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5-Chloro-6-nitroso-2-norbornene dimer as a motif for supramolecular assembly

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The title compound, 1,2-bis(5-chloronorbornen-6-yl)diazene 1,2-dioxide, $C_{14}H_{16}Cl_2N_2O_2$, has a crystallographic centre of symmetry. The norbornane cages are *trans*-oriented and the nitroso groups are in positions 3 and 6. This compound might be used as a starting point for the construction of two different polymeric structures due to the photochromism observed in the solid state.

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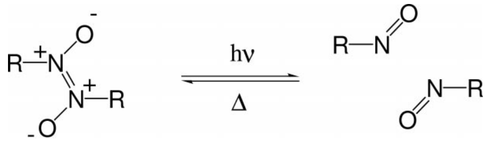
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.030
wR factor = 0.083
Data-to-parameter ratio = 10.3

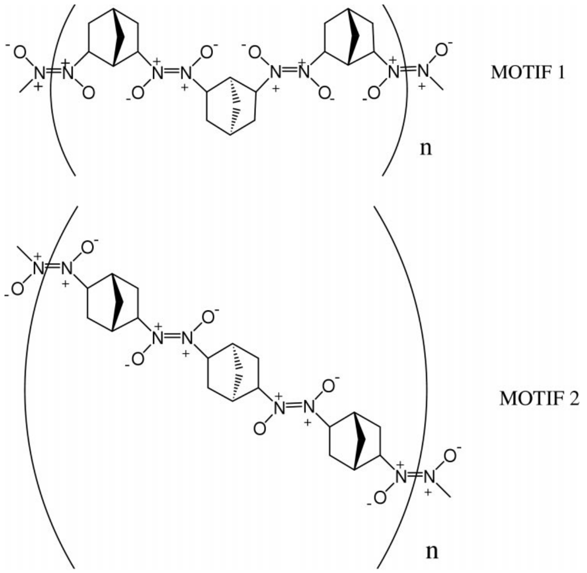
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Recently, we found that the monomer–dimer equilibrium of C-nitroso compounds could be used as a system for supramolecular self-assembly (see below, monomer–dimer equilibrium of C-nitroso compounds), because the azodioxide dimer affords photochromism in the solid state (Vančik *et al.*, 2001). Basic nitroso monomeric units convenient for the construction of supramolecular structures should have a rigid carbon skeleton with two azo groups which serve as chemical receptors oriented in proper spatial positions.



Here we propose the polymeric structures that may have nitroso groups on 2- and 6- (MOTIF 1) or on 3- and 6- (MOTIF 2) positions of the norbornane skeleton.



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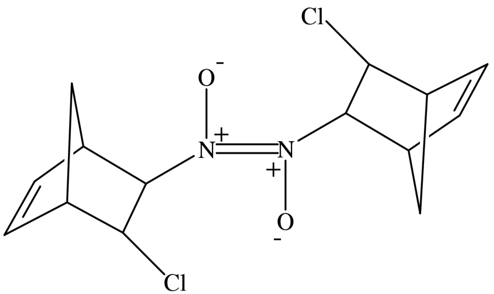
Possibilities of such structures depend on the stereochemistry of the basic motif, such as the title structure, (I) (see below), which has only one azodioxide group. The C═C double bond on each norbornene unit is a functionality on which additional nitroso groups, necessary for the polymer formation, could be added.



(I)

The inversion centre is located at the midpoint of the N═N bond which connects two monomeric units into the dimer structure (Fig. 1). The norbornene cages are *trans*-oriented.

Experimental

The title compound was prepared by direct addition of NOCl to norbornadiene (Ciattoni *et al.*, 1964; Metzger & Meier, 1971, 1990; Miller, 1961). Crystals of (I) were obtained by evaporation from a dichloromethane solution containing a few drops of tetrahydrofuran at 277 K.

Crystal data

$C_{14}H_{16}Cl_2N_2O_2$
$M_r = 315.19$
Monoclinic, $P2_1/n$
$a = 5.9247 (7)$ Å
$b = 13.5925 (11)$ Å
$c = 8.3407 (7)$ Å
$\beta = 95.452 (8)^\circ$
$V = 668.7 (7)$ Å^3
$Z = 2$

$D_x = 1.565$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 18.5–25.3^\circ$
$\mu = 0.49$ mm^{-1}
$T = 100 (5)$ K
Prism, colourless
0.18 × 0.16 × 0.12 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.920$, $T_{\max} = 0.968$
1527 measured reflections
1364 independent reflections
1076 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.025$
$\theta_{\max} = 26.3^\circ$
$h = -7 \rightarrow 7$
$k = -16 \rightarrow 0$
$l = 0 \rightarrow 10$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > (F^2)] = 0.030$
$wR(F^2) = 0.083$
$S = 1.02$
1364 reflections
132 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.40P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.011$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0055 (12)

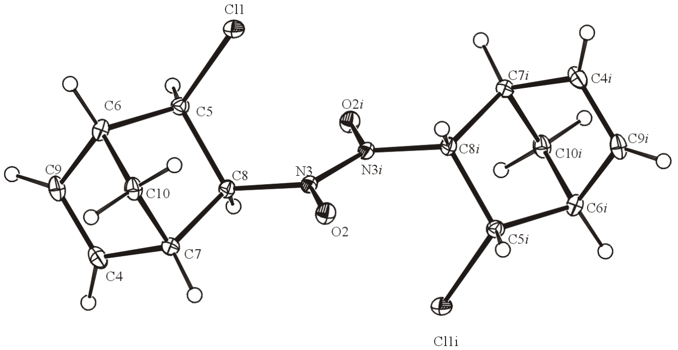


Figure 1
An *ORTEP*II (Johnson, 1976) drawing of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 1
Selected geometric parameters (Å, °).

Cl1—C5	1.796 (2)	N3—C8	1.481 (2)
O2—N3	1.268 (2)	N3—N3$^{\rm i}$	1.315 (2)
O2—N3—C8	123.01 (14)	Cl1—C5—C8	112.90 (11)
O2—N3—N3$^{\rm i}$	120.92 (10)	N3—C8—C5	113.24 (15)
N3$^{\rm i}$—N3—C8	116.02 (12)	N3—C8—C7	111.39 (14)
Cl1—C5—C6	110.55 (12)		

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

All H-atom positional and $U_{\rm iso}$ parameters were refined. C—H bond lengths lie between 0.91 (2) and 0.99 (2) Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *SET*4 and *CELDIM* in *CAD*-4 *Software* (Enraf–Nonius, 1989); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *PLATON* (Spek, 1990).

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