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Structure of 4-Azatricyclo[4.3.1.1^{3,8}]undecan-5-one (Homoazaadamantanone)

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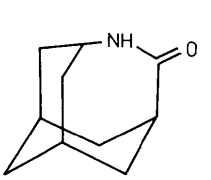
Abstract. $C_{10}H_{15}NO$, $M_r = 165{\cdot}24$, monoclinic, $P2_1/n$, $a = 17{\cdot}219$ (1), $b = 6{\cdot}4465$ (5), $c = 16{\cdot}064$ (2) Å, $\beta = 95{\cdot}95$ (1)°, $V = 1773{\cdot}5$ (3) Å^3, $Z = 8$, $D_m = 1{\cdot}23$ (1), $D_x = 1{\cdot}24$ (1) g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5{\cdot}91$ cm^{-1}, $F(000) = 720$, $T = 295$ K. Final $R = 0{\cdot}0474$ for 1936 unique observed reflections. In the unit cell, there are two symmetrically independent molecules. The amide group of the first conformational type molecule shows pyramidal arrangement of bonds at N, but this group of the second molecule is almost planar. Each conformational type forms a cyclic dimer by means of inter-amide hydrogen bonds.

Introduction. The structure of the title compound (I) was determined as part of a series of studies on the potential occurrence of non-planar amide groups in amides and peptides (Ealick & van der Helm, 1977; Bláha *et al.*, 1978; Bláha & Maloň, 1980; Kálal, Bláha & Langer, 1984). This lactam is one of the model compounds in which the *cis*-amide group is embedded in a rigid tricyclic skeleton. Determination of properties characteristic for a non-planar amide group, *e.g.* dependence of chiroptical parameters on the extent and character of deviation from planarity, could be the starting point for finding other similar deviations in flexible amides (peptides) in solution (Bláha & Maloň, 1980).



(I)

Experimental. Title compound kindly provided by Dr J. Smolíková. Colorless prismatic crystals grown from solution in acetone. Molecular formula confirmed by elemental analysis. Crystal density determined by flotation in CCl_4/heptane and preliminary cell dimensions and space group from oscillation and Weissenberg photographs recorded with Cu $K\alpha$ radiation; final cell dimensions refined on 15 diffractometer reflections with $63{\cdot}8 < 2\theta < 96{\cdot}7°$. Crystal 0·15 × 0·25 × 0·15 mm, Syntex $P2_1$ automated diffractometer with graphite monochromator, Cu $K\alpha$ radiation, $(\sin\theta/\lambda)_{max} = 0{\cdot}5617$ Å^{-1}. θ–2θ scan technique, $0 \le h \le 19$, $-7 \le k \le 0$, $-18 \le l \le 18$; in range up to $2\theta = 120°$, 2651 unique reflections measured, 1936 observed with $I > 1{\cdot}96\sigma_I$. Three standard reflections (200, 0$\bar{2}$0, 004) monitored after every 47 reflections showed decreasing intensity throughout data collection (to 86, 87, 88%, respectively, of initial values). The measurements were reduced to the same scale with the program *INTER* (Langer, 1973). Corrections made for Lorentz and polarization factors, not for absorption. Structure solved using direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Refinement on $|F|$ by full-matrix LS method using *SHELX*76 (Sheldrick, 1976). H atoms calculated in theoretical positions. In final stage of refinement all atoms included. Correction for secondary extinction as $F_c^{corr} = F_c(1-gF_c^2/\sin\theta)$, where $g = 1{\cdot}65\ (9) \times 10^{-6}$. Refinement was stopped when $(\Delta/\sigma)_{max} < 0{\cdot}07$; total number of parameters refined 338. Final $R = 0{\cdot}0474$, $wR = 0{\cdot}0508$ for observed reflections, 0·0702 and 0·0596 respectively for all reflections with $w = 2{\cdot}067/[\sigma_F^2 + (0{\cdot}03F)^2]$, where σ_F is taken from counting statistics. Final difference Fourier synthesis on all reflections did not show any significant feature, the maximum being 0·21 and minimum −0·30 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Geometrical parameters as torsional angles, mean planes, bond distances and comparison of coordinates of atomic subsets calculated with program *PARST*83 (Nardelli, 1983).

