organic compounds

(E)-Methyl 2,6-dichloro-N-cyano-benzimidate

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The molecule of the title compound, $C_9H_6Cl_2N_2O$, displays an E conformation about the C=N double bond. The N-cyanoimidate fragment is substantially planar [maximum deviation 0.010 (4) Å] and perpendicular to the benzene ring [dihedral angle = 88.50 (14)°]. In the crystal packing, intermolecular Cl···Cl interactions [3.490 (2) Å] are observed.

Related literature

For the synthesis of substituted cyanoimidates, see: Huffman & Schaefer (1963). For the crystal structures of compounds containing the N-cyanoimidate fragment, see: Zöllinger et al. (2006); Ponomareva et al. (1995); Jäger et al. (1996). For details of halogen···halogen interactions, see: Desiraju & Parthasarathy (1989).
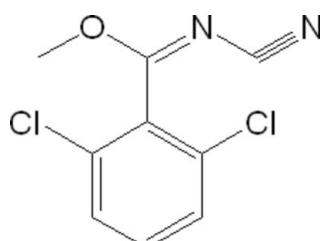
Experimental

Crystal data

$C_9H_6Cl_2N_2O$	V = 2128.2 (16) Å^3
M_r = 229.06	Z = 8
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
a = 21.199 (4) Å	μ = 0.58 mm^{-1}
b = 8.548 (3) Å	T = 291 K
c = 15.005 (4) Å	0.52 × 0.46 × 0.28 mm
β = 128.49 (4)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	1948 independent reflections
Absorption correction: spherical (WinGX; Farrugia, 1999)	1167 reflections with $I > 2\sigma(I)$
	R_{int} = 0.016
T_{min} = 0.754, T_{max} = 0.855	3 standard reflections
2116 measured reflections	every 120 reflections
	intensity decay: 3.8%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054	129 parameters
$wR(F^2)$ = 0.170	H-atom parameters constrained
S = 1.04	$\Delta\rho_{max}$ = 0.30 e Å^{-3}
1948 reflections	$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Data collection: DIFRAC (Gabe & White, 1993); cell refinement: DIFRAC; data reduction: NRCVAX (Gabe et al., 1989); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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supporting information

(*E*)-Methyl 2,6-dichloro-*N*-cyanobenzimidate

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S1. Comment

In the course of our studies aimed to prepare substituted cyanoimidates (Huffman & Schaefer, 1963) from the corresponding aromatic aldehyde by oxidation using 1-bromopyrrolidine-2,5-dione, the title compound was obtained in 84% yield, and its crystal structure is reported herein.

The molecule of the title compound (Fig. 1) displays an *E* conformation about the C═N double bond. The O—C═N—C≡N *N*-cyanoimidate fragment is substantially planar [maximum deviation 0.010 (4) Å for atom N2] and forms a dihedral angle of 88.50 (14)° with the plane of the benzene ring. As far as the authors are aware, crystal structures reporting the presence of the *N*-cyanoimidate fragment are very rare, the only examples found in the literature being 1-(2,3-dibromo-10-oxo-7,8-dihydro-6H,10H-dipyrrolo[1,2-a:1′,2′-d]pyrazin-5-yl)-2-(2,6-dimethylphenyl)-3-cyanoisourea monohydrate (Zöllinger *et al.*, 2006), *catena*-poly-[(*μ*⁶-benzoylcyanamido)-thallium(I)] (Ponomareva *et al.*, 1995) and tris(ethylenediamine)-nickel(II) bis[2-methyl-4-chlorophenoxy(cyanamido)acetate] (Jäger *et al.*, 1996). In the crystal structure, molecules are connected by intermolecular Cl···Cl interactions of 3.490 (2) Å (Desiraju & Parthasarathy, 1989) into one-dimensional chains running parallel to [101].

S2. Experimental

A mixture of 2,6-dichlorobenzaldehyde (1 mmol), H_2NCN (3 equiv) and t-BuONa (3 equiv) in MeOH (8 ml) was stirred for 30 min at room temperature, then N-bromosuccinimide (NBS; 3 equiv) was added. After stirring for 12 h at 323 K, the mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1–25:1 *v/v*) as eluent to give the title compound in 84% yield. Colourless crystals suitable for X-ray analysis were obtained by slow evaporation of a petroleum ether/acetyl acetate solution (25:1 *v/v*) at room temperature.

