

(E)-Methyl 2,6-dichloro-N-cyano-benzimidateXiao-Ai Wu,^a Ping Yin,^a Ling He,^a Zi-Cheng Li^b and Wen-Cai Huang^{b*}^aKey Laboratory of Drug Targeting and Drug-Delivery Systems of the Ministry of Education, Department of Medicinal Chemistry, West China School of Pharmacy, Sichuan University, Chengdu, 610041, People's Republic of China, and^bDepartment of Pharmaceutical and Bioengineering, School of Chemical Engineering, Sichuan University, Chengdu 610065, People's Republic of China
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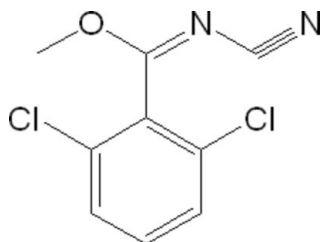
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Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.054; wR factor = 0.170; data-to-parameter ratio = 15.1.

The molecule of the title compound, $\text{C}_9\text{H}_6\text{Cl}_2\text{N}_2\text{O}$, displays an *E* conformation about the $\text{C}=\text{N}$ 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 $\text{Cl}\cdots\text{Cl}$ 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 \cdots halogen interactions, see: Desiraju & Parthasarathy (1989).

**Experimental***Crystal data*

$\text{C}_9\text{H}_6\text{Cl}_2\text{N}_2\text{O}$
 $M_r = 229.06$
 Monoclinic, $C2/c$
 $a = 21.199$ (4) Å
 $b = 8.548$ (3) Å
 $c = 15.005$ (4) Å
 $\beta = 128.49$ (4)°

$V = 2128.2$ (16) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.58$ mm⁻¹
 $T = 291$ K
 $0.52 \times 0.46 \times 0.28$ mm

Data collection

Enraf–Nonius CAD-4
 diffractometer
 Absorption correction: spherical
 (*WinGX*; Farrugia, 1999)
 $T_{\min} = 0.754$, $T_{\max} = 0.855$
 2116 measured reflections

1948 independent reflections
 1167 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$
 3 standard reflections
 every 120 reflections
 intensity decay: 3.8%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.170$
 $S = 1.04$
 1948 reflections

129 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.30$ e Å⁻³
 $\Delta\rho_{\min} = -0.32$ 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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2343).

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supplementary materials

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

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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*-cyanoimide 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*-cyanoimide 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-[(μ⁶-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].

Experimental

A mixture of 2,6-dichlorobenzaldehyde (1 mmol), H₂NCN (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/ethyl acetate solution (25:1 *v/v*) at room temperature.

Refinement

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

Figures

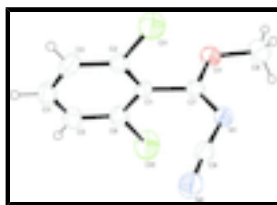


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.

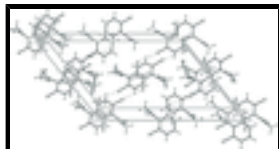


Fig. 2. Crystal packing of the title compound approximately viewed along the *b* axis. Cl...Cl interactions are shown as dotted lines.

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

Crystal data

$C_9H_6Cl_2N_2O$	$F_{000} = 928$
$M_r = 229.06$	$D_x = 1.430 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-C 2yc$	Cell parameters from 28 reflections
$a = 21.199 (4) \text{ \AA}$	$\theta = 4.8\text{--}9.2^\circ$
$b = 8.548 (3) \text{ \AA}$	$\mu = 0.58 \text{ mm}^{-1}$
$c = 15.005 (4) \text{ \AA}$	$T = 291 \text{ K}$
$\beta = 128.49 (4)^\circ$	Block, colourless
$V = 2128.2 (16) \text{ \AA}^3$	$0.52 \times 0.46 \times 0.28 \text{ mm}$
$Z = 8$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.016$
Radiation source: fine-focus sealed tube	$\theta_{\text{max}} = 25.5^\circ$
Monochromator: graphite	$\theta_{\text{min}} = 2.5^\circ$
$T = 291 \text{ K}$	$h = -25 \rightarrow 17$
$\omega/2\theta$ scans	$k = 0 \rightarrow 10$
Absorption correction: for a sphere (WinGX; Farrugia, 1999)	$l = -18 \rightarrow 18$
$T_{\text{min}} = 0.754$, $T_{\text{max}} = 0.855$	3 standard reflections
2116 measured reflections	every 120 reflections
1948 independent reflections	intensity decay: 3.8%
1167 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.1053P)^2]$
$wR(F^2) = 0.170$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1948 reflections	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
129 parameters	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$
	Extinction correction: SHELXL97 (Sheldrick, 2008),
	$F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Primary atom site location: structure-invariant direct methods Extinction coefficient: 0.0069 (15)
 Secondary atom site location: difference Fourier map

