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4,4,7,7-Tetramethylazacyclononan-2-one

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Abstract

$C_{12}H_{23}NO$ is monoclinic, $C2/c$, with $a = 26{\cdot}244\ (19)$, $b = 11{\cdot}957\ (5)$, $c = 26{\cdot}645\ (15)$ Å, $\beta = 118{\cdot}90\ (6)°$, $V = 7319{\cdot}9$ Å^3 at 138 ± 2 K, $Z = 24$. The intensities of 6205 unique reflections were measured at 138 ± 2 K using Cu $K\alpha$ radiation. The structure was solved by direct methods and refined by least-squares methods to final R factors of 0·065 for 3986 observed reflections and 0·114 for all data. The three molecules in the asymmetric unit are almost identical. The molecules adopt a conformation in which the amide group is *transoid* and markedly non-planar with a torsion angle of 147°. The molecules are packed through N—H···O hydrogen bonds in a double helix along the b axis, leading to a pseudo-hexagonal symmetry for the crystal structure.

Introduction

Characteristic features of medium-ring lactams in the crystalline state have been studied in detail by Dunitz & Winkler (1975). One important feature of these compounds is the non-planarity of the amide group, which has also been observed in a number of polycyclic lactams (Ealick & van der Helm, 1977; Ealick, Washecheck & van der Helm, 1976). Smolikova, Havel, Vasickova, Vitek, Svoboda & Bláha (1974) have studied the effect of geminal methyl substitution in ten- and nine-membered lactams. According to them, the introduction of the substituents manifests itself by a decreased number of conformers, that is by a greater rigidity of the molecule. Substitution of the methyl groups at positions 4,4,7,7 favors a conformation with a *trans* amide group, while substitutions at 5,5,8,8 lead exclusively to a conformer with a *cis* amide group. The crystal structure of 5,5,8,8-tetramethylazacyclononan-2-one has been reported earlier (van der Helm & Ealick, 1979). We now report the structure of 4,4,7,7-tetramethylazacyclononan-2-one in the crystalline state.

Long, thin, needle-shaped crystals of the compound were obtained from an ethanol–water solution by slow evaporation at room temperature. Cell parameters and intensity data were obtained at 138 ± 2 K with a CAD-4 counter diffractometer controlled by a PDP8/e computer and fitted with a low-temperature set-up. Cell parameters were determined by least-squares fit to $+2\theta$ and -2θ values of 24 reflections measured with Cu $K\alpha_1$ ($\lambda = 1{\cdot}54051$ Å) radiation.

Intensities of all independent reflections with $2\theta \leq 130°$ were measured using Cu $K\bar{\alpha}$ radiation and applying θ–2θ scan techniques. The scan width for each reflection was calculated as $(0{\cdot}90 + 0{\cdot}14 \tan\theta)°$. A receiving aperture of variable width of $(3{\cdot}5 + 0{\cdot}86 \times$

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tan θ) mm and a constant height of 6 mm was located 173 mm from the crystal. The maximum scan time for a reflection was 50 s. The orientation of the crystal was automatically checked every 200 reflections, and an intensity monitor was measured every 40 min of X-ray exposure. In all, 6206 independent reflections were measured, out of which 2089 were considered unobserved $[I \leq 2\sigma(I)]$. The intensity data were scaled by the use of the monitor reflection by averaging its intensities for three consecutive measurements. For 85% of the data, the monitor intensity varied within 3%, and for the remainder it varied up to 8–9%. Lorentz and polarization corrections were applied.

