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The disordered molecular structure of (3a*RS*,7a*RS*)-1,3-dinitrosooctahydro-1*H*-benzimidazole

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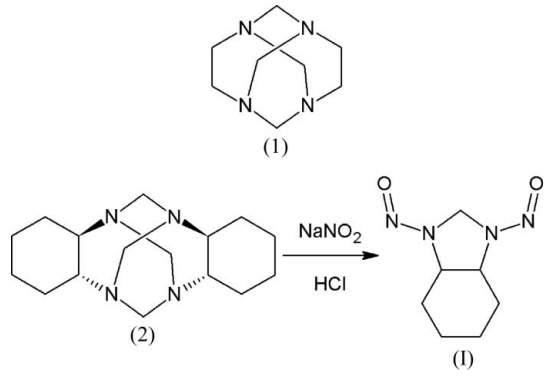
The title compound, $C_7H_{12}N_4O_2$, was obtained by nitrosation of the aminal cage (2*R*,7*R*,11*S*,16*S*)-1,8,10,17-tetraazapentacyclo[8.8.1.1^{8,17}.0^{2,7}.0^{11,16}]icosane. The crystal structure is a racemic mixture of *RR* and *SS* enantiomers. The asymmetric unit contains two crystallographically independent half-molecules, one having two partially occupied conformers with refined occupancy factors of 0.747 (3) and 0.253 (3). The molecules sit across twofold axes. The unique molecules each form chains parallel to [001], with molecules connected by intermolecular C—H···O hydrogen bonds. The bonding between adjacent chains is weak. The analysis of eight different crystals confirmed the presence of disordered and nondisordered molecules in the same structure as a regular feature.

Comment

Our group (at the Universidad Nacional de Colombia, Bogotá) has previously explored the reaction of nitrous acid with cyclic aminals, which are actually tertiary amines. Previously, we reported the synthesis and complete characterization by NMR of a heterocyclic secondary *N*,*N*′-dinitrosoamine by reaction of the macrocyclic aminal 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane [TATD, (1)] with nitrous acid (sodium nitrite/HCl) (Rivera *et al.*, 1997). The chemistry of *N*-nitrosoamines is a subject of considerable interest with regard to their strong carcinogenic and mutagenic properties (Di Salvo *et al.*, 2008). Recently, we have been interested in the cyclic aminal (2*R*,7*R*,11*S*,16*S*)-1,8,10,17-tetraazapentacyclo-[8.8.1.1^{8,17}.0^{2,7}.0^{11,16}]icosane, (2). In a further exploration of its synthetic utility, aminal (2) was reacted with sodium nitrite in an acidic medium. We found that the nitrosation of (2) was similar to the reaction of (1); it also proceeded under mild conditions (273–278 K) to give the corresponding title compound, (3a*RS*,7a*RS*)-1,3-dinitrosooctahydro-1*H*-benzimidazole, (I), in 70–75% yields (see Scheme). The structure of the *N*-nitrosoamine obtained was investigated in solution and in the solid state by IR, NMR (^{1}H and ^{13}C, and short- and long-range coupling experiments), mass spectrometry and X-ray methods. Crystallographic information on *N*,*N*′-dinitroso compounds in the Cambridge Structural Database (CSD, Version 5.32; Allen, 2002) is limited. In particular, the O═N—NCH_2N—N═O fragment is quite rare and a search of the CSD for compounds containing structures that match this fragment retrieved no hits.



As reported in the literature, *N*-nitroso compounds typically display two absorption bands in their IR spectra due to stretching of the N═O and N—N bonds between 1460 and 1440 cm^{-1}, and near 1050 cm^{-1}, respectively (Sousa *et al.*, 2005). These characteristic bands are observed in the IR spectrum of (I) at 1455 and 1112 cm^{-1}.

The ^{1}H NMR spectrum of (I) only shows signals corresponding to the *syn* isomer. The influence of the nitroso group on the chemical shift values is evident in the signals of the aminal protons of the imidazolidine ring, which appear at a lower field (5.20 p.p.m.) than the corresponding aminal protons in the aminal precursor (2).

