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# 1,4-Bis[chloro(hydroxyimino)methyl]benzene *N*,*N*′-dimethylformamide disolvate

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**Key indicators**

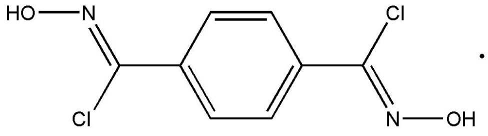
Single-crystal X-ray study
$T$ = 294 K
Mean $\sigma$(C–C) = 0.003 Å
$R$ factor = 0.040
$wR$ factor = 0.104
Data-to-parameter ratio = 16.1

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

The structure of the centrosymmetric title compound, $C_8H_6Cl_2N_2O_2 \cdot 2C_3H_7NO$, shows that the hydroximoyl chloride substituent has an essentially planar arrangement and the dihedral angle between this plane and the benzene plane is 18.3 (4)°. The hydroximoyl chloride group has a *cis* configuration. The packing can be described as a polymeric arrangement of molecules linked through O—H···O hydrogen bonds.

## Comment

For many years, nitrile oxides have contributed significantly to modern organic synthesis in the field o 1,3-dipolar compounds (Kozikowski, 1984; Kanemasa & Tsuge, 1990), since they readily undergo a variety of 1,3-dipolar cycloaddition reactions. One of the most common methods for the generation of nitrile oxides is dehydrohalogenation of hydroximoyl halides (Kim *et al.*, 1993; Kim & Ryu, 1993). Hence, hydroximoyl chlorides are precursors of nitrile oxides and have received much attention. In this paper, the structure of the title compound, (I), is reported.



$\cdot 2C_3H_7NO$

(I)

The centrosymmetric structure of (I) is illustrated in Fig. 1. The bond lengths and angles have normal values, except for those of the hydroximoyl chloride group (Table 1). The C1—N1 bond length of 1.266 (3) Å is much shorter than the typical C═N bond distance and is also shorter than the oxime C—N distance (Luck & Mendenhall, 2000; Kedziorek *et al.*, 2003; Soylu *et al.*, 2004). The N1—O1 bond length of 1.387 (2) Å is slightly longer than that of 2,6-dimethyl-1,4-benzoquinone 4-monooxime (Odabasoglu *et al.*, 2005). The Cl—C bond lengths are in the range 1.732 (6)–1.746 (7) Å, in agreement with values reported in the literature (Busetti *et al.*, 1980; Sutherland & Ali-Adib, 1987). The O1—N1—C1—Cl1 torsion angle of −0.8 (3)° describes a *cis* configuration of the molecule about the C1—N1 bond. The hydroximoyl chloride substituent (C1/Cl1/N1/O1) has an essentially planar arrangement, with a mean deviation of 0.003 (2) Å, and the dihedral angle between this plane and the benzene plane is 18.3 (4)°. The dimethylformamide (DMF) molecule is approximately planar [within 0.006 (3) Å, excluding H atoms]. This plane makes dihedral angles of 13.8 (4) and 9.2 (3)° with the hydroximoyl chloride group and the benzene ring, respectively. The packing

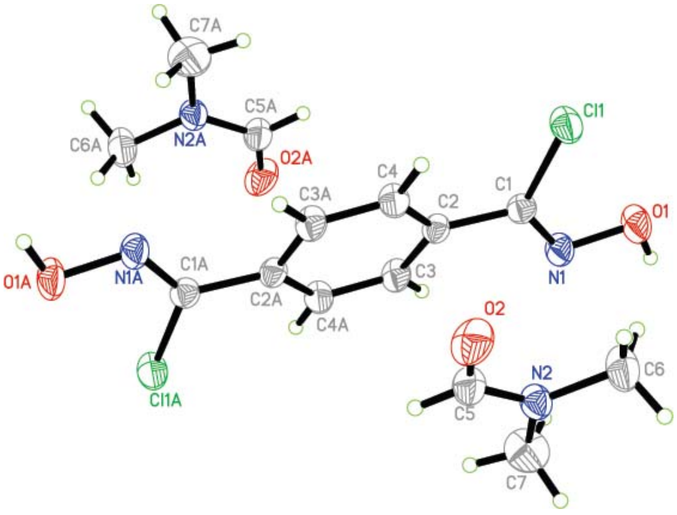


**Figure 1**
The molecular structure of (I) drawn with 30% probability ellipsoids. Atoms with the suffix A are generated by the symmetry code $(2 - x, 1 - y, 2 - z)$.