S3. Refinement

H atoms were positioned geometrically (C—H = 0.93–0.96 Å) and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl H atoms.
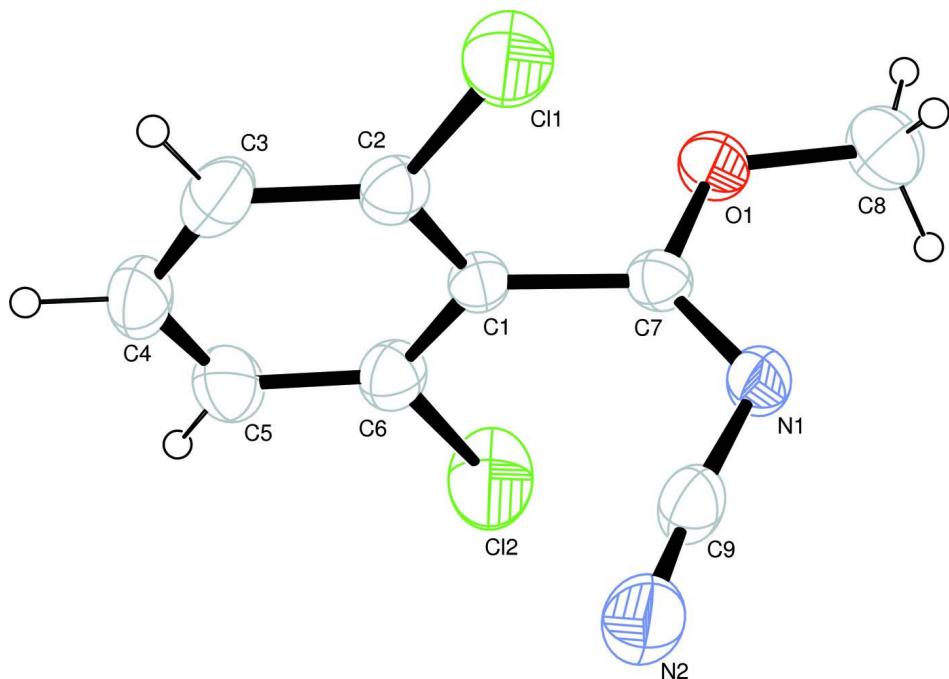
Figure 1

The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.
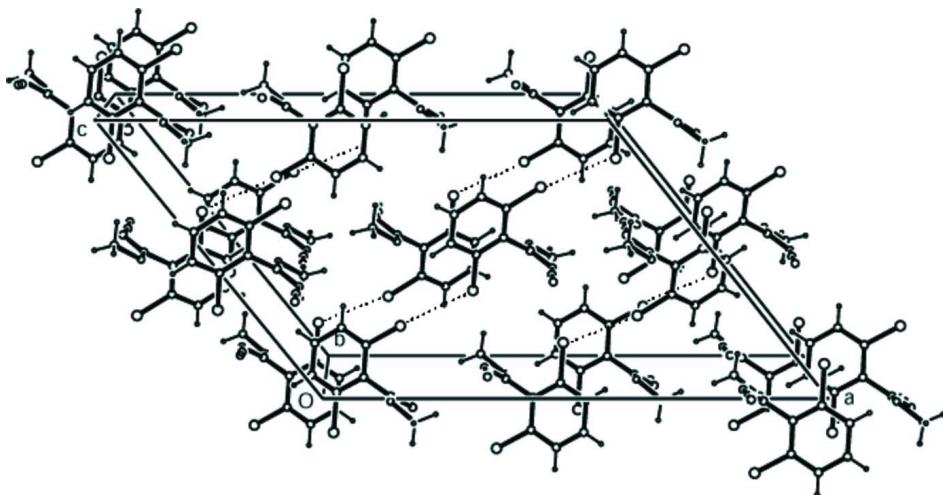
Figure 2

Crystal packing of the title compound approximately viewed along the *b* axis. Cl···Cl interactions are shown as dotted lines.

