Tri-*tert*-butyl 3-oxo-4-oxa-1,8,11-triazaspiro[5.6]dodecane-1,8,11-tri-acetate

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The title compound, C₂₆H₄₅N₃O₈, is a bicyclic molecule; the seven-membered diazepane ring has a twisted-chair conformation and the six-membered morpholine ring has a boat conformation.

Comment

The chemistry of 1,4-diazepane-based ligands is attracting increasing attention since these ligands have strong binding capabilities with different metal ions, including main group metals, transition metals and lanthanides (Comba *et al.*, 2009; Ge *et al.*, 2007, 2009; Peralta *et al.*, 2005; Rey *et al.*, 2007). In particular, it has been proposed that gadolinium(III) complexes of 6-amino-6-methylperhydro-1,4-diazepinetetraacetic acid (AAZTA) ligands are good candidates as MRI (magnetic resonance imaging) contrast agents due to their good thermodynamic stability, kinetic inertness and high relaxivity at neutral pH (Aime *et al.*, 2004).

Recently, we reported the syntheses and characterization of new bifunctional AAZTA ligands with hydroxy side chains, and the crystal structures of their gadolinium and europium complexes (Sengar *et al.*, 2008, 2009). The title compound, (I), was used as a precursor for one of the bifunctional ligands with

Figure 1

The molecular structure of (I), showing one of the molecules in the unit cell, with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

a hydroxy arm and the complete synthesis and spectroscopic characterization of (I) was provided (Sengar *et al.*, 2009). We report herein the molecular structure of compound (I) determined by X-ray crystallography (Fig. 1).

Compound (I) crystallizes with two independent molecules in the asymmetric unit and these exhibit similar conformations. The r.m.s. deviation of the two molecules based on a fit of all non-H atoms is 0.353 Å, calculated by *PLATON* (Spek, 2009). The maximum deviations were observed for the *tert*-butyl ester groups. As expected, compound (I) contains two rings, *viz.* a seven-membered 1,4-diazepane ring with a twisted-chair conformation and a six-membered morpholine ring which adopts a boat conformation (Fig. 1). For the seven-membered ring, the approximate plane can be defined by N4/C29/N5/C27, with atoms C30, C43 and C28 deviating above and below this plane. For the six-membered ring, atoms C44 and C46 occupy the prow and stern positions, respectively. The two rings are connected to each other *via* spiro atom C43 in a near orthogonal fashion; the dihedral angles for the N5/C30/C43/N6 and N4/C27/C43/C44 planes are $-87.0(2)^\circ$ and $-71.9(2)^\circ$, respectively [$-85.6(2)^\circ$ and $-72.8(2)^\circ$, respectively, for the other molecule in the unit cell].

The diazepane and morpholine rings in the two molecules have slightly different puckering parameters (Cremer & Pople, 1975), as given in Table 1. The puckering parameters for the seven-membered ring in (I) are different from the values for the AAZTA chelate (Table 1) or the protonated diazepane (daza-3HCl-3H₂O) chelate (Romba *et al.*, 2006). This shows that a large degree of flexibility is associated with the diazepane ring, which gives rise to the different puckering parameters for noncoordinated ligands. However, upon metal coordination, the diazepane ring adopts a pseudo-chair conformation and all three N atoms coordinate to the metal ion in a facial mode (Aime *et al.*, 2008).

Experimental

Compound (I) was synthesized according to the literature procedure of Sengar *et al.* (2009). Colorless crystals suitable for X-ray analysis were obtained by slow evaporation from a dichloromethane solution of (I) in air.

Crystal data

$C_{26}H_{45}N_3O_8$	$\gamma = 100.168 (3)^\circ$
$M_r = 527.65$	$V = 2982.5 (8) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 4$
$a = 11.1304 (17) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 15.250 (2) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 18.098 (3) \text{ \AA}$	$T = 203 \text{ K}$
$\alpha = 99.305 (4)^\circ$	$0.24 \times 0.18 \times 0.13 \text{ mm}$
$\beta = 90.010 (3)^\circ$	

Data collection

Bruker SMART APEX CCD diffractometer	21467 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	11582 independent reflections
$T_{\min} = 0.962$, $T_{\max} = 0.980$	7769 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.052$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$	667 parameters
$wR(F^2) = 0.170$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\max} = 0.58 \text{ e \AA}^{-3}$
11582 reflections	$\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$

Table 1

Puckering parameters for (I) and the AAZTA chelate.

All calculations made using PLATON (Spek, 2009).

	Diazepane ring		Morpholine ring		Diazepane in AAZTA†
	Molecule 1	Molecule 2	Molecule 1	Molecule 2	
q_2 (°)	0.510 (2)	0.537 (2)	0.638 (2)	0.653 (2)	0.641 (7)
q_3 (°)	0.676 (2)	0.675 (2)	0.031 (2)	0.026 (2)	0.633 (7)
φ_2 (°)	69.0 (3)	67.2 (2)	55.1 (2)	59.3 (2)	65.7 (6)
φ_3 (°)	323.7 (2)	323.5 (2)			16.2 (6)

† Aime *et al.* (2008).

H atoms were placed in calculated positions and refined using a riding model [$C-H = 0.97 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$ for methyl H

atoms, and $C-H = 0.98 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$ for methylene H atoms].

Data collection: SMART (Bruker, 2003); cell refinement: SAINT-Plus (Bruker, 2003); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3037). Services for accessing these data are described at the back of the journal.

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