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gem-Chloronitrosocyclododecane, $(CH_2)_{n-1}CNOCl$, with $n = 12$

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Key indicators

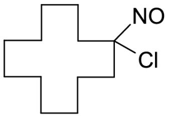
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.054
wR factor = 0.155
Data-to-parameter ratio = 18.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{12}H_{22}ClNO$, adopts the square conformation [3333] observed in other known saturated twelve-membered rings. Disorder is observed, resulting from exchange of the chloro and nitroso substituents.

Comment

gem-Chloronitroso compounds are used in organic syntheses and mechanistic studies, particularly as precursors of aliphatic nitro derivatives (Marchand & Suri, 1984; Marchand *et al.*, 1988) and of vicinal dinitro compounds (Wade *et al.*, 1987; Paquette *et al.*, 1988).



(I)

The molecular structure of the title compound, (I), is shown in Fig. 1. The torsion angles (Table 1) indicate that the cyclododecane ring is in a square conformation [3333], as in other saturated twelve-membered rings reported previously (Groth, 1979*a*,*b*, 1980). Although the skeleton of the cyclododecane ring does not exhibit any observable disorder, the chloro and nitroso groups are disordered (Fig. 2). There are two possible orientations, Cl1/N1/O1 and Cl2/N2/O2, each with 50% occupancy. This can be explained as an orientational

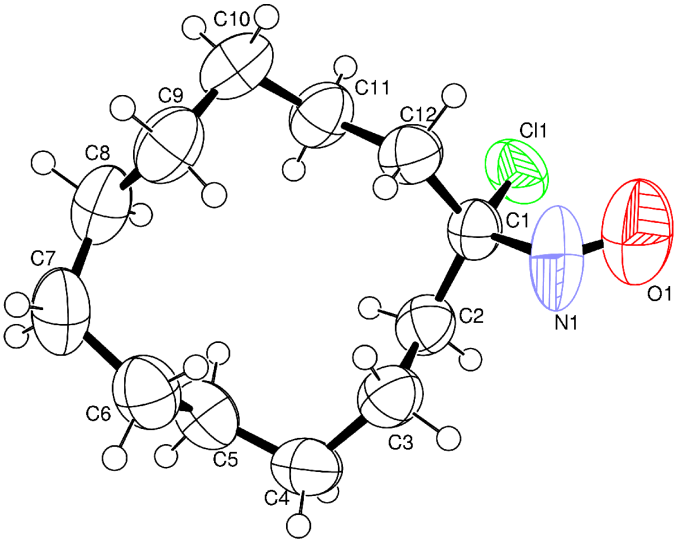


Figure 1
Molecular structure of (I), showing 50% probability displacement ellipsoids. Only one orientation of the disordered chloro and nitroso groups is shown.

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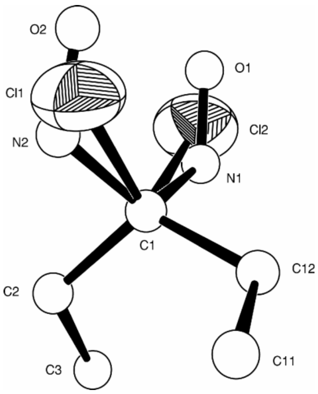

Figure 2
The disorder of the chloro and nitroso groups.

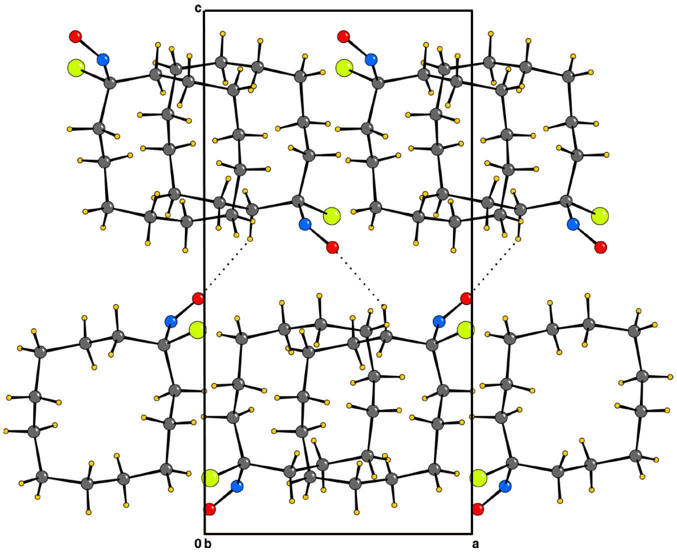

Figure 3
Crystal structure of (I), viewed down the *b* axis. Dotted lines indicate H bonds.

