(Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1347). Services for accessing these data are described at the back of the journal.

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(±)-(3′aα,4′α,6′aα)-3′,3′a,4′,6′a-Tetrahydro-5,5,*N*,*N*-tetramethylspiro[1,3-dioxane-2,2′(1′*H*)-pentalene]-4′-acetamide, a triclinic crystal structure with local monoclinic pseudosymmetry

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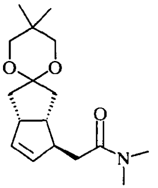
Abstract

The crystal packing in the title compound, $C_{17}H_{27}NO_3$, shows layers with local pseudo-monoclinic symmetry. The two independent molecules are related by local non-crystallographic glide planes and screw axes. Adjacent layers are displaced by a distance of about 1.61 Å in the *a* direction, resulting in an overall triclinic symmetry of the structure.

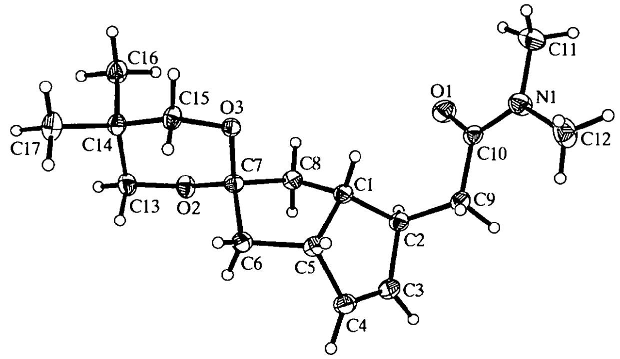
Comment

The structure of the title compound, (I), contains two crystallographically independent molecules (1 and 2). The geometries of both molecules are very similar. Inspection of the fractional coordinates shows that both independent molecules are related by a local non-crystallographic glide plane almost perpendicular to the *a* axis, with a translation vector of 0.5**b**. The equation of this pseudo-glide plane in crystal coordinates is approximately $9.48x + 0y - 1.61z = 1.56$. The angle between the *a* axis and the normal to this pseudo-glide plane is only 0.6°. The pseudo-glide plane is continuous in the crystallographic *b* direction. In the *c* direction, however, the pseudo-glide plane only acts in one unit cell and shows a shift of about one sixth of the length of the *a* axis between adjacent cells. The pseudo-glide symmetry can be combined with the crystallographic inversion center to give an additional pseudo-twofold screw axis parallel to **a** and displaced from the origin by ±**b**/4 and +**c**/2. These pseudosymmetry elements can be easily identified using the program *BUNYIP* (Hester & Hall, 1996) or by a combined coordinate midpoint and translation analysis as described by Kálmán & Argay (1998).

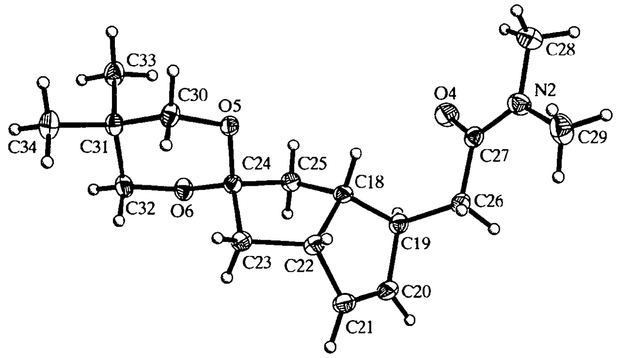


(I)