Discussion. The molecule of the lactam under study (I) consists of two six-membered rings and one seven-membered ring. A view of the independent part of the structure with the numbering scheme is shown in Fig. 1. The fractional atomic coordinates and B_{eq} values are given in Table 1, selected bond lengths and angles in

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Table 2.* The crystal packing and hydrogen bonds can be seen in Fig. 2. Two types of hydrogen bonds were found, the first having distances N(4*A*)–H(5*A*) = 0·90 (3), H(5*A*)···O(1*A*^{i}) = 2·01 (3), N(4*A*)···O(1*A*^{i}) = 2·903 (3) Å, and angle N(4*A*)–H(5*A*)···O(1*A*^{i}) = 176 (3)°, the second having N(4*B*)–H(5*B*) = 0·95 (3), H(5*B*)···O(1*B*^{ii}) = 1·95 (3), N(4*B*)···O(1*B*^{ii}) = 2·897 (3) Å and angle N(4*B*)–H(5*B*)···O(1*B*^{ii}) = 179 (3)°. For symmetry code see Fig. 2.

Deviations of the *cis*-amide group from planarity can be described by the three independent parameters τ' (Winkler & Dunitz, 1971), χ_C and χ_N (Warshel, Levitt & Lifson, 1970). The parameter τ' describes rotation about the C′–N bond and the values of χ_C and χ_N describe the non-planar arrangement of bonds about C′ and N atoms respectively. The definition of the parameters τ', χ_C, χ_N with their values for the lactam under study are given in Table 3.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and thermal parameters, bond distances and angles involving H atoms and weighted mean planes for the amide group have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42435 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

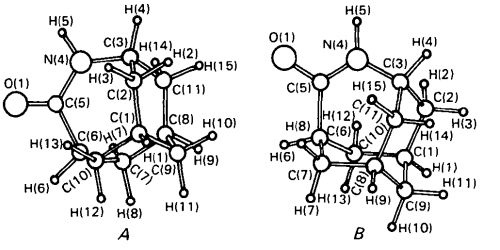

Fig. 1. Projection of the structure with numbering scheme.

Table 1. *Fractional atomic coordinates* (×10^4) *and* B_{eq} (Å^2) *values with e.s.d.'s in parentheses*

	x	*y*	*z*	B_{eq}*
C(1*A*)	6722 (2)	5868 (5)	466 (2)	4·1 (1)
C(2*A*)	6690 (2)	4334 (5)	−255 (2)	4·2 (1)
C(3*A*)	6698 (2)	2075 (5)	35 (2)	4·0 (1)
N(4*A*)	5927 (1)	1393 (4)	249 (1)	3·8 (1)
C(5*A*)	5532 (2)	2163 (4)	841 (1)	3·5 (1)
O(1*A*)	4860 (1)	1531 (3)	927 (1)	4·8 (1)
C(6*A*)	5891 (2)	3846 (4)	1411 (2)	3·8 (1)
C(7*A*)	6649 (2)	3176 (6)	1924 (2)	4·5 (1)
C(8*A*)	7366 (2)	3270 (5)	1445 (2)	4·6 (1)
C(9*A*)	7439 (2)	5444 (5)	1081 (2)	4·7 (1)
C(10*A*)	5998 (2)	5864 (5)	934 (2)	4·3 (1)
C(11*A*)	7346 (2)	1680 (5)	741 (2)	4·9 (1)
C(1*B*)	11393 (2)	3346 (5)	2442 (2)	4·7 (1)
C(2*B*)	11733 (2)	2572 (6)	1661 (2)	4·7 (1)
C(3*B*)	11250 (2)	3160 (5)	855 (2)	3·9 (1)
N(4*B*)	10564 (1)	1822 (4)	669 (1)	4·1 (1)
C(5*B*)	9958 (2)	1644 (4)	1115 (2)	3·8 (1)
O(1*B*)	9403 (1)	472 (3)	878 (1)	5·1 (1)
C(6*B*)	9949 (2)	2861 (5)	1916 (2)	4·1 (1)
C(7*B*)	9916 (2)	5204 (5)	1756 (2)	4·8 (1)
C(8*B*)	10702 (2)	6177 (5)	1632 (2)	4·7 (1)
C(9*B*)	11279 (2)	5684 (6)	2390 (2)	5·3 (1)
C(10*B*)	10623 (2)	2297 (6)	2580 (2)	4·8 (1)
C(11*B*)	11031 (2)	5448 (5)	841 (2)	4·5 (1)