disorder of the molecule around the local pseudo-twofold axis passing through atoms C1 and C7, exchanging the two substituents. Fig. 3 shows the packing of the molecules, which is stabilized by C—H⋯O interactions (Table 2) and van der Waals forces.

Experimental

The title compound, (I), was synthesized by a reported procedure (Karim, 2003). In a 100 ml two-necked flask, 10 mmol of cyclododecanoneoxime in 10 ml of dry diethyl ether was cooled to 263 K in an ice–salt bath; chlorotrimethylsilane (12 mmol) was introduced through a dropping funnel. The mixture was stirred magnetically, and isoamyl nitrite (12 mmol) was slowly introduced through a dropping funnel over 15 min. The reaction mixture was left to stir for 1.5 h. Water (10 ml) was added. The organic layer, after separation, was washed with water (20 ml) twice and dried over Na_2SO_4. The solvent was removed on a rotary evaporator under reduced pressure, and the residue was chromatographed on silica gel (60–120 mesh). Elution with petroleum ether (b.p. 313–333 K) moved down a blue band, which was identified as (I). Single crystals of (I) were grown from a chloroform solution by slow evaporation.

Crystal data

$C_{12}H_{22}ClNO$
$M_r = 231.76$
Orthorhombic, $P2_12_12_1$
$a = 8.3801\ (19)$ Å
$b = 9.543\ (2)$ Å
$c = 16.348\ (4)$ Å
$V = 1307.4\ (5)$ Å^3
$Z = 4$
$D_x = 1.177$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 600 reflections
$\theta = 2.5$–$28.1°$
$\mu = 0.27$ mm^{-1}
$T = 293\ (2)$ K
Block, blue
0.30 × 0.20 × 0.15 mm

Data collection

Bruker SMART APEX diffractometer
φ–ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.821$, $T_{max} = 0.960$
11 518 measured reflections

3072 independent reflections
1998 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 28.1°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 11$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.155$
$S = 0.95$
3072 reflections
163 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0985P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}
Absolute structure: Flack (1983), 1239 Friedel pairs
Flack parameter = 0.00 (10)

Table 1
Selected torsion angles (°).

C12—C1—C2—C3	−62.1 (3)	C6—C7—C8—C9	−63.5 (3)
C1—C2—C3—C4	156.64 (19)	C7—C8—C9—C10	158.4 (2)
C2—C3—C4—C5	−74.4 (3)	C8—C9—C10—C11	−72.5 (3)
C3—C4—C5—C6	−73.1 (3)	C9—C10—C11—C12	−74.4 (3)
C4—C5—C6—C7	162.5 (2)	C10—C11—C12—C1	161.1 (2)
C5—C6—C7—C8	−64.3 (3)	C2—C1—C12—C11	−64.1 (3)

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C2—H2*B*⋯O1^i	0.97	2.69	3.533 (8)	145
C3—H3*B*⋯O2^i	0.97	2.71	3.467 (8)	135
C4—H4*A*⋯O2^{ii}	0.97	2.91	3.511 (8)	121

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

The chloro and nitroso groups show disorder and there are two possible orientations, Cl1/N1/O1 and Cl2/N2/O2, each with 50% occupancy. Fitting the light atoms of the nitroso group near the heavier Cl atom yielded large displacement parameters. Restraints were applied for C—N and N—O bond distances to give reasonable values. The N and O atoms were refined anisotropically with restraints for approximate isotropy. H atoms were positioned geometrically and treated as riding, with C—H distances of 0.97 Å and $U_{iso}(H) = 1.2U_{eq}$(parent).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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