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.54862 (5)	0.67130 (14)	0.65350 (8)	0.0881 (5)
C12	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 (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0583 (5)	0.1217 (9)	0.0646 (6)	0.0019 (5)	0.0285 (5)	0.0127 (5)
C12	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)

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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, °)

C11—C2	1.724 (3)	C2—C3	1.389 (4)
C12—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—C12	119.2 (3)
C6—C1—C7	121.3 (3)	C5—C6—C12	119.8 (3)
C1—C2—C3	121.1 (3)	N1—C7—O1	121.0 (3)
C1—C2—C11	119.5 (2)	N1—C7—C1	125.6 (2)
C3—C2—C11	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—C12	-2.1 (4)
C7—C1—C2—C3	-176.1 (3)	C4—C5—C6—C1	0.6 (5)
C6—C1—C2—C11	178.8 (2)	C4—C5—C6—C12	178.7 (3)
C7—C1—C2—C11	1.9 (4)	C9—N1—C7—O1	179.2 (3)
C1—C2—C3—C4	-0.6 (5)	C9—N1—C7—C1	0.2 (4)
C11—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—C12	-178.9 (2)	C6—C1—C7—O1	93.8 (3)

Fig. 1

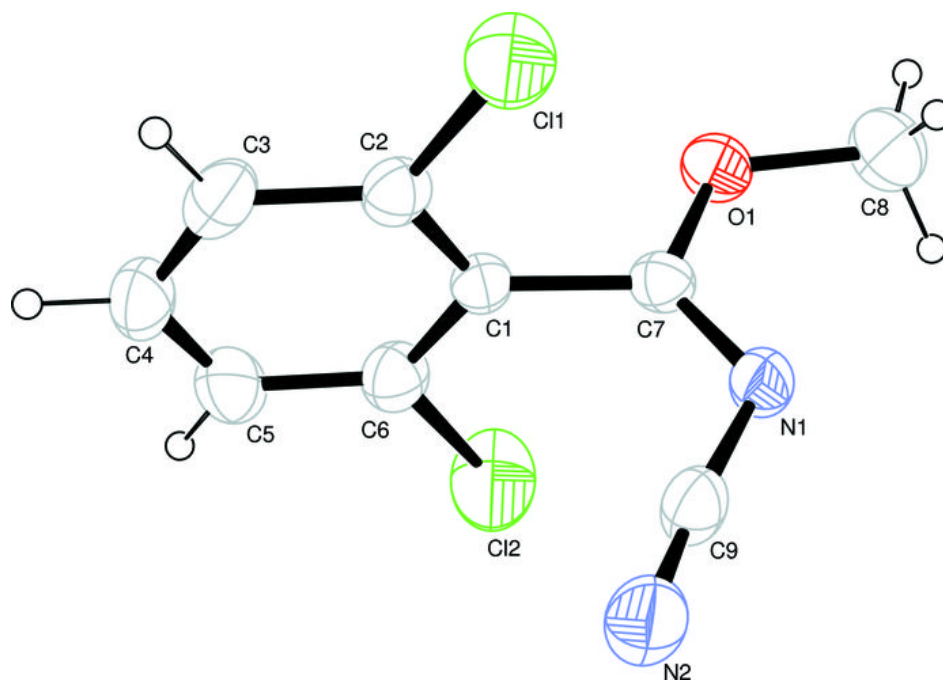


Fig. 2