The molecular structure of (I) is presented in Fig. 1, and selected geometric parameters are given in Table 1. The compound is monoclinic (space group *P*2/*c*), with two crystallographically independent half-molecules (half-molecule *M*1 formed by atoms O1/C1–C4 and half-molecule *M*2 formed by atoms O2/C5–C8) in the asymmetric unit and overall *Z* = 4. Molecules *M*1 and *M*2 both have twofold symmetry, with atoms C1 (for *M*1) and C5 (for *M*2) located on the twofold axes. The entire molecule *M*2 is disordered and adopts two unequally occupied orientations. Molecule *M*1 is fully ordered.

In the first attempt at modelling the disorder, we described two overlapping conformations, *A* and *B*, of *M*2. The positions of the atoms were refined independently, whereas the displacement parameters (isotropic for close positions and anisotropic for positions further away) were constrained so that they were the same for corresponding atoms from each of the disordered positions of the molecule; a common site-occupation factor was refined for the atoms of each disordered conformation while constraining the sum of the two occupancies to unity. Refinement of this structural model con-

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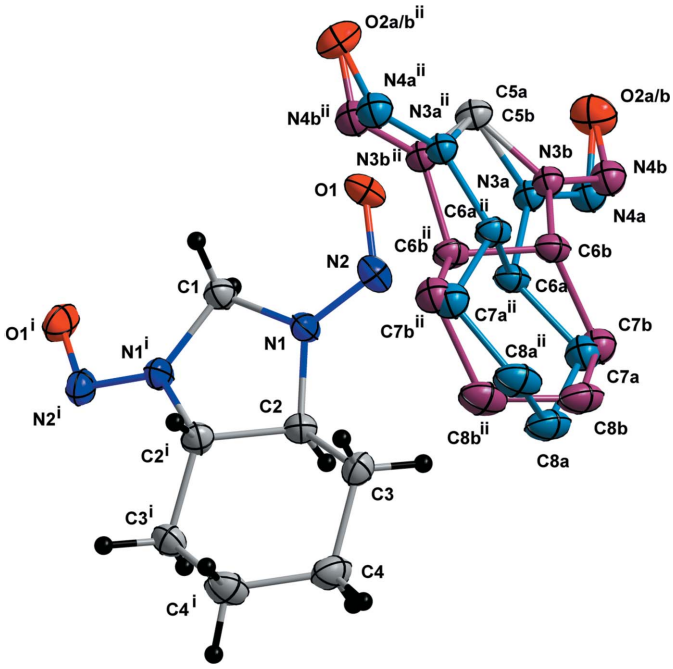

Figure 1
The molecular structure of (I), including two independent molecules and showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms in the disordered molecule have been omitted for clarity. [Symmetry codes: (i) $-x+2, y, -z+\frac{3}{2}$; (ii) $-x+1, y, -z+\frac{1}{2}$.]

tained 120 parameters and converged with R_{obs} = 0.043, with the largest difference-map residuals being 0.30 and −0.31 e Å^{-3}, indicating a good fit of the structural model to the experimental data. The occupancies of conformations *A* and *B* refined to 0.734 (2) and 0.266 (2), respectively. However, the refined geometries of conformations *A* and *B* were significantly different, particularly for the N—NO groups.

Prior to drawing conclusions from the differences between conformations *A* and *B*, it was necessary to test whether the diffraction data were sufficiently sensitive for refinement of such weakly occupied positions of *B*. Indeed, the average electron density of carbon with an occupancy of 0.266 (2) is less than that of two H atoms. For this test, we used a rigid-body approach available in the crystallographic package *JANA2006* (Petříček *et al.*, 2006). The atoms of position *A* of molecule *M*2 obtained from the structure model described above were taken as the model molecule. Atom C5, sitting on the twofold axis, was used as a reference point for the calculation of symmetry restrictions of molecular parameters. Together with the parameters of the model molecule, we refined a translation vector and three rotation angles transforming the model molecule (including orientation of anisotropic displacement parameters) to the actual position *A*, and another translation vector and three rotation angles transforming the model molecule to the actual position *B*. The reference point located on the twofold axis led to symmetry restrictions of the translation vectors such that molecules *A* and *B* were both still located on the twofold axis. Since the model molecule was originally taken from position *A* of *M*2, the first translation vector was very short and the corresponding rotation angles zero. The occupancy factors converged to 0.747 (3) and 0.253 (3) for *A* and *B*, respectively, which are close to the values from the split-atom model. Surprisingly, the resulting *R* value was 0.040 and the largest difference-map residuals were 0.28 and −0.25 e Å^{-3} (*i.e.* slightly better than the previous model), whereas the number of refined parameters (124) remained almost the same. This meant that the different geometries of *A* and *B* were not confirmed and should both be considered identical.