* $B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j$.

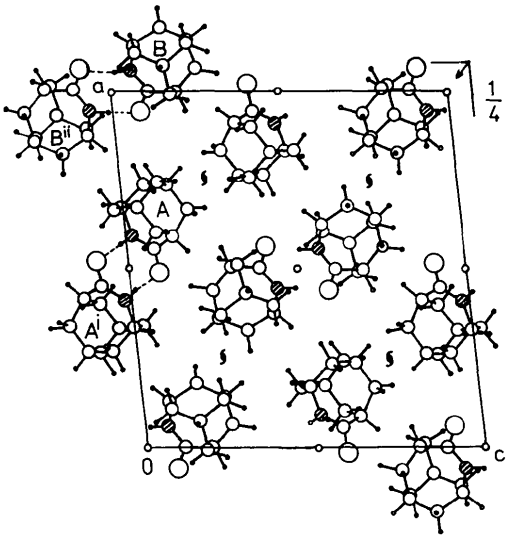

Fig. 2. Crystal packing in the projection along the *b* axis. N atoms are shaded. The hydrogen bonds forming the cyclic dimers are shown. Symmetry code: (i) $\bar{x}+1, \bar{y}, \bar{z}$; (ii) $\bar{x}+2, \bar{y}, \bar{z}$.

Table 2. *Bond lengths* (Å) *and angles* (°) *for A and B lactam molecules*

	A	*B*		*A*	*B*		*A*	*B*
C(1)–C(2)	1·520 (5)	1·523 (5)	C(3)–C(11)	1·528 (4)	1·522 (5)	C(6)–C(10)	1·531 (4)	1·536 (4)
C(1)–C(9)	1·524 (4)	1·521 (5)	N(4)–C(5)	1·322 (3)	1·331 (4)	C(7)–C(8)	1·522 (5)	1·523 (5)
C(1)–C(10)	1·521 (5)	1·525 (5)	C(5)–O(1)	1·248 (4)	1·246 (4)	C(8)–C(9)	1·529 (5)	1·523 (4)
C(2)–C(3)	1·529 (5)	1·513 (4)	C(5)–C(6)	1·510 (4)	1·508 (4)	C(8)–C(11)	1·524 (5)	1·518 (5)
C(3)–N(4)	1·473 (4)	1·468 (4)	C(6)–C(7)	1·532 (5)	1·532 (5)			
C(9)–C(1)–C(10)	109·2 (3)	109·8 (3)	C(3)–N(4)–C(5)	126·8 (2)	126·9 (2)	C(6)–C(7)–C(8)	114·0 (3)	114·2 (3)
C(2)–C(1)–C(10)	114·1 (3)	112·9 (3)	N(4)–C(5)–C(6)	119·8 (2)	119·5 (3)	C(7)–C(8)–C(11)	113·0 (3)	113·3 (3)
C(2)–C(1)–C(9)	109·9 (3)	109·8 (3)	N(4)–C(5)–O(1)	120·6 (2)	120·5 (3)	C(7)–C(8)–C(9)	109·4 (3)	108·9 (3)
C(1)–C(2)–C(3)	112·9 (3)	113·5 (3)	O(1)–C(5)–C(6)	119·6 (2)	120·0 (3)	C(9)–C(8)–C(11)	109·2 (3)	109·6 (3)
C(2)–C(3)–C(11)	111·6 (3)	111·6 (3)	C(5)–C(6)–C(10)	111·7 (2)	113·3 (3)	C(1)–C(9)–C(8)	108·6 (3)	108·7 (3)
C(2)–C(3)–N(4)	112·1 (2)	112·7 (3)	C(5)–C(6)–C(7)	113·3 (2)	111·9 (2)	C(1)–C(10)–C(6)	113·3 (3)	113·6 (3)
N(4)–C(3)–C(11)	112·6 (2)	111·9 (3)	C(7)–C(6)–C(10)	111·6 (3)	111·2 (3)	C(3)–C(11)–C(8)	113·4 (3)	113·6 (3)