The structure was determined by direct methods (Karle & Karle, 1966) using the program *MULTAN* (Germain, Main & Woolfson, 1971). All non-hydrogen atoms of the three molecules (designated *A*, *B* and *C*) in the asymmetric unit were obtained from the *E* map calculated with the 375 largest *E* values ($E > 1{\cdot}85$). These atoms were refined first isotropically and then with anisotropic thermal parameters. All H atoms, except six, were located from a difference Fourier map and were refined isotropically. Refinements were carried out by using a block-diagonal (3 × 3, 6 × 6) least-squares program (Ahmed, 1966). The scattering factors for C, O and N atoms were taken from *International Tables for X-ray Crystallography* (1974) and those for H from Stewart, Davidson & Simpson (1965). The refinement was discontinued when the parameter shifts were less than a third of their corresponding standard deviations. The final difference Fourier map was featureless except around molecule *B*, where it contained six peaks with heights ranging from 0·4 to 0·7 e Å^{-3}. No satisfactory explanation could be provided for these peaks except that molecule *B* is probably slightly disordered. Refinements with fractional occupancy at those peak positions did not improve the discrepancy factor. It was, therefore, decided to leave these peaks out of any structure factor calculations. The final *R* factor is 0·065 for 3986 reflections included in the least-squares refinements (some of the observed reflections were excluded by using a logical routine; van der Helm & Nicholas, 1970) and 0·113 for all reflections. The final positional parameters and the equivalent isotropic thermal parameters are listed in Table 1.* The atom-numbering scheme is shown in Fig. 1.

Table 1. *Positional parameters and equivalent isotropic thermal parameters for non-hydrogen atoms* ($U_{eq} = 1/6\pi^2 \sum_i \sum_j b_{ij}\,\mathbf{a}_i . \mathbf{a}_j$)

Three amide hydrogen parameters are listed at the bottom of the table.

	x (×10^5)	y (×10^4)	z (×10^5)	U_{eq} (Å^2)
Molecule *A*				
O	62070 (9)	2316 (2)	82553 (9)	0·0253 (10)
N	57147 (10)	3476 (2)	74942 (10)	0·0202 (12)
C(2)	61688 (13)	3206 (3)	80007 (13)	0·0192 (15)
C(3)	66656 (14)	4027 (3)	82137 (14)	0·0238 (15)
C(4)	70960 (13)	3729 (3)	79844 (14)	0·0250 (15)
C(4*a*)	74602 (15)	4781 (4)	80577 (15)	0·0412 (20)
C(4*b*)	74972 (14)	2781 (3)	83383 (15)	0·0361 (19)
C(5)	67787 (13)	3423 (3)	73378 (13)	0·0254 (15)
C(6)	65293 (13)	2227 (3)	71848 (13)	0·0224 (15)
C(7)	59805 (14)	2071 (3)	65965 (13)	0·0221 (15)
C(7*a*)	61007 (15)	2452 (3)	61154 (14)	0·0321 (18)
C(7*b*)	58346 (14)	819 (3)	65162 (14)	0·0284 (17)
C(8)	54465 (13)	2708 (3)	65464 (13)	0·0242 (15)
C(9)	53398 (13)	2659 (3)	70633 (14)	0·0240 (16)
Molecule *B*				
O	54637 (9)	−1034 (2)	87716 (9)	0·0269 (12)
N	57090 (10)	146 (2)	82545 (10)	0·0212 (12)
C(2)	56649 (13)	−132 (3)	87202 (14)	0·0227 (15)
C(3)	59285 (14)	705 (3)	92022 (13)	0·0238 (14)
C(4)	65805 (14)	434 (3)	96254 (14)	0·0283 (17)
C(4*a*)	66321 (19)	−485 (4)	100397 (15)	0·0492 (23)
C(4*b*)	68533 (15)	1504 (4)	99701 (15)	0·0392 (20)
C(5)	69223 (15)	190 (3)	92945 (15)	0·0368 (18)
C(6)	68624 (15)	−984 (3)	90559 (15)	0·0372 (18)
C(7)	69013 (14)	−1117 (3)	84967 (14)	0·0268 (16)
C(7*a*)	74852 (16)	−611 (4)	85839 (18)	0·0470 (24)
C(7*b*)	68949 (19)	−2390 (4)	83658 (18)	0·0507 (23)
C(8)	64048 (15)	−536 (3)	79703 (15)	0·0362 (19)
C(9)	57807 (14)	−665 (3)	78841 (13)	0·0273 (16)
Molecule *C*				
O	57988 (9)	5687 (2)	70781 (9)	0·0257 (11)
N	50257 (10)	6870 (2)	67996 (10)	0·0207 (13)
C(2)	55485 (13)	6579 (3)	68580 (13)	0·0219 (15)
C(3)	57806 (13)	7379 (3)	65849 (13)	0·0226 (14)
C(4)	55785 (14)	7042 (3)	59452 (13)	0·0242 (15)
C(4*a*)	59501 (15)	6079 (3)	59307 (15)	0·0329 (17)
C(4*b*)	56774 (15)	8069 (3)	56603 (15)	0·0353 (18)
C(5)	49196 (14)	6753 (3)	56109 (13)	0·0240 (16)
C(6)	47402 (13)	5584 (3)	57124 (13)	0·0232 (15)
C(7)	41304 (13)	5477 (3)	56666 (13)	0·0229 (15)
C(7*a*)	36619 (15)	5910 (3)	50804 (14)	0·0323 (18)
C(7*b*)	40215 (14)	4224 (3)	57121 (15)	0·0320 (18)
C(8)	40719 (14)	6114 (3)	61345 (14)	0·0257 (15)
C(9)	45844 (13)	6057 (3)	67484 (13)	0·0241 (16)
	x (×10^3)	y (×10^3)	z (×10^3)	U (Å^2)
Peptide H atoms				
H(*A*)	575 (1)	414 (3)	736 (1)	0·05 (1)
H(*B*)	586 (1)	76 (3)	826 (1)	0·03 (1)
H(*C*)	487 (2)	765 (2)	661 (2)	0·06 (1)