A CIF file was generated as the free atomic model because the rigid-body approach is not included in the CIF dictionary. Therefore, refinement of the structure model included in the CIF would bring back our free atomic model with different molecular geometries for *A* and *B*. As a logical step, we constructed another rigid-body model with three positions for the model molecule, including configurations *A* and *B* of *M*2, and nondisordered molecule *M*1. Refinement of this structure model had 71 parameters and converged with R_{obs} = 0.054; the largest difference-map residuals were 0.43 and −0.32 e Å^{-3}. Taking into account the considerably lower number of parameters, we could conclude that all molecules of (I) have almost the same geometry within the resolution of our diffraction experiment. However, the increase in the *R* value of the last structure model by 0.014 cannot be ignored, and some slight differences in geometry between *M*1 and *M*2 cannot be excluded. Thus, we took as the final structure model the one with independently refined *M*1 and *M*2 molecules, where the disordered positions for *M*2 are based on the translated and rotated positions obtained from the refinement of a common model molecule.

X-ray crystallography reveals a nearly planar structure for the N atom in the heterocyclic five-membered ring in both molecules *M*1 and *M*2, where the sums of the internal bond angles around the N atoms are 360.08 (10) and 360.0 (2)°, respectively. The presence of planar N atoms in all fused five-membered rings imposes some conformational rigidity on these molecules, which is evident from the values of the relevant torsion angles for *M*1 [C1—N1—N2—O1 = −3.4 (2)°, C2—N1—C1—N1^{i} = 13.72 (12)°, C1—N1—C2—C2^{i} = −34.46 (16)° and N1—C2—C2^{i}—N1^{i} = 38.92 (17)°] and the puckering parameters Q = 0.376 (2) Å and φ = 126.0 (3)° (Cremer & Pople, 1975). These values indicate that the N1—C1—N1^{i}—C2—C2^{i} five-membered ring adopts a conformation that is significantly deformed (twisted on the C2—C2^{i} bond), with the C atoms oriented *endo* and *exo* with respect to the reference plane defined by atoms N1, C1 and N1^{i} [symmetry code: (ii) $-x+2, y, -z+\frac{3}{2}$]. This orientation is very close to a half-chair conformation. Analogously, the disordered molecule (*M*2) shows puckering parameters and torsion angles that indicate a conformation twisted around the C6—C6^{ii} bond [symmetry code: (ii) $-x+1, y, -z+\frac{1}{2}$]. In addition, the N—NO moieties are nearly coplanar with the imidazolidine rings. The dihedral angles between the planes defined by atoms O1/N1/N2 and N1/C1/N1^{i} and between the planes defined by atoms O2/N3/N4 and N3/C5/N3^{ii} are 13.84 (13) and 15.2 (3)°, respectively.

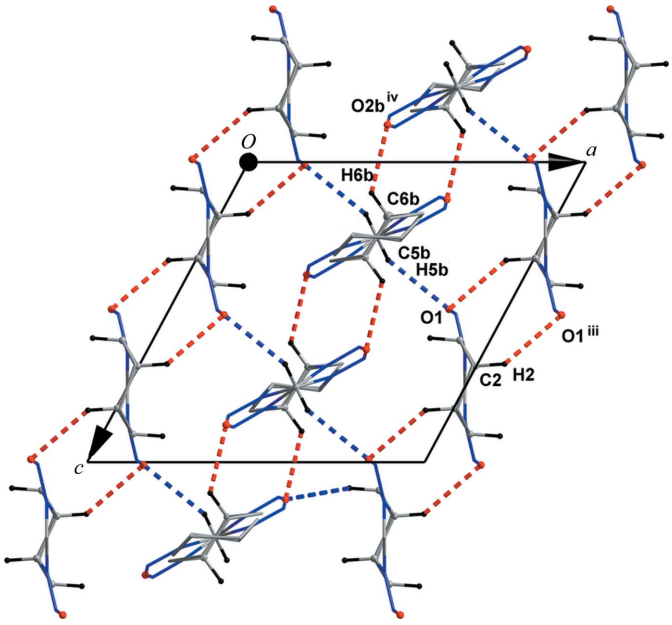

Figure 2
The packing of the molecules of (I), viewed along the *b* axis. Hydrogen bonds are drawn as dashed lines (in the electronic version of the journal, blue dashed lines indicate weak inter-chain hydrogen bonds). Only H atoms participating in hydrogen bonds are shown. [Symmetry codes: (iii) $-x+2, y+1, -z+1$; (iv) $-x+1, -y+1, -z$.]