The crystal packing (Fig. 2) shows layers parallel to the *ab* plane with approximate monoclinic symmetry. The symmetry of the layer corresponds to structural class $P_{l(XY)}2_1/b$, $Z = 4\,(1)$, using the nomenclature of Zorky (1996). Adjacent layers are displaced by a distance of about 1.61 Å along the *a* axis. This displacement results in a triclinic symmetry of the three-dimensional crystal structure. Without this displacement the structure would be monoclinic with space group $P2_1/b$ (*a* axis unique), but with intermolecular H···H contacts between adjacent layers as short as 2.04 Å, which, obviously, is too short. A similar pseudosymmetric structure has been observed by Bats *et al.* (1999). The five-membered rings are *cis*-connected about the C1—C5 and the C18—C22 bonds. These bonds have lengths of 1.563 (2) Å and are slightly lengthened with respect to a normal C—C single bond of 1.54 Å. The cyclopentene ring has an envelope conformation, with atoms C1 and C18 0.30 and 0.31 Å, respectively, outside the plane of the other four ring atoms. Atoms C8 and C25 are in axial positions, while atoms C6 and C23 are in pseudo-equatorial positions with respect to the cyclopentene rings. The central cyclopentane ring has a conformation intermediate between a C7,C8-twist and a C8-envelope for molecule 1, and between a C24,C25-twist and a C25-envelope for molecule 2. The six-membered dioxane rings have chair conformations. Atoms C6, C16, C23 and C33 are in axial positions, and atoms C8, C17, C25 and C34 are in equatorial positions with respect to the dioxane rings. The axial C6—C7 and C23—C24 bonds are about 0.027 Å longer than the equatorial C7—C8 and C24—C25 bonds. An inspection of the Cambridge Structural Database (Allen & Kennard, 1993) shows this bond-length difference to occur in many spiro-connected dioxane derivatives. So far, however, only Solans *et al.* (1985) have reported this effect in the literature. A steric repulsion between hydrogen atoms H6*B* and H15*B* [distance 2.22 (2) Å], and H23*B* and H30*B* [distance 2.16 (2) Å] may be responsible for this bond-length difference. The C7—O3 and C24—O5 distances are slightly longer than the corresponding C7—O2 and C24—O6 bonds. The bond angles about O3 and O5 are about 2° larger than those about O2 and O6, and the bond angles about the spiro atoms C7 and C24 are rather unsymmetrical. Also, these effects may depend on the intramolecular H···H repulsions. The amide bonds are almost planar. The torsion angles about the C(O)—N bonds are about 4°. The crystal packing shows only very weak electrostatic intermolecular O···H interactions, with distances more than 0.2 Å longer than the van der Waals contact distances.



Molecule 1



Molecule 2

Fig. 1. The structures of the two independent molecules of (I) shown with 50% probability displacement ellipsoids.

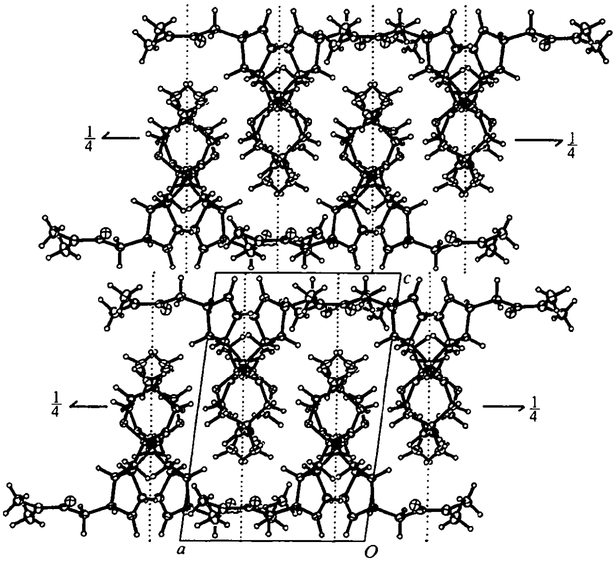


Fig. 2. The crystal packing of (I) shown down the *b* axis. The pseudo-glide planes have been indicated by dotted lines and the pseudo-twofold screw axes by arrows.