(*E*)-Methyl 2,6-dichloro-*N*-cyanobenzimidate

Crystal data

$C_9H_6Cl_2N_2O$	$b = 8.548$ (3) Å
$M_r = 229.06$	$c = 15.005$ (4) Å
Monoclinic, *C*2/*c*	$\beta = 128.49$ (4)°
Hall symbol: -C 2yc	$V = 2128.2$ (16) Å^3
$a = 21.199$ (4) Å	$Z = 8$

$F(000) = 928$

$D_x = 1.430$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 28 reflections

$\theta = 4.8–9.2°$

$\mu = 0.58$ mm^{-1}

$T = 291$ K

Block, colourless

$0.52 \times 0.46 \times 0.28$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega/2\theta$ scans

Absorption correction: for a sphere (*WinGX*; Farrugia, 1999)

$T_{min} = 0.754$, $T_{max} = 0.855$

2116 measured reflections

1948 independent reflections

1167 reflections with $I > 2\sigma(I)$

$R_{int} = 0.016$

$\theta_{max} = 25.5°$, $\theta_{min} = 2.5°$

$h = -25\rightarrow17$

$k = 0\rightarrow10$

$l = -18\rightarrow18$

3 standard reflections every 120 reflections

intensity decay: 3.8%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.170$

$S = 1.04$

1948 reflections

129 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1053P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.30$ e Å^{-3}

$\Delta\rho_{min} = -0.32$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$

Extinction coefficient: 0.0069 (15)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.54862 (5)	0.67130 (14)	0.65350 (8)	0.0881 (5)
Cl2	0.24528 (6)	0.72469 (18)	0.26898 (9)	0.1121 (6)
O1	0.36902 (14)	0.4760 (2)	0.5066 (2)	0.0672 (7)
N1	0.35148 (15)	0.7020 (3)	0.5663 (2)	0.0563 (7)
N2	0.3600 (2)	0.9913 (4)	0.5784 (3)	0.0866 (10)
C1	0.40050 (16)	0.7037 (3)	0.4547 (2)	0.0472 (7)
C2	0.48117 (18)	0.7300 (3)	0.5135 (3)	0.0545 (8)
C3	0.5094 (2)	0.8077 (4)	0.4632 (3)	0.0675 (9)
H3	0.5642	0.8259	0.5039	0.081*

C4	0.4550 (3)	0.8571 (4)	0.3523 (3)	0.0745 (10)
H4	0.4735	0.9086	0.3179	0.089*
C5	0.3742 (2)	0.8318 (4)	0.2917 (3)	0.0750 (10)
H5	0.3379	0.8664	0.2169	0.090*
C6	0.3471 (2)	0.7542 (4)	0.3432 (3)	0.0613 (9)
C7	0.37157 (16)	0.6295 (3)	0.5129 (2)	0.0486 (7)
C8	0.3474 (3)	0.3932 (4)	0.5685 (4)	0.0930 (13)
H8A	0.3881	0.4102	0.6487	0.139*
H8B	0.3433	0.2833	0.5525	0.139*
H8C	0.2966	0.4312	0.5453	0.139*
C9	0.3568 (2)	0.8581 (4)	0.5699 (3)	0.0619 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0583 (5)	0.1217 (9)	0.0646 (6)	0.0019 (5)	0.0285 (5)	0.0127 (5)
Cl2	0.0589 (6)	0.1721 (13)	0.0731 (7)	−0.0024 (6)	0.0252 (5)	0.0231 (7)
O1	0.0903 (16)	0.0367 (12)	0.0958 (17)	0.0011 (10)	0.0684 (15)	0.0009 (10)
N1	0.0733 (17)	0.0436 (14)	0.0707 (16)	−0.0010 (11)	0.0540 (15)	0.0000 (11)
N2	0.129 (3)	0.0544 (18)	0.122 (3)	−0.0121 (17)	0.100 (3)	−0.0177 (17)
C1	0.0566 (16)	0.0401 (14)	0.0550 (16)	0.0025 (12)	0.0397 (14)	−0.0008 (12)
C2	0.0587 (17)	0.0537 (17)	0.0574 (17)	0.0016 (13)	0.0393 (15)	−0.0039 (13)
C3	0.0639 (19)	0.070 (2)	0.087 (2)	−0.0075 (16)	0.056 (2)	−0.0115 (18)
C4	0.103 (3)	0.069 (2)	0.090 (3)	0.000 (2)	0.079 (2)	0.0017 (19)
C5	0.096 (3)	0.078 (2)	0.066 (2)	0.013 (2)	0.058 (2)	0.0132 (18)
C6	0.0620 (18)	0.068 (2)	0.0564 (18)	0.0022 (15)	0.0382 (16)	0.0003 (15)
C7	0.0502 (15)	0.0413 (15)	0.0535 (16)	0.0004 (12)	0.0319 (13)	−0.0001 (12)
C8	0.123 (3)	0.050 (2)	0.144 (4)	−0.004 (2)	0.101 (3)	0.014 (2)
C9	0.080 (2)	0.055 (2)	0.076 (2)	−0.0076 (16)	0.0612 (19)	−0.0101 (16)

