5,5,8,8-Tetramethylazacyclononan-2-one

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Abstract. $C_{12}H_{23}NO$, triclinic, $P\bar{1}$, $a = 6\cdot1478\,(7)$, $b = 8\cdot4647\,(8)$, $c = 12\cdot323\,(2)$ Å, $\alpha = 105\cdot00\,(1)$, $\beta = 98\cdot22\,(1)$, $\gamma = 102\cdot70\,(1)°$, $V = 590\cdot5$ Å^3, $T = 138$ K, $Z = 2$. The final R value is $4\cdot6\%$ for all 2434 data. The molecule contains a *cis* amide bond which deviates only slightly from planarity.

Introduction. A number of small-ring polycyclic lactams (Ealick & van der Helm, 1975, 1977; Ealick, Washecheck & van der Helm, 1976) as well as several medium-ring lactams (Dunitz & Winkler, 1975) exhibit varying degrees of amide-group non-planarity. The structure of caprylolactam (Winkler & Dunitz, 1975a) shows a *transoid* non-planar amide group with a torsion angle of 148°. Deviations from planarity have also been observed in cyclic peptides.

The title compound was prepared by Smolikova, Havel, Vasickova, Vitek, Svoboda & Bláha (1974) as part of a more general study to examine the conformation of medium-ring lactams using infrared spectroscopy. Crystalline material for this study was provided by Professor K. Bláha and was used without further recrystallization. Infrared studies show that the title compound has a pronounced preference for the *cis* amide conformation in both the solid state and solution. The purpose of this investigation was to determine the geometrical parameters of a potentially non-planar *cis* amide group and to determine the conformation of the nine-membered ring.

A well formed prismatic single crystal was selected for intensity measurements and unit-cell determination. The intensities of 2434 unique intensities [2298 with $I > 2\sigma(I)$] with $2\theta \le 150°$ were measured using θ–2θ scan techniques. The scan and aperture width were $(0\cdot9 + 0\cdot09 \tan \theta)°$ and $(4\cdot0 + 0\cdot9 \tan \theta)$ mm respectively. The maximum time per reflection was 90 s. The orientation of the crystal was automatically checked every 100 reflections and an intensity monitor was measured every 30 reflections. The intensity of the monitor reflection decreased by as much as 10% owing to ice formation on the crystal. It was necessary to de-ice the crystal four times during the data collection. All intensities were brought to a common scale by means of the monitor reflection. There was no indication of decomposition of the compound. All measurements were made at 138 K on a Nonius CAD-4 automatic

diffractometer. No correction was made for the absorption of X-rays.

The structure was solved by direct methods (Karle & Karle, 1966) using the program *MULTAN* (Germain, Main & Woolfson, 1971). The H atoms were located using a difference Fourier map based on the partially refined positions of the O, N and C atoms. The structure was refined using block-diagonal least-squares techniques (Ahmed, 1966) with anisotropic thermal parameters for C, N and O atoms and isotropic thermal parameters for H atoms. The refinement was terminated when all shifts for non-hydrogen atoms were less than the corresponding estimated standard deviations. The error in an observation of unit weight, $[\sum w(F_o - F_c)^2/(m - n)]^{1/2}$, where m = number of observations and n = number of parameters, is 0·87 e. The R value $(R = \sum \|kF_o| - |F_c\|/\sum |kF_o|)$ for all data based on the final parameters (Tables 1 and 2) is 0·046.*

Scattering factors for C, N and O atoms were taken from *International Tables for X-ray Crystallography*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34133 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* $(\times 10^5)$ *for* O, N *and* C *atoms*

The standard deviation for the last digit is given in parentheses.

	x	y	z
N(1)	31278 (15)	3332 (11)	10870 (7)
C(2)	19660 (18)	−12221 (13)	3858 (9)
C(3)	−2501 (17)	−21718 (12)	6010 (8)
C(4)	1371 (16)	−34478 (12)	12633 (8)
C(5)	−5314 (16)	−31533 (12)	24463 (8)
C(6)	3773 (16)	−12874 (12)	32011 (8)
C(7)	29445 (16)	−5049 (12)	33396 (8)
C(8)	36251 (16)	13122 (12)	32534 (8)
C(9)	25175 (17)	13967 (12)	20713 (8)
O(2)	27253 (15)	−19159 (10)	−4388 (7)
C(5a)	4341 (18)	−42982 (13)	30499 (9)
C(5b)	−31415 (18)	−36703 (14)	22503 (9)
C(8a)	62242 (18)	18860 (14)	34248 (9)
C(8b)	28671 (18)	25341 (13)	41803 (9)

(1962) and those for H atoms from Stewart, Davidson & Simpson (1965). The weights of F in the least-squares calculation were determined from $\sigma(I)$, which was in turn based on counting statistics (van der Helm, Ealick & Burks, 1975). In the structure factor analysis, the value of $w\Delta F^2$ did not show a significant variation with either $|F_o|$ or $\sin^2 \theta$, with the exception of 17 high-intensity reflections, which seem to be affected by extinction in that $|F_c| > |F_o|$.