Discussion

The bond distances and angles of the three molecules in the asymmetric unit are listed in Tables 2 and 3 respectively, along with those observed in the unsubsituted caprylolactam (Winkler & Dunitz, 1975). The torsion angles for the molecules are given in Table 4. The three molecules in the asymmetric unit have closely

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* Lists of structure factors, anisotropic thermal parameters and hydrogen atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35727 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

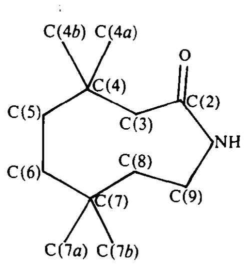

Fig. 1. Atom-numbering scheme in 4,4,7,7-tetramethylazacyclononan-2-one.

similar dimensions and assume the same general type of conformation. It is interesting to note that all nine endocyclic bond distances are longer in the present compound than in the unsubstituted caprylolactam. The average lengthening is 0·015 Å. Precisely the same observation was made when 5,5,8,8-tetramethylazacyclononan-2-one was compared with the unsubstituted caprylolactam. The cause for this effect must be the tetramethyl substitution. A stereoview of the single molecule is shown in Fig. 2. The molecule assumes a conformation in which the amide group is *transoid*, as predicted by Smolikova *et al.* (1974). The amide bond torsion angle of 146·8 (4)° (average for the three molecules) is similar to that observed in the unsubstituted caprylolactam. In fact, the 4,4,7,7-tetramethyl substitution seems to have little effect on the conformation of the amide unit, as can be seen from the conformational angles (Tables 4 and 5). Methyl substitution, however, causes significant conformational changes in the hydrocarbon part of the molecule. Torsion angles C(4)–C(5)–C(6)–C(7), C(5)–C(6)–C(7)–C(8) and C(6)–C(7)–C(8)–C(9) are all significantly different from those in unsubstituted caprylolactam and from the calculated values for the *trans*-cyclononene ring (Ermer & Lifson, 1973).

Table 2. *Bond distances* (Å) *in the three molecules, their average values and corresponding distances in unsubstituted caprylolactam*