The geometry of the N—NO group in *M*1 is similar to that observed in related compounds (Simonov *et al.*, 2005), as is evident from the O1—N2 bond length of 1.2482 (18) Å, which is between a double (1.13 Å) and single bond (1.49 Å) (Hartung *et al.*, 1996). This type of structure has been observed in other *N*-nitrosoamines (Simonov *et al.*, 2005) where it was associated with the possibility of conjugation and redistribution of the electron density, in contradiction with the representation shown in the Scheme. In contrast, the geometric parameters in *M*2 (*M*2*A* and *M*2*B* have identical geometry because of the constraints used in the refinement, as described above) fall within the mean for N—O bond distances (Simonov *et al.*, 2005). The N4*A*—O2*A* distance of 1.266 (3) Å in *M*2 is slightly longer than that in *M*1. The fused six-membered ring for *M*2*A* (C6*A*/C7*A*/C8*A*/C8*A*^{ii}/C7*A*^{ii}/C6*A*^{ii}) exhibits a chair conformation, with puckering parameters Q = 0.571 (3) Å, θ = 172.7 (3)° and φ = 150 (2)°, and the bond lengths and angles are distorted with respect to the normal bond values for an ideal chair conformation of a cyclohexane ring (1.528 Å and 111.1°, respectively; Geise *et al.*, 1971). Furthermore, the C—C bonds shared by the two rings and their vicinal C—C bonds are shorter than the other C—C distances in the cyclohexyl ring. The shortening of these bonds might be attributed to the polarization effect of the N—NO group. By comparison, the six-membered ring of *M*1 (C2/C3/C4/C2^{i}/C3^{i}/C4^{i}) adopts a chair conformation, with puckering parameters Q = 0.608 (2) Å, θ = 172.90 (3)° and φ = 150.0 (15)°.

In the crystal structure of (I) (Fig. 2), C—H···O hydrogen bonds involving the methine groups of the fused rings link adjacent molecules of the same independent type into centrosymmetric dimers which then extend, by virtue of the molecular twofold symmetry, into extended chains propagating along the *c* axis. In addition, the chains of *M*1 and *M*2 molecules are crosslinked by another weak intermolecular C—H···O hydrogen bond (Table 2). Atom C5 acts as a hydrogen-bond donor to atom O1, producing a chain running parallel to the [101] direction. It is interesting to compare the hydrogen-bond pattern of the nondisordered molecule (*M*1) with that of the disordered molecule (*M*2). In *M*1, where the cyclohexane ring does not exhibit molecular disorder, two intermolecular hydrogen bonds link the molecules to their *M*1 neighbours and should be structurally important. For the disordered molecule, only one intermolecular hydrogen bond is significant, and bonding between adjacent chains is very weak.

We believe that the differences in the geometric parameters and hydrogen-bond geometry between *M*1 and *M*2 might be rationalized in terms of electronic delocalization of the N—NO moiety and/or dipole interactions (Abraham *et al.*, 1972). To provide more relevant data for this theory, quantum chemical calculations were performed on the isolated atomic coordinates derived from the X-ray diffraction experiment to obtain optimized structural parameters. For both structures, full optimizations using *ab initio* Hartree–Fock (HF) and density functional theory with the 6-31G** basis set were performed using the *GAUSSIAN98* program package (Frisch *et al.*, 1998). The results for both methods show that both molecules converge to the same minimum. Selected optimized bond lengths and angles are given in Table 1 for comparison with the X-ray crystallographic data. The largest differences are for the nondisordered molecule (*M*1), suggesting that the computed geometric parameters are in closer agreement with the disordered molecule (*M*2).

