. The set of transformations that leads from the orthorhombic to the f.c.c. lattice is:

orthorhombic \longrightarrow hexagonal \longrightarrow rhombohedral \longrightarrow face centered cubic

$$\mathbf{A}_1 = \begin{bmatrix} 0 & \frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & 1 \\ \frac{3}{4} & 0 & 0 \end{bmatrix} \quad \mathbf{A}_2 = \begin{bmatrix} -\frac{1}{3} & \frac{1}{3} & \frac{1}{3} \\ -\frac{1}{3} & -\frac{2}{3} & \frac{1}{3} \\ \frac{2}{3} & \frac{1}{3} & \frac{1}{3} \end{bmatrix} \quad \mathbf{A}_3 = \begin{bmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix}$$

Therefore

$$\begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix}_{\text{f.c.c.}} = \{\mathbf{A}_3\} \{\mathbf{A}_2\} \{\mathbf{A}_1\} \begin{bmatrix} a \\ b \\ c \end{bmatrix}_{\text{orthorh.}}$$

One of us (LMA) had financial support from Grant AI08202 from the National Institutes of Health.

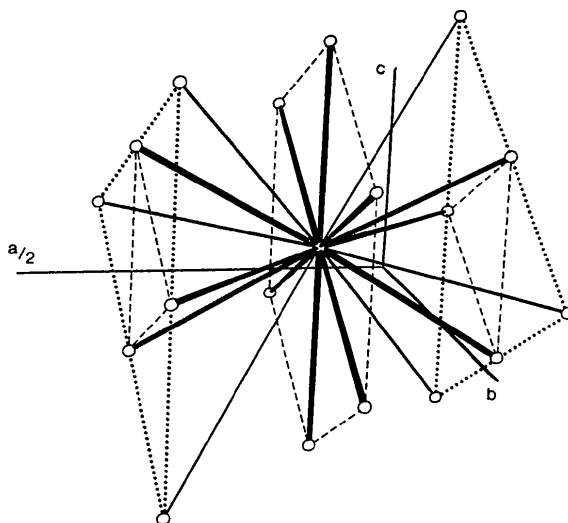


Fig. 2. Packing of AZBN molecules in the orthorhombic crystals. The positions of the molecules are represented by circles. One central molecule (fractional coordinates: $0.12, 0.18, 0.20$) and its 18 nearest neighbors are shown. First nearest neighbors are connected to the central molecule by thick bonds and second nearest neighbors by thin bonds. Contacts within the f.c.c. type packing planes for first nearest neighbors (---) and second nearest neighbors (···) are indicated.

References

- AMZEL, L. M. (1967). Ph. D. Dissertation. Univ. of Buenos Aires.
 AMZEL, L. M., CUCARELLA, M. C. M. & BECKA, L. N. (1971). *J. Phys. Chem.* **75**, 1073–1079.

- GERMAIN, C., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* **B26**, 274–285.
 HAMILTON, W. C., ROLLETT, J. S. & SPARKS, R. A. (1965). *Acta Cryst.* **18**, 129–130.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–246. Birmingham: Kynoch Press.
 WESTRUM, E. F. JR (1967). *Ann. Rev. Phys. Chem.* **18**, 135.