Table 3. *Parameters and angles* (°) *describing the geometry of the amide group*

Parameter definition	Values for the title lactam Molecule *A*	Molecule *B*
$\omega_1 = \omega\lvert C(6)–C(5)–N(4)–C(3)\rvert$	−3·5 (4)	−1·8 (4)
$\omega_2 = \omega\lvert O(1)–C(5)–N(4)–H(5)\rvert$	5 (2)	0 (2)
$\omega_3 = \omega\lvert O(1)–C(5)–N(4)–C(3)\rvert$	175·6 (2)	178·7 (3)
$\omega_4 = \omega\lvert C(6)–C(5)–N(4)–H(5)\rvert$	−174 (2)	179 (2)
$\tau' = 2\tau = \omega_1 + \omega_2$	2 (2)	−2 (2)
$\chi_C = \omega_1 - \omega_3 + \pi$ (mod 2π)	0·9 (4)	−0·5 (5)
$\chi_N = \omega_2 - \omega_3 + \pi$	9 (2)	1 (2)

These parameters along with the statistical χ^2 value for the mean plane through the amide group of molecule *A* (345·6) indicate much more significant deviation from planarity than for *B* (38·9). An especially significant contribution to the non-planarity is represented by the value of χ_N for molecule *A*. It corresponds to out-of-plane bending at the N(4*A*) atom. Values of χ_C of both molecules *A* and *B* represent the small contribution of bending at the C(5*A*) and C(5*B*) atoms respectively. The contribution of twisting about the C(5)—N(4) bond is also small as can be seen from values of the parameter τ'. Comparison of coordinates of the atomic subsets *A* and *B* shows significant differences in these molecules in any projection.

Thus, the *A* molecule contains a *cis*-amide group with a significant non-planarity contribution from pyramidal bond arrangement at N; on the other hand, this group of the *B* molecule is nearly planar. Molecules *A* are connected by inter-amide hydrogen bonds into cyclic dimers as are molecules *B*. No hydrogen bonds of the type *A*···*B* were found.

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Structure of 5,5,7,7,8,8-Hexachloro-4-methoxy-2-methyl-5,6,7,8-tetrahydro-6-quinolinone*

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Abstract. $C_{11}H_7Cl_6NO_2$, $M_r = 397·9$, triclinic, $P\bar{1}$, $a = 8·801$ (1), $b = 9·285$ (1), $c = 10·099$ (1) Å, $\alpha = 92·69$ (1), $\beta = 102·70$ (1), $\gamma = 111·38$ (1)°, $V = 742·3$ Å^3, $Z = 2$, $D_m = 1·774$ (2), $D_x = 1·780$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1·15$ mm^{-1}, $F(000) = 396$, $T = 293$ K. $R = 0·048$ for 1981 observed reflections. The pyridine moiety is planar. The cyclohexene ring has five atoms coplanar and C(7) deviating by 0·67 (1) Å from this plane. The presence of Cl atoms on vicinal C atoms induces strong van der Waals interactions which results in a staggered conformation and unusual bond lengths.

Introduction. The title compound was prepared by reacting 4-methoxy-2-methyl-6-acetamidoquinoline with sulfuryl chloride at 298 K for 48 h and the subsequent removal of sulfuryl chloride at 323–333 K (Moghe, Pol & Mhaskar, 1985). The structure was established by the X-ray studies.

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