Experimental

A solution in ethanol and water (1:1 *v*/*v*, 5 ml) of the aminal (2*R*,7*R*,11*S*,16*S*)-1,8,10,17-tetraazapentacyclo[8.8.1.1^{8,17}.0^{2,7}.0^{11,16}]-icosane, (2) (407 mg, 1.48 mmol), prepared beforehand following a previously described procedure (Glister *et al.*, 2005), was cooled to 283 K using an ice–water bath. The solution was treated with sodium nitrite (450 mg, 6.50 mmol) and concentrated hydrochloric acid was added dropwise until a pH value of 3 was obtained. The mixture was stirred for 15 min until precipitation of a colourless solid occurred. The resulting solid was collected by filtration and recrystallized from propan-2-ol (yield 70%, m.p. 413–415 K). Single crystals of racemic (I) were grown from a propan-2-ol solution by slow evaporation of the solvent at room temperature over a period of about two weeks.

Crystal data

$C_7H_{12}N_4O_2$
M_r = 184.2
Monoclinic, $P2/c$
a = 10.8128 (8) Å
b = 8.4293 (4) Å
c = 10.9321 (9) Å
β = 118.192 (8)°
V = 878.20 (12) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 0.88 mm^{-1}
T = 120 K
0.37 × 0.18 × 0.07 mm

Table 1
Comparison of the experimental and optimized geometric parameters of molecules *M*1 and *M*2 (Å, °).

DFT denotes density functional theory and HF denotes Hartree–Fock theory. The geometries of *M*2*A* and *M*2*B* were constrained to be identical.

*M*1/*M*2	*M*1	*M*2	DFT, 6-31G(dp)	HF, 6-31G(dp)
N2—O1/N4—O2	1.2482 (18)	1.266 (3)	1.231	1.182
N2—N1/N4—N3	1.3014 (17)	1.299 (5)	1.327	1.304
N1—C1/N3—C5	1.4583 (13)	1.462 (2)	1.468	1.459
N1—C2/N3—C6	1.4746 (18)	1.465 (3)	1.463	1.455
C2—C3/C6—C7	1.513 (2)	1.505 (4)	1.521	1.517
C2—C2^{i}/C6—C6^{ii}	1.510 (3)	1.507 (4)	1.533	1.517
C3—C4/C7—C8	1.534 (2)	1.528 (4)	1.547	1.541
C4—C4^{i}/C8—C8^{ii}	1.522 (3)	1.535 (4)	1.546	1.540
O1—N2—N1/O2—N4—N3	113.73 (12)	113.6 (4)	113.85	115.27
N2—N1—C1/N4—N3—C5	124.21 (10)	124.2 (2)	124.23	122.14
N2—N1—C2/N4—N3—C6	124.42 (12)	124.2 (2)	123.99	120.97
C1—N1—C2/C5—N3—C6	111.35 (9)	111.60 (15)	111.78	111.28
C3—C2—C2^{i}/C7—C6—C6^{ii}	110.62 (16)	112.0 (2)	110.84	110.72
C2—C3—C4/C6—C7—C8	105.76 (12)	106.9 (3)	106.64	106.80
C3—C4—C4^{i}/C7—C8—C8^{ii}	113.30 (17)	114.1 (2)	113.77	113.55

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

Data collection

Agilent Xcalibur diffractometer with an Atlas (Gemini Ultra Cu) detector
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)
T_{min} = 0.549, T_{max} = 1.000
6725 measured reflections
1376 independent reflections
1163 reflections with $I > 3\sigma(I)$
R_{int} = 0.024
θ_{max} = 62.2°

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.115
S = 1.92
1376 reflections
122 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

H atoms were positioned geometrically and kept in ideal positions during the refinement, with C—H = 0.96 Å and U_{iso}(H) = 1.2U_{eq}(parent). One of the molecules is disordered and its atoms are divided over two sites [occupancy ratio = 0.747 (3):0.253 (3)]. In order to describe the disordered molecule, orientational disorder of the complete *M*2 molecule as a rigid body was applied; see *Comment* for details.

Data collection: *CrysAlis PRO* (Agilent, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *JANA2006*.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1^{i}	0.96	2.47	3.244 (3)	137.15
C5*B*—H5*B*···O1	0.96	2.48	3.3213 (15)	146.93
C6*B*—H6*B*···O2*B*^{ii}	0.96	2.38	3.111 (4)	132.53

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+1, -y+1, -z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: UK3034). Services for accessing these data are described at the back of the journal.

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