Table 3. *Selected geometric parameters (Å, °) for (II)*

C5—C6	1.477 (5)	C7—C8	1.476 (4)
C5—C10	1.512 (4)	C8—C9	1.504 (4)
C6—C7	1.302 (5)		
C6—C5—C10	115.2 (3)	C7—C8—C9	114.2 (3)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O1···O2^{i}	1.00 (4)	1.75 (5)	2.740 (3)	173 (4)

Symmetry code: (i) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4.95 cm for (I) and 3.99 cm for (II); the detector swing angle was −30°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of the data collection and analysing the duplicate reflections, and was found to be negligible. Both structures were solved by direct methods and refined by full-matrix least-squares techniques; all H atoms were located from successive difference Fourier maps and refined isotropically. Though all the atoms in the structure of (I) had been located, the refinement did not converge and showed an *R* value of 0.174 (*wR* = 0.507). Nearly equal lengths for the *a* [9.7322 (6) Å] and *c* [9.7382 (6) Å] axes suggested the possibility of a rotational twin, with the *a* and *c* axes interchanged. Accordingly, the structure was refined with *TWIN* 001, 0$\bar{1}$0, 100 and *BASF* instructions, with equal values for *a* and *c* lengths, and it converged to the present *R* value with twin components of 0.720 (2) and 0.280 (2). The slightly low reflection-to-parameter ratios of 9.8 are due to the fact that the H-atom parameters were refined.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1234). Services for accessing these data are described at the back of the journal.

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The 3,3,6,6-Tetramethyl *cis-transoid-cis*-Photocyclodimer of *tert*-Butyl 2,5-Dihydro-5,5-dimethyl-2-oxo-1*H*-pyrrole-1-carboxylate

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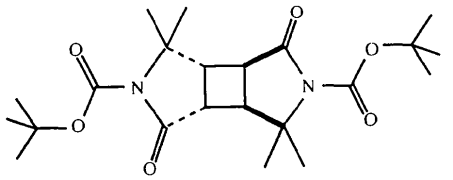
Abstract

The X-ray structure of di-*tert*-butyl *cis-transoid-cis*-perhydro-3,3,6,6-tetramethyl-1,4-dioxocyclobuta[1,2-*c*:3,4-*c*′]dipyrrole-2,5-dicarboxylate, $C_{22}H_{34}N_2O_6$, which is the major photocyclodimer obtained on hexadeuterioacetone-sensitized irradiation of the monomeric *tert*-butyl 2,5-dihydro-5,5-dimethyl-2-oxo-1*H*-pyrrole-1-carboxylate, was determined in order to establish its constitution and configuration unambiguously.

Comment

The photochemical behaviour of 5,5-dimethyl-1*H*-pyrrol-2(5*H*)-one (Ihlefeld & Margaretha, 1992) parallels that of the pyrimidine bases of DNA, such as uracil or thymine. Direct irradiation (Ihlefeld & Margaretha, 1992) or hexadeuterioacetone-sensitized irradiation (Wrobel & Margaretha, 1997) affords a mixture of two dimers, (*A*) (major) and (*B*) (minor), whose structures were previously assigned on the basis of their ^{1}H NMR spectra only, because suitable single crystals could not be obtained. We have prepared the title compound,

(I), determined its structure by X-ray analysis, and then converted it to the major dimer (*A*), mentioned above, by double N-deprotection. In this way, we were able to confirm the proposed structure for this compound unambiguously.



(I)

The asymmetric unit consists of one half of the molecule, with the cyclobutane ring across a centre of inversion. The molecule adopts a staircase-like conformation, with an exactly flat butane ring in the middle of the molecule and two rather flat pyrrole rings [puckering parameters (Cremer & Pople, 1975): Q = 0.210 (1) Å and Φ = 148.5 (4)°] connected to it. Each pyrrole ring adopts an envelope conformation, with atom C5 out of the plane (Köll *et al.*, 1982).

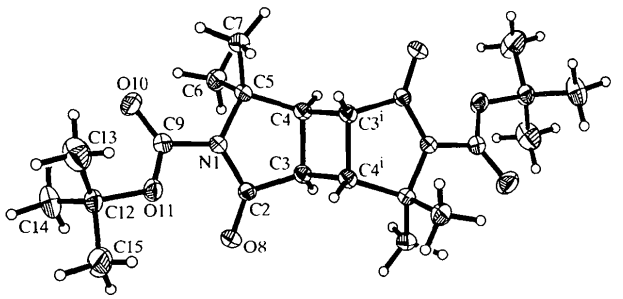


Fig. 1. *ORTEP*II (Johnson, 1976) plot, as implemented in *SHELXTL-Plus* (Sheldrick, 1992), of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. [Symmetry code: (i) $-x$, $-y$, $1-z$.]

Experimental

The title compound, (I), is the main product (42% yield) from hexadeuterioacetone-sensitized irradiation of *tert*-butyl 2,5-dihydro-5,5-dimethyl-2-oxo-1*H*-pyrrole-1-carboxylate, and subsequent chromatographic work-up (Wrobel & Margaretha, 1997). Suitable single crystals, decomposing at 466 K, were obtained from acetone. Conversion of (I) to *cis-transoid-cis*-perhydro-3,3,6,6-tetramethylcyclobuta[1,2-*c*:3,4-*c*′]dipyrrole-1,4-dione, (*A*), was achieved by stirring (I) in CH_2Cl_2 in the presence of trifluoroacetic acid (Wolman, 1968) at room temperature.