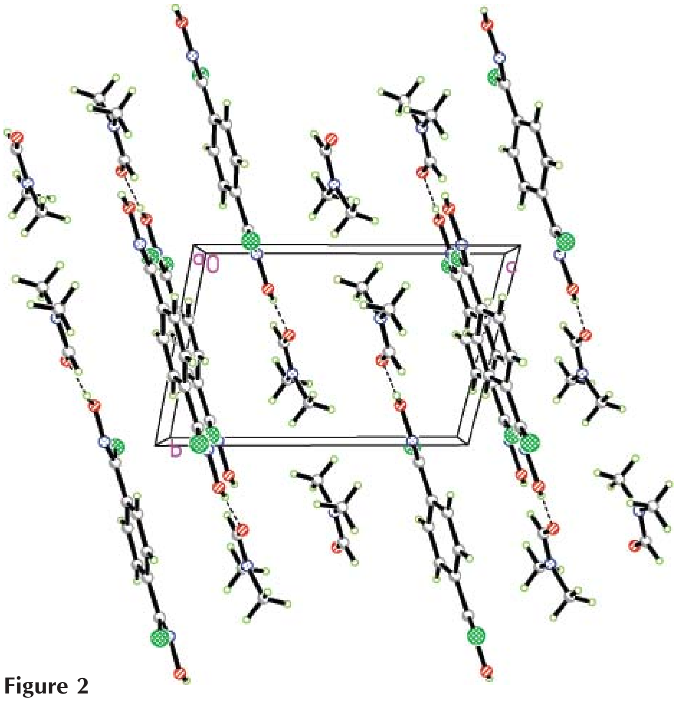


**Figure 2**
The crystal structure of (I), viewed along the *a* axis. Dashed lines indicate hydrogen bonds.

can be described as a polymeric arrangement of molecules linked through O—H···O hydrogen bonds (Fig. 2 and Table 2); atom O1 of the hydroximoyl chloride group acts as a hydrogen-bond donor and atom O2 atom of DMF at $(x, y - 1, z)$ acts as an acceptor.

## Experimental

Hydroxylamine hydrochloride (3.0 mmol) in water (6.0 ml) was added dropwise to terephthalaldehyde (1.0 mmol) in ethanol (6.0 ml). The mixture was stirred for 30 min, then cooled and $Na_2CO_3$ (1.0 ml, 1.0 *M*) was added dropwise. After the addition was complete, the reaction mixture was stirred for an additional 1 h, then diluted with water (50 ml). The precipitate was filtered and washed with water to give the 1,4-benzenedialdoxime. *N*-Chlorosuccinimide (1.1 mmol) was added to the stirred oxime (1.0 mmol) in dimethylformamide at 298 K. After 30 min, the mixture was cooled (ice bath) and then diluted with water (50 ml). The precipitate was filtered off and washed with water to give compound (I). $^1H$ NMR ($CDCl_3$): δ 7.90 (*s*, 4H), 9.13 (*s*, 2H). Single crystals of (I) suitable for X-ray analysis were obtained by recrystallization from a DMF solution.

### *Crystal data*

$C_8H_6Cl_2N_2O_2 \cdot 2C_3H_7NO$
$M_r = 379.24$
Triclinic, $P\overline{1}$
$a = 6.2021$ (18) Å
$b = 7.600$ (2) Å
$c = 10.849$ (3) Å
$\alpha = 100.589$ (4)°
$\beta = 92.777$ (5)°
$\gamma = 113.518$ (4)°
$V = 456.7$ (2) Å$^3$
$Z = 1$
$D_x = 1.379$ Mg m$^{-3}$
Mo *K*α radiation
Cell parameters from 1128 reflections
$\theta = 3.2$–25.6°
$\mu = 0.38$ mm$^{-1}$
$T = 294$ (2) K
Block, colorless
0.40 × 0.26 × 0.22 mm

### *Data collection*

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.843$, $T_{max} = 0.920$
2599 measured reflections
1856 independent reflections
1373 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 26.4°$
$h = -7 \rightarrow 6$
$k = -8 \rightarrow 9$
$l = -13 \rightarrow 11$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.104$
$S = 1.04$
1856 reflections
115 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.1801P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å$^{-3}$
$\Delta\rho_{min} = -0.23$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cl1—C1 | 1.740 (2) | N1—O1 | 1.387 (2) |
| N1—C1 | 1.266 (3) | C1—C2 | 1.477 (3) |
| | | | |
| C1—N1—O1 | 113.36 (18) | N1—C1—Cl1 | 122.12 (17) |
| N1—C1—C2 | 120.19 (19) | C2—C1—Cl1 | 117.69 (15) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···O2$^{i}$ | 0.86 (3) | 1.79 (3) | 2.609 (2) | 159 (3) |

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

The H atom bonded to the O atom was refined isotropically. All other H atoms were positioned geometrically, with C—H = 0.93–0.98 Å, and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve

*Acta Cryst.* (2005). E**61**, o1970–o1972 Liu *et al.* • $C_8H_6Cl_2N_2O_2 \cdot 2C_3H_7NO$ **o1971**

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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