SHORT STRUCTURAL PAPERS

Medium-Ring Compounds. XIX. Caprolactam: Structure Refinement

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Abstract. Monoclinic, $C2/c$, $a=19.28$ (2), $b=7.78$ (1), $c=9.57$ (1) Å, $\beta=112.39$ (10)°, $C_6H_{11}ON$, $M=113.16$, $Z=4$, $D_m=1.12$, $D_x=1.133$ g cm^{-3}. The previously reported structure has been refined with new three-dimensional intensities.

Introduction. Intensities from a crystal of dimensions $0.35 \times 0.32 \times 0.20$ mm were collected on an automated Hilger–Watts Y290 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.71069$ Å, $\mu=0.80$ cm^{-1}). All reflexions with θ less than 23° were measured; in the range $23° < \theta < 30°$ only those with intensity significantly above background (as determined by a quick-scan) were measured. The measurements led to 1017 independent $|F_o|$ values. The coordinates given by Nitta, Haisa, Yasuoka, Kasami, Tomiie & Okaya (1965) for the C, N and O atoms served as starting model for a series of six cycles of full-matrix least-squares analysis with anisotropic temperature factors. The H atoms were then included at calculated positions (all consistent with peaks observed in a difference synthesis); their positions and isotropic temperature factors were refined by two further cycles of least-squares analysis with the criteria proposed by Huber-Buser (1971). Scattering factors for C, N and O were taken from *International Tables for X-ray Crystallography* (1962), for H from Stewart, Davidson & Simpson (1965). The final R was 0.048.*

Table 2. *Caprolactam: atomic coordinates* ($\times 10^3$, *e.s.d.'s in parentheses) and isotropic temperature factors for* H *atoms*

E.s.d.'s for the B values are about 1.0 Å^2.

	x/a	y/b	z/c	B (Å^2)
H(1) C(2)	394 (2)	21 (5)	379 (4)	6.8
H(2) C(2)	438 (2)	25 (5)	266 (4)	6.0
H(1) C(3)	514 (2)	194 (5)	470 (4)	8.5
H(2) C(3)	463 (2)	342 (5)	333 (4)	5.7
H(1) C(4)	422 (2)	222 (5)	589 (4)	6.6
H(2) C(4)	468 (2)	414 (5)	593 (4)	9.0
H(1) C(5)	338 (2)	454 (6)	540 (4)	7.7
H(2) C(5)	357 (2)	508 (5)	388 (4)	7.7
H(1) C(6)	290 (2)	167 (5)	416 (4)	5.7
H(2) C(6)	234 (2)	346 (5)	327 (4)	5.9
H(N)	241 (2)	293 (5)	118 (4)	8.8

Discussion. The structure described by Nitta *et al.* (1965) is confirmed by the present work but its accuracy is considerably improved (Tables 1 and 2). Bond lengths, bond angles and torsion angles are given in Table 3. The molecule adopts a chair conformation with an approximate mirror plane passing through C(4) and the midpoint of the N–C(1) bond (Fig. 1). The *cis*-amide group does not deviate significantly from planarity, the out-of-plane parameters (Winkler & Dunitz, 1971) being $\chi_N=6.5(3.0)°$, $\chi_C=-0.8$ (0.4)° and $\tau= -0.6$ (1.5)°, and its dimensions are quite close to those of the 'standard' *cis*-peptide unit (Ramachandran & Sasisekharan, 1968). The torsion angles in the seven-membered ring agree well with those obtained by Ermer & Lifson (1973) for *cis*-cycloheptene but show some serious discrepancies from those calculated for caprolactam itself (Warshel, Levitt & Lifson, 1970),

Table 1. *Caprolactam: atomic coordinates (*e. s. d.'s in parentheses*) and vibrational tensor components for* C, N *and* O *atoms (all* $\times 10^4$)

The U_{ij} values (in Å^2) correspond to the temperature-factor expression $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{12}hka^*b^*\ldots)]$ and have standard deviations in the range 0.0008–0.0028 Å^2.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	3372 (1)	1288 (2)	504 (1)	730	856	576	154	276	−79
N	2904 (1)	2508 (2)	2071 (2)	615	664	523	105	250	−1
C(1)	3428 (1)	1605 (2)	1814 (2)	583	493	545	−4	254	−13
C(2)	4094 (1)	992 (3)	3143 (2)	627	623	630	92	254	66
C(3)	4573 (1)	2440 (3)	4094 (3)	636	889	701	−88	155	86
C(4)	4275 (2)	3200 (3)	5221 (3)	1029	830	615	−192	140	−53
C(5)	3511 (2)	4069 (3)	4513 (2)	1217	677	669	16	419	−103
C(6)	2892 (1)	2880 (3)	3567 (2)	794	752	584	130	371	1

presumably because of inadequacies in the force field used for the amide group (Lifson, 1973).