Discussion. An *ORTEP* stereoview of a single molecule is shown in Fig. 1. The structure consists of a nine-membered lactam (caprylolactam) substituted with two methyl groups at each of C(5) and C(8). The amide group assumes a *cis* conformation owing to the restrictions of the ring conformation imposed by the methyl groups at C(5) and C(8). The *cis* conformation was predicted for this compound, both in solution and the solid state, based on its IR spectrum (Smolikova *et al.*, 1974). In unsubstituted caprylolactam (Winkler & Dunitz, 1975a) the amide group is *trans* and non-planar while in protonated caprylolactam hydro-chloride (Winkler & Dunitz, 1975b), the amide group is *cis* with only a small amount of non-planarity. In dilute solution, the difference in free energy between the *cis* and *trans* forms of caprylolactam is estimated as less than 4·2 kJ mol^{-1} (Hallam & Jones, 1970) with the *cis* form preferred. The parameters of non-planarity χ_n, χ_c and $\tau[=\frac{1}{2}(w_1 + w_2)]$ (Winkler & Dunitz, 1971) are

3·0, −1·4 and −1·6°, respectively, and the deviation from planarity is minor.

Bond distances are shown in Fig. 2 and bond angles in Fig. 3. The amide bond length of 1·346 (1) Å is somewhat longer than the value of 1·32 Å suggested by Ramachandran & Sasisekharan (1968) for the standard *cis* peptide unit although the C−O bond length of 1·242 (1) Å agrees with the predicted value. These values are in good agreement with the values of C−N = 1·340 (2) and C−O = 1·250 (2) Å (corrected for thermal motion) reported for caprolactam (Winkler & Dunitz, 1975c) which contains a planar *cis*-amide bond. The bond angles in the nine-membered ring are all significantly larger than 109·5°, as is generally observed in medium-ring compounds.

Torsion angles are given in Table 3. The ring conformation does not resemble those observed for *trans*-amide caprylolactam (Winkler & Dunitz, 1975a), *cis*-amide protonated caprylolactam hydrochloride (Winkler & Dunitz, 1975b), or methylthiocaprylo-lactam (Flippen, 1972) or that calculated for *cis*-cyclo-nonane (Ermer & Lifson, 1973). There is, however, a resemblance to the most stable conformation (D_3 symmetry) calculated for cyclononane (Hendrickson, 1967a) (Table 3). The largest deviation occurs because of the planar amide linkage, and this is compensated primarily by the endocyclic conformations around the two neighboring bonds [C(2)−C(3) and C(9)−N(1)].

Table 2. *Positional parameters* $(\times 10^3)$ *and isotropic thermal parameters* (Å^2) *for hydrogen atoms*

H atoms are given the number of the C or N atom to which they are attached.

|	x	y	z	B
H(1)	445 (2)	80 (2)	90 (1)	2·3 (3)
H(3)A	−106 (2)	−134 (2)	98 (1)	1·9 (2)
H(3)B	−123 (2)	−283 (2)	−19 (1)	2·3 (3)
H(4)A	−81 (2)	−462 (2)	78 (1)	2·1 (3)
H(4)B	181 (2)	−347 (2)	136 (1)	2·1 (3)
H(6)A	−54 (2)	−59 (2)	288 (1)	1·7 (2)
H(6)B	2 (2)	−125 (2)	397 (1)	2·2 (3)
H(7)A	384 (2)	−46 (2)	412 (1)	2·0 (3)
H(7)B	359 (2)	−125 (2)	274 (1)	2·2 (3)
H(9)A	82 (2)	112 (2)	194 (1)	1·8 (2)
H(9)B	308 (2)	261 (2)	207 (1)	2·0 (3)
H(5a)A	214 (2)	−396 (2)	323 (1)	2·4 (3)
H(5a)B	−4 (3)	−421 (2)	380 (1)	2·8 (3)
H(5a)C	−12 (3)	−550 (2)	255 (1)	3·0 (3)
H(5b)A	−368 (3)	−350 (2)	300 (1)	2·6 (3)
H(5b)B	−379 (2)	−301 (2)	182 (1)	2·2 (3)
H(5b)C	−381 (2)	−492 (2)	178 (1)	2·4 (3)
H(8a)A	679 (3)	118 (2)	281 (1)	2·6 (3)
H(8a)B	697 (3)	183 (2)	420 (1)	3·1 (3)
H(8a)C	675 (3)	308 (2)	339 (1)	3·1 (3)
H(8b)A	118 (3)	222 (2)	407 (1)	3·3 (3)
H(8b)B	358 (3)	254 (2)	497 (1)	2·9 (3)
H(8b)C	337 (3)	372 (2)	416 (1)	3·0 (3)
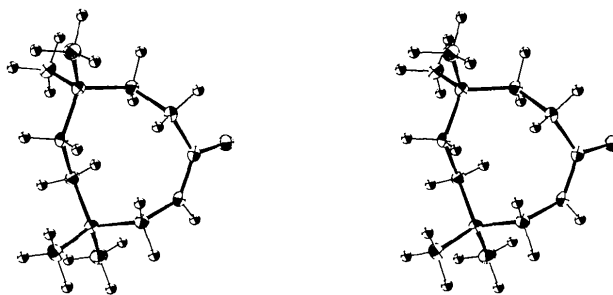
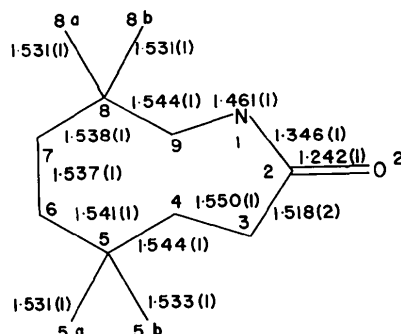Fig. 1. Stereoview of a single molecule (Johnson, 1965).