	A	*B*	*C*	Average	Caprylo-lactam*
C(2)–O	1·240 (4)	1·238 (4)	1·240 (4)	1·239	1·233
N–C(2)	1·338 (4)	1·343 (5)	1·350 (4)	1·344	1·334
C(2)–C(3)	1·507 (5)	1·507 (5)	1·498 (5)	1·504	1·500
C(3)–C(4)	1·563 (5)	1·562 (5)	1·573 (5)	1·566	1·535
C(4)–C(5)	1·552 (5)	1·560 (5)	1·554 (5)	1·555	1·534
C(5)–C(6)	1·544 (5)	1·517 (6)	1·539 (5)	1·533	1·515
C(6)–C(7)	1·544 (5)	1·550 (6)	1·550 (5)	1·548	1·531
C(7)–C(8)	1·543 (5)	1·543 (5)	1·531 (5)	1·539	1·537
C(8)–C(9)	1·533 (5)	1·548 (6)	1·537 (5)	1·539	1·522
C(9)–N	1·466 (5)	1·460 (5)	1·467 (4)	1·464	1·448
C(4)–C(4*a*)	1·534 (5)	1·517 (6)	1·522 (5)	1·524	
C(4)–C(4*b*)	1·524 (5)	1·535 (6)	1·530 (5)	1·530	
C(7)–C(7*a*)	1·530 (5)	1·557 (6)	1·537 (5)	1·541	
C(7)–C(7*b*)	1·535 (5)	1·560 (6)	1·542 (5)	1·546	

* Winkler & Dunitz (1975).

Table 3. *Bond angles* (°) *in the three molecules, their average values and corresponding angles in unsubstituted caprylolactam*

The standard deviation (if not indicated) is 0·3°.

	A	*B*	*C*	Average	Caprylo-lactam*
O–C(2)–N	123·8	123·4	123·6	123·7	122·4
O–C(2)–C(3)	121·8	122·0	122·1	122·0	122·3
N–C(2)–C(3)	114·2	114·5	114·1	114·3	115·0
C(2)–C(3)–C(4)	111·2	111·7	111·1	111·3	108·4
C(3)–C(4)–C(5)	112·7	111·1	112·2	112·0	115·1
C(4)–C(5)–C(6)	116·3	116·0	116·9	116·4	117·4
C(5)–C(6)–C(7)	116·6	117·1	116·9	116·9	119·0
C(6)–C(7)–C(8)	113·0	114·1	113·6	113·6	116·5
C(7)–C(8)–C(9)	117·1	117·3	117·7	117·4	114·1
C(8)–C(9)–N	109·5	107·8	108·4	108·6	109·4
C(9)–N–C(2)	124·2	123·9	123·5	123·9	122·8
C(3)–C(4)–C(4*a*)	106·7	110·9	109·7		
C(3)–C(4)–C(4*b*)	110·0	106·9	106·4		
C(4*a*)–C(4)–C(4*b*)	109·2	108·5	109·3		
C(5)–C(4)–C(4*a*)	107·5	113·7	111·5		
C(5)–C(4)–C(4*b*)	110·6	105·4	107·6		
C(6)–C(7)–C(7*a*)	110·2	109·5	109·9		
C(6)–C(7)–C(7*b*)	107·8	108·4	107·3		
C(7*a*)–C(7)–C(7*b*)	108·2	108·4	108·7		
C(8)–C(7)–C(7*a*)	109·1	107·4	108·3		
C(8)–C(7)–C(7*b*)	108·3	108·8	108·9		
C(9)–N–H(N)	116 (2)	113 (2)	117 (2)	115	116
C(2)–N–H(N)	113 (2)	117 (2)	114 (2)	115	118

* Winkler & Dunitz (1975).

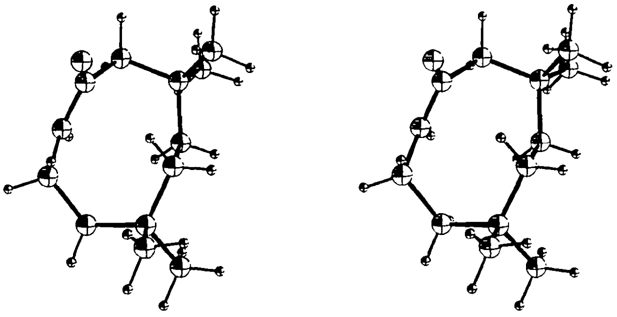

Fig. 2. A stereoview of the single molecule of 4,4,7,7-tetramethylazacyclononan-2-one. Thermal ellipsoids are drawn at the 50% probability level (Johnson, 1965).