Experimental

The required racemic allylic alcohol *exo*-7,7-(2,2-dimethyl-1,3-propylenedioxy)-*cis*-bicyclo[3.3.0]oct-3-en-2-ol was obtained together with its *endo*-epimer by a base-promoted epoxide-opening reaction (Apparu & Barrelle, 1978) following the method described by Carceller *et al.* (1984), Piers & Moss (1985) and Demuth & Schaffner (1982). The *exo*-epimer was easily separated from the less polar *endo*-epimer by column chromatography. The allylic alcohols were subjected separately to Claisen rearrangements (Felix *et al.*, 1969). Thus, *exo*-7,7-(2,2-dimethyl-1,3-propylendioxy)-*cis*-bicyclo-[3.3.0]oct-3-en-2-ol (900 mg, 4.0 mmol) was dissolved in dried xylene and heated to 393 K. Dimethylacetamidedimethylacetal (2.93 ml, 20 mmol) was added and the resulting solution was boiled for 10 h under reflux with cooling. Vacuum distillation of the solvent yielded a brown oil, which was purified by chromatography. The yield of the desired compound (I) was 1.08 g (3.7 mmol, 92%). The product was recrystallized from diethyl ether by the dropwise adding of *n*-pentane (m.p. 380–382 K). In a similar reaction, the racemic epimeric *endo*-allylic alcohol was subjected to the same Claisen rearrangement. The corresponding *endo*-epimer of (I) was obtained in a somewhat lower yield (78%, longer reaction time required) as an oil, which did not crystallize.

Crystal data

$C_{17}H_{27}NO_3$
$M_r = 293.41$
Triclinic
$P\bar{1}$
$a = 9.4850\,(13)$ Å
$b = 11.769\,(2)$ Å
$c = 14.596\,(2)$ Å
$\alpha = 104.889\,(12)°$
$\beta = 96.663\,(12)°$
$\gamma = 90.451\,(9)°$
$V = 1562.8\,(4)$ Å^3
$Z = 4$
$D_x = 1.247$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 213 reflections
$\theta = 3–23°$
$\mu = 0.084$ mm^{-1}
$T = 135$ K
Block
$1.02 \times 0.52 \times 0.24$ mm
Pale yellow

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: numerical, based on six indexed crystal faces (Sheldrick, 1996)
$T_{\min} = 0.930$, $T_{\max} = 0.981$
24 913 measured reflections
7688 independent reflections

7473 reflections with $I > 0$
$R_{\rm int} = 0.051$
$\theta_{\max} = 29.85°$
$h = -11 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 20$
332 standard reflections
frequency: 540 min
intensity decay: none

Refinement

Refinement on F
$R = 0.056$
$wR = 0.052$
$S = 1.070$
7473 reflections
595 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0009F_o^4]$

$(\Delta/\sigma)_{\max} = 0.015$
$\Delta\rho_{\max} = 0.4322$ e Å^{-3}
$\Delta\rho_{\min} = -0.200$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL* (direct methods) (Sheldrick, 1996). Program(s) used to refine structure: *LSFM* in *MolEN* (Fair, 1990). Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *CIF* in *MolEN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1316). Services for accessing these data are described at the back of the journal.

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4-(1*H*-1,2,4-Triazol-1-yl)phenol[†]

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Abstract

The secondary structure of the title compound, $C_8H_7N_3O$, consists of O—H···N hydrogen-bonding catemers, similar to those of the parent 1,2,4-triazole, where the molecules are linked by N—H···N bonds. Chains related by translation are linked by C—H(triazole)···O/N interactions to give a tertiary structure of corrugated sheets parallel to the *ac* plane. The quaternary structure is due to C—H(Ph)···O contacts and to the stacking of triazole rings from centrosymmetrically related sheets.

Comment

The solid state chemistry of simple phenols has received much attention due to the great variety of structures they present (Perrin *et al.*, 1987). Similarly, heterocyclic compounds, especially azoles, bearing hydroxyphenyl substituents have been studied for their photophysical properties, for instance by ourselves (Catalán *et al.*, 1992, 1995; Foces-Foces *et al.*, 1998). These compounds are also used as ligands in coordination chemistry (La Monica & Ardizzoia, 1997), and a most

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[†] Alternative name: 1-(4-hydroxyphenyl)-1*H*-1,2,4-triazole.