Fig. 2. Bond distances (Å). Standard deviations are between 0·0014 and 0·0015 Å.
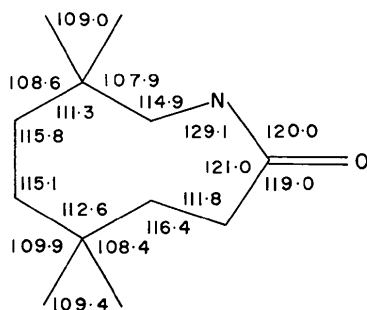
Fig. 3. Bond angles (°). Additional bond angles are C(4)—C(5)—C(5a) = 107·6, C(5b)—C(5)—C(6) = 108·9, C(7)—C(8)—C(8b) = 110·8, C(8a)—C(8)—C(9) = 109·3°. Standard deviations are between 0·08 and 0·10°.

The crystal structure is composed of hydrogen-bonded dimeric pairs about the centers of symmetry ($\frac{1}{2}$,0,0). The hydrogen-bond dimensions are N—H = 0·91, H···O = 2·018, N···O = 2·927 Å and α = 176·8°. The next-closest intermolecular contact is 2·26 Å between two H(7)A atoms related by a center of symmetry at ($\frac{1}{2}$,0,$\frac{1}{2}$).

Table 3. Torsion angles (°)

Standard deviations for the observed conformational angles are between 0·12 and 0·15°.

	Observed	Calculated*
C(9)—N(1)—C(2)—C(3)	−3·8	−56
N(1)—C(2)—C(3)—C(4)	−96·8	−56
C(2)—C(3)—C(4)—C(5)	119·1	125
C(3)—C(4)—C(5)—C(6)	−47·2	−56
C(4)—C(5)—C(6)—C(7)	−51·8	−56
C(5)—C(6)—C(7)—C(8)	137·2	125
C(6)—C(7)—C(8)—C(9)	−60·3	−56
C(7)—C(8)—C(9)—N(1)	−60·0	−56
C(8)—C(9)—N(1)—C(2)	97·9	125
C(9)—N(1)—C(2)—O(2)	177·6	
H(N1)—N(1)—C(2)—C(3)	179·2	
H(N1)—N(1)—C(2)—O(2)	0·6	

* Conformational angles calculated for the most stable cyclononane ring (D_3 symmetry) (Hendrickson, 1967a).

The primary factor determining the conformation of the present molecule is the *gem*-dimethyl substitution at C(5) and C(8). It is predicted that the adjacent bonds of C(5) and C(8), in pairs, should be *gauche* with the same sign, or both C(5) and C(8) should be bounded by bonds of the same dihedral-angle sign (Smolikova *et al.*, 1974; Hendrickson, 1967b). In addition, because of the twofold axes of the approximate D_3 symmetry of the cyclononane ring, all four should have the same sign, as is the case (Table 3). This, therefore, fixes an approximate C_2 axis for the molecule as a whole, *i.e.* from C(2) to the midpoint of C(6)—C(7), relating the two *gem*-dimethyl groups. In Fig. 1 this can be seen to be the case.

There are a number of short H···H intramolecular distances (<2·3 Å). All involve the H atoms bonded to the atoms of the ring, and most are of the type H[C(n)]···H[C(n ± 3)], as can be expected owing to the approximate D_3 symmetry of the ring. The 22 C—H distances vary between 0·98 and 1·03 Å.

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