Analysis of the experimental thermal-motion tensors in terms of rigid-body translational and librational motion (Schomaker & Trueblood, 1968) leads to reasonably good agreement between observed and calculated tensor components [$\langle \Delta U_{i,j})^2 \rangle^{1/2} = 0.0020$ Å^2, $\langle \sigma^2(U_{i,j}) \rangle^{1/2} = 0.0017$ Å^2]. Contributions from internal
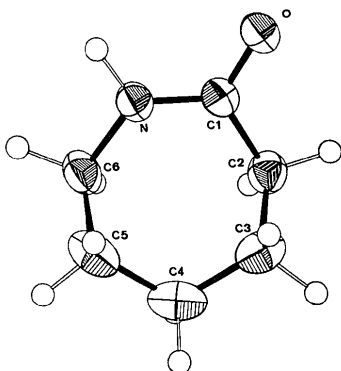

Fig. 1. The caprolactam molecule (with atom numbering shown) viewed along a direction perpendicular to the mean plane of the seven-membered ring. The vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965).
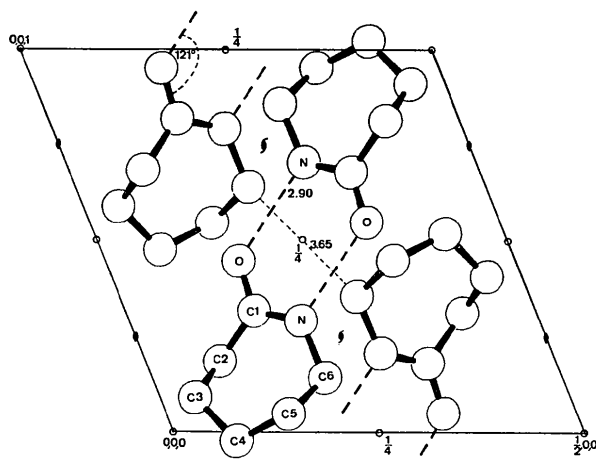

Fig. 2. Caprolactam: crystal structure projected down [010].

molecular vibrations must be rather small or else they are remarkably well simulated by the rigid-body motion. The large vibration amplitudes of C(3), C(4) and C(5) seem to be due mainly to libration about an axis passing roughly through the midpoint of the amide bond and nearly perpendicular to the plane of the amide group. This libration axis is associated with the smallest eigenvalue (17·1 deg^2) but the three atoms mentioned lie furthest away from it. The corrections for librational motion to the bond lengths amount to 0·008–0·016 Å (Table 3). Corrections to the angles are negligible.

The crystal structure (Fig. 2) is built from centrosymmetric pairs of molecules linked by hydrogen bonds (N–H⋯O, 2·90 Å). The shortest distance between methylene carbon atoms of different molecules is 3·65 Å, corresponding to normal van der Waals interactions.

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Table 3. *Caprolactam: molecular parameters (bond lengths corrected for molecular libration are in parentheses)*

The e.s.d.'s are 0·002–0·003 Å for bond lengths, 0·2° for bond angles and 0·4° for torsion angles not involving H atoms.

C(1)–O	1·242 (1·250) Å	O——C(1)–N	120·9°	C(6)–N——C(1)–C(2)	−4·2°
N——C(1)	1·327 (1·340)	O——C(1)–C(2)	120·6	N——C(1)–C(2)–C(3)	−63·1
C(1)–C(2)	1·501 (1·513)	N——C(1)–C(2)	118·5	C(1)–C(2)–C(3)–C(4)	81·9
C(2)–C(3)	1·519 (1·535)	C(1)–C(2)–C(3)	113·6	C(2)–C(3)–C(4)–C(5)	−63·5
C(3)–C(4)	1·522 (1·534)	C(2)–C(3)–C(4)	113·9	C(3)–C(4)–C(5)–C(6)	60·7
C(4)–C(5)	1·525 (1·539)	C(3)–C(4)–C(5)	114·8	C(4)–C(5)–C(6)–N	−77·0
C(5)–C(6)	1·509 (1·525)	C(4)–C(5)–C(6)	113·9	C(5)–C(6)–N——C(1)	67·8
C(6)–N	1·470 (1·480)	C(5)–C(6)–N	113·7	C(6)–N——C(1)–O	176·6
		C(6)–N——C(1)	125·5		
C–H	0·99–1·10 (4)	H——C–H	105–109 (3)	H(N)–N–C(1)–O	3
N–H	1·06	H(N)–N–C(6)	113 (2)	H(N)–N–C(1)–C(2)	−178
		H(N)–N–C(1)	122 (2)		