Crystal data

$C_{22}H_{34}N_2O_6$
M_r = 422.51
Cu $K\alpha$ radiation
λ = 1.54178 Å
Monoclinic
$C2/c$
a = 17.298 (1) Å
b = 10.738 (1) Å
c = 12.453 (1) Å
β = 95.43 (1)°
V = 2302.7 (3) Å^3
Z = 4
D_x = 1.219 Mg m^{-3}
D_m not measured
Cell parameters from 25 reflections
θ = 41.3–45.7°
μ = 0.724 mm^{-1}
T = 173 (1) K
Block
0.8 × 0.7 × 0.7 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
2555 measured reflections
2417 independent reflections
2368 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
θ_{max} = 76.26°
$h = -21 \rightarrow 21$
$k = -13 \rightarrow 3$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.114
S = 1.078
2417 reflections
159 parameters
H-atom treatment: mixed
$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 2.4367P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.366 e Å^{-3}
$\Delta\rho_{min}$ = −0.223 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0105 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.3920 (16)	C3—C4	1.5456 (16)
N1—C9	1.4127 (17)	C3—C4^i	1.5601 (16)
N1—C5	1.5002 (15)	C4—C5	1.5413 (17)
C2—O8	1.2190 (15)	C5—C7	1.5233 (18)
C2—C3	1.5070 (17)	C5—C6	1.5289 (18)
C2—N1—C9	125.25 (11)	C5—C4—C3	107.01 (10)
C2—N1—C5	112.94 (10)	C5—C4—C3^i	120.02 (10)
C9—N1—C5	120.44 (10)	C3—C4—C3^i	89.24 (9)
O8—C2—N1	126.54 (12)	N1—C5—C7	112.16 (10)
O8—C2—C3	125.19 (12)	N1—C5—C6	109.65 (10)
N1—C2—C3	108.25 (10)	C7—C5—C6	110.95 (11)
C2—C3—C4	105.32 (10)	N1—C5—C4	101.65 (9)
C2—C3—C4^i	109.07 (10)	C7—C5—C4	113.15 (10)
C4—C3—C4^i	90.76 (9)	C6—C5—C4	108.87 (10)

Symmetry code: (i) $-x$, $-y$, $1-z$.

H atoms were included using a riding model (*SHELXL*97; Sheldrick, 1997), but their displacement parameters were refined freely; rigid methyl groups were allowed to rotate, thus contributing one additional parameter each.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD-4 EXPRESS*. Data reduction: *CAD-SHEL* (Kopf, 1987). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1992). Software used to prepare material for publication: *PLATON*95 (Spek, 1990).

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(Z)-5-(2-Naphthylmethylene)-4-oxo-2-thioxo-1,3-thiazolidine-3-acetic Acid Dimethyl Sulfoxide Solvate

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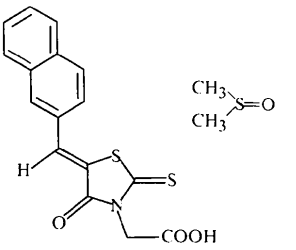
Abstract

The title acid (1-H-NOTA), as well as its methoxy derivative (1-OCH_3-NOTA), exhibit aldose reductase (AR) inhibitor activity and co-crystallize with dimethyl sulfoxide (DMSO), *i.e.* $C_{16}H_{11}NO_3S_2.C_2H_6OS$. The skeleton of 1-H-NOTA is highly planar, except for the acetic acid group. This conformation confers on the molecule a geometry that complements that of the AR active pocket. 1-H-NOTA molecules are held together by van der Waals and ring-to-ring interactions. The stability of the crystal is enhanced by an O—H···O hydrogen bond [O···O 2.554 (5) Å] which links the DMSO to 1-H-NOTA through its carboxy group.

Comment

Complications of non-insulin-dependent diabetes mellitus (NIDDM) are caused by glucidic metabolism disorders characterized by enhanced activity of aldose reductase (Cogan *et al.*, 1984; Kador *et al.*, 1985; Benfield, 1986; Raskin & Rosenstock, 1987; Kinoshita & Nishimura, 1984). Consequently, AR inhibition is an appropriate approach to prevent NIDDM complications. In the search for new AR inhibitors, over 30 new compounds have been synthesized (Fresneau, 1996). Two of them, 1-H-NOTA and its derivative 1-OCH_3-NOTA, exhibit activities comparable to those of well known AR inhibitors (Kinoshita & Nishimura, 1984; Kador *et al.*, 1985, 1987; Benfield, 1986; Raskin & Rosenstock, 1987; Sarges & Oates, 1993; Tomlinson *et al.*, 1994). 1-OCH_3-NOTA has AR inhibition activity one order of magnitude greater than that of 1-H-NOTA. Molecular modelling suggests that a stable NOTA-AR complex may be formed by numerous hydrophobic and hydrogen-bond interactions between the host and guest molecules. In order to determine the structural features required for potential AR inhibitor molecules, and in particular those for NOTA, we have investigated the crystal structure of 1-OCH_3-NOTA.DMSO (TranQui *et al.*, 1998) and here we report the structure of 1-H-NOTA.DMSO



1-H-NOTA

The molecular geometry and atom-numbering scheme are shown in Fig. 1. As expected, the heavy-atom skeleton, apart from the carboxy group, is planar. DMSO, used as solvent, is also present in the crystal. The displacement parameters of its atoms (S3, C17, C18 and O4) are similar to those of the other atoms in the structure, indicating that DMSO can be considered as co-crystallized with the inhibitor molecule. It helps to stabilize the crystal by forming a strong hydrogen bond (O2···O4) which links the two molecular species through the carboxylic acid group of 1-H-NOTA.