Such conformational changes have resulted in an asymmetric ring skeleton for the present stucture, whereas the ring skeleton of the unsubstituted caprylolactam has approximate C_2 symmetry. In 5,5,8,8-tetramethylazacyclononan-2-one (van der Helm & Ealick, 1979), the nine-membered ring possesses approximate D_3 symmetry. In a five-membered fragment (1–5) of the ring, the position of the middle atom, atom (3), can be of three types, *W*, *Y* and *Z*, which are defined by the torsion angles of the bonds 2–3 and 3–4. These torsion angles for type *W* are (±60, ∓60°), for type *Y* (±60, ±60°) and for type *Z* (180, ±60°) (Smolikova *et al.*, 1974). These authors also predicted that geminal methyl groups would occupy the most

Table 4. *Torsion angles* (°)

Standard deviations for the conformational angles in the present structure are between 0·3 and 0·6° for those involving non-hydrogen atoms only and between 1·5 and 2·0° for those involving H.

	A	*B*	*C*	Average	Caprylo-lactam*	Calculated†
C(9)–N–C(2)–C(3)	146·6	146·6	147·3	146·8	148·4	150·5
N–C(2)–C(3)–C(4)	−88·1	−90·8	−90·2	−89·7	−88·8	−88·8
C(2)–C(3)–C(4)–C(5)	44·5	47·4	46·0	46·0	65·8	59·4
C(3)–C(4)–C(5)–C(6)	−79·5	−81·5	−79·1	−80·0	−109·2	−108·1
C(4)–C(5)–C(6)–C(7)	149·9	149·0	148·7	149·2	64·2	66·8
C(5)–C(6)–C(7)–C(8)	−64·2	−64·4	−66·2	−64·9	66·7	66·8
C(6)–C(7)–C(8)–C(9)	−42·9	−43·3	−41·8	−42·7	−109·3	−108·1
C(7)–C(8)–C(9)–N	81·2	81·4	81·4	81·3	58·3	59·4
C(8)–C(9)–N–C(2)	−110·0	−110·3	−110·6	−110·3	−90·5	−88·8
C(9)–N–C(2)–O	−27·4	−28·4	−27·4	−27·7	−25·8	
O–C(2)–C(3)–C(4)	86·0	84·3	84·6	85·0	85·5	
H(N)–N–C(2)–O	−179	−178	180	−179	177	
H(N)–N–C(2)–C(3)	−5	−3	−5	−4	−9	

* Winkler & Dunitz (1975).

† Torsion angles calculated for *trans*-cyclononene (Ermer & Lifson, 1973).

Table 5. *Out-of-plane deformation parameters* (°)

	A	*B*	*C*	Average	Caprylo-lactam*
χ_C	−6·0 (4)	−5·0 (4)	−5·3 (4)	−5·4 (4)	−5·8
χ_N	28·4 (14)	30·4 (14)	27·4 (14)	28·7 (14)	23·1
τ	163·8 (14)	164·3 (14)	163·6 (14)	163·9 (14)	162·9

* Winkler & Dunitz (1975).

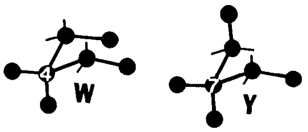

Fig. 3. Conformation around atoms C(4) and C(7). Conformation types are designated according to Smolikova *et al.* (1974).

Table 6. *Hydrogen-bond parameters*

A prime indicates an atom at: $1 - x, -1 + y, \frac{3}{2} - z$.

	D–*A* (Å)	*D*–H (Å)	*A*–H (Å)	*D*–H–*A* (°)
N(*A*)–H(*A*)···O(*B*)	2·916 (3)	0·89 (4)	2·03 (4)	177 (4)
N(*C*)–H(*C*)···O(*A*)	2·904 (4)	0·83 (3)	2·08 (3)	178 (3)
N′(*B*)–H′(*B*)···O(*C*)	2·891 (4)	1·04 (4)	1·85 (4)	175 (4)