Geometric parameters (Å, º)

Cl1—C2	1.724 (3)	C2—C3	1.389 (4)
Cl2—C6	1.724 (4)	C3—C4	1.374 (5)
O1—C7	1.314 (3)	C3—H3	0.9300
O1—C8	1.451 (4)	C4—C5	1.367 (5)
N1—C7	1.278 (4)	C4—H4	0.9300
N1—C9	1.338 (4)	C5—C6	1.385 (5)
N2—C9	1.143 (4)	C5—H5	0.9300
C1—C2	1.370 (4)	C8—H8A	0.9600
C1—C6	1.382 (4)	C8—H8B	0.9600
C1—C7	1.486 (4)	C8—H8C	0.9600
C7—O1—C8	117.2 (3)	C4—C5—H5	120.4
C7—N1—C9	117.1 (3)	C6—C5—H5	120.4
C2—C1—C6	118.8 (3)	C1—C6—C5	120.9 (3)
C2—C1—C7	119.9 (3)	C1—C6—Cl2	119.2 (3)
C6—C1—C7	121.3 (3)	C5—C6—Cl2	119.8 (3)

C1—C2—C3	121.1 (3)	N1—C7—O1	121.0 (3)
C1—C2—Cl1	119.5 (2)	N1—C7—C1	125.6 (2)
C3—C2—Cl1	119.4 (2)	O1—C7—C1	113.4 (2)
C4—C3—C2	119.0 (3)	O1—C8—H8A	109.5
C4—C3—H3	120.5	O1—C8—H8B	109.5
C2—C3—H3	120.5	H8A—C8—H8B	109.5
C5—C4—C3	121.1 (3)	O1—C8—H8C	109.5
C5—C4—H4	119.5	H8A—C8—H8C	109.5
C3—C4—H4	119.5	H8B—C8—H8C	109.5
C4—C5—C6	119.2 (3)	N2—C9—N1	174.8 (4)
C6—C1—C2—C3	0.8 (4)	C7—C1—C6—Cl2	−2.1 (4)
C7—C1—C2—C3	−176.1 (3)	C4—C5—C6—C1	0.6 (5)
C6—C1—C2—Cl1	178.8 (2)	C4—C5—C6—Cl2	178.7 (3)
C7—C1—C2—Cl1	1.9 (4)	C9—N1—C7—O1	179.2 (3)
C1—C2—C3—C4	−0.6 (5)	C9—N1—C7—C1	0.2 (4)
Cl1—C2—C3—C4	−178.6 (3)	C8—O1—C7—N1	−3.7 (4)
C2—C3—C4—C5	0.4 (5)	C8—O1—C7—C1	175.4 (3)
C3—C4—C5—C6	−0.4 (5)	C2—C1—C7—N1	89.7 (4)
C2—C1—C6—C5	−0.8 (5)	C6—C1—C7—N1	−87.1 (4)
C7—C1—C6—C5	176.0 (3)	C2—C1—C7—O1	−89.4 (3)
C2—C1—C6—Cl2	−178.9 (2)	C6—C1—C7—O1	93.8 (3)