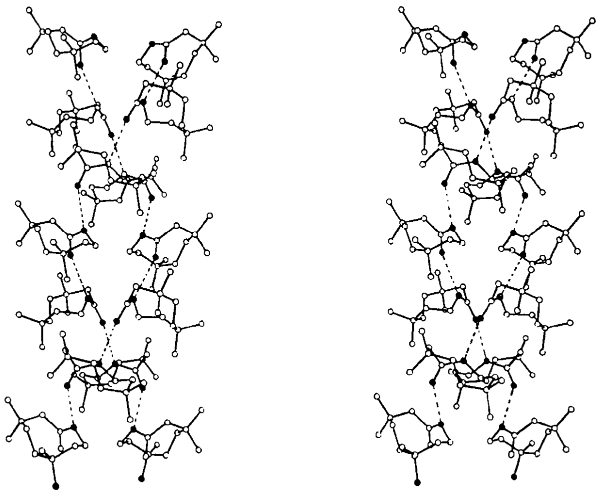

Fig. 4. A stereoview of the double-helical packing of the molecules. The pitch of the helix is twice the length of the *b* axis.

energetically advantageous positions, leading to only type *Y* for the substitution site (3) out of the three possible types. This proved to be true in the case of 5,5,8,8-tetramethylazacyclononan-2-one, where both substitution sites are of the *Y* type. But, in the present structure, the two substitution sites are different. While atom C(7) is of type *Y*, atom C(4) assumes type *W* (Fig. 3). However, the torsion angles about bonds C(3)–C(4) and C(4)–C(5) of 46 and −80° deviate significantly from the ideal values of 60 and −60°, as do the corresponding torsion angles around C(7) (−65, −43° compared to ideal values of −60, −60°).

The out-of-plane deformation of the amide group is described in terms of twisting (τ) and bending (χ_C, χ_N) parameters as defined by Winkler & Dunitz (1971). The values of these parameters are listed in Table 5. The average χ_C, χ_N and τ are −5·4 (5), 28·7 (14), and 163·9 (14)° respectively. These values are in agreement with the observation that when the amide group is significantly non-planar, the carbonyl end of the amide group has a much greater resistance to out-of-plane bending than the nitrogen end. The χ_N value of 28·7° in the present structure is slightly larger than that in caprylolactam (23·1°), while the χ_C value in the present molecule is nearly the same as in its unsubstituted counterpart (5·8°). The difference in χ_N may be attributed to the indirect effect of the methyl substitution on the hydrocarbon part of the molecule. The correlation between χ_N and the corresponding lengthening of the C—N bond has been discussed by Baker, Hossain & van der Helm (1981). The C—N bond length of 1·344 (4) Å in the present structure is about six standard deviations longer than that normally observed in planar peptides. There is, however, no noticeable shortening of the corresponding C=O bond.

The three molecules of the asymmetric unit are linked together through strong intermolecular N—H···O hydrogen bonds. All hydrogen-bond parameters are listed in Table 6. The molecules are packed so as to form an endless helix around the crystallographic twofold axis. The resulting double helix is shown in a stereodiagram in Fig. 4. The amide units constitute the inner core of the helix while the methyl groups lie on the periphery.

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Hexaphenyl Group IV*a* Ethers*

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Abstract

The crystal structures of hexaphenyl Group IV*a* ethers, Ph_3MONPh_3 (in which $M \neq N$) for Si, Ge and Sn have been solved by the Patterson method using diffractometer data and refined by full-matrix least-squares methods. Crystals of $Ph_3SiOGePh_3$ and $Ph_3GeOSnPh_3$ are triclinic in space group $P\bar{1}$, $Z = 2$, with *a* = 11·000 (3), *b* = 9·719 (2), *c* = 15·449 (3) Å, *α* = 92·69 (1), *β* = 103·06 (1), *γ* = 109·49 (1)° and *a* = 11·264 (3), *b* = 9·744 (2), *c* = 15·627 (4) Å, *α* = 92·60 (2), *β* = 103·35 (2) and *γ* = 109·48 (2)°, respectively; those for $Ph_3SiOSnPh_3$ are in $P2_1/n$, $Z = 4$ with *a* = 19·886 (5), *b* = 17·621 (4), *c* = 8·830 (2) Å and *β* = 90·07 (2)°. The metalloid atoms are disordered in all these structures. For $Ph_3SiOGePh_3$ (R = 0·042 with a population parameter of 0·503, hence complete disorder), the *M*—O bond lengths are

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