



6-Chloro-1-phenylindoline-2,3-dione: absolute structure, non-linear optical and charge-transport properties

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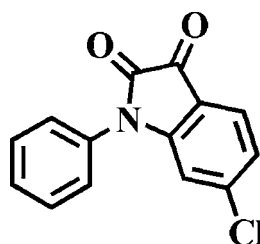
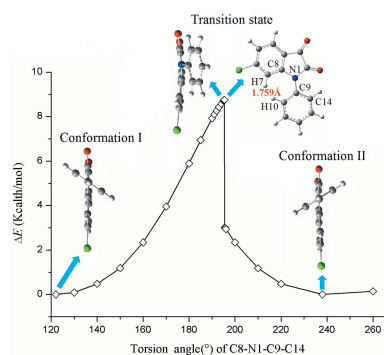
Keywords: crystal structure; absolute structure; isatin derivatives; frozen chiral conformation; SHG effect; charge-transport property.**CCDC reference:** 1528555**Supporting information:** this article has supporting information at journals.iucr.org/e

In the title compound, C₁₄H₈ClNO₂, the dihedral angle between the isatin moiety (r.m.s. deviation = 0.014 Å) and the phenyl ring is 51.8 (1)°. All molecules have the same 'frozen chiral' conformation in the non-centrosymmetric *P*2₁2₁ space group. A polycrystalline sample of the title compound exhibits a considerable second-order non-linear optical effect (frequency doubling of 1064 nm light to output 532 nm light). In the crystal, molecules are linked by C—H···O hydrogen bonds, generating chains along the [100] direction. Based on a DFT calculation, [100] proves to be the most favourable direction for charge transport and the title crystal could be used as a hole-transport material because of its high hole mobility.

1. Chemical context

Derivatives of isatin, also called indoline-2,3-dione, have drawn great attention for their biological and pharmacological properties such as anticonvulsant (Prakash *et al.*, 2010), anti-cancer (Abadi *et al.*, 2006) and anti-HIV (Bal *et al.*, 2005) activities. The isatin skeleton can be found in analytical reagents, pesticides and dye intermediates. Isatin derivatives are also versatile precursors in the synthesis of a variety of heterocyclic compounds. However, the opto-electronic properties of isatin derivatives are rarely investigated.

The crystal structures of many isatin derivatives have been reported, among the analogues of the title compound are 6-bromo-1-butylindoline-2,3-dione (Ji *et al.*, 2009), 1-ethyl-5-iodoindoline-2,3-dione (Wang *et al.*, 2014), 6-chloroindoline-2,3-dione (Golen & Manke, 2016), 1-benzyl-5-fluoroindoline-2,3-dione (Sharmila *et al.*, 2015) and 1-phenylindoline-2,3-dione (Shukla & Rajeswaran, 2011). The synthesis of the title compound was reported in 2014 (Bergman & Stensland, 2014). Recently, we prepared this compound by a different method, which involves the use of O₂ in air as oxidant. Herein, we report the crystal structure and some opto-electronic properties of this compound.



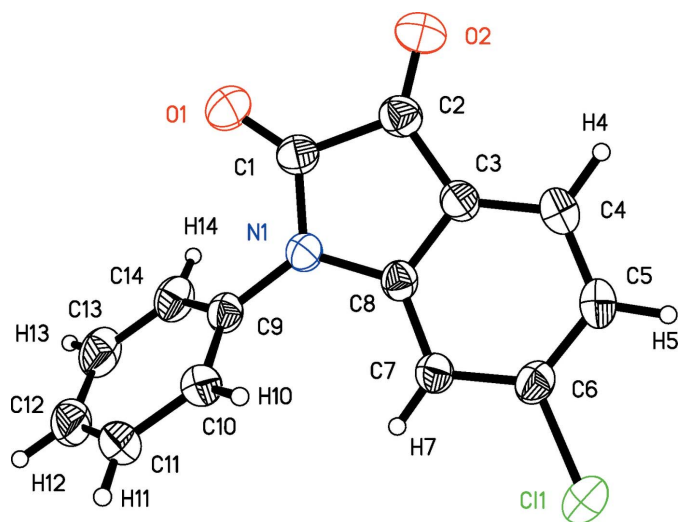


Figure 1
The molecular structure of the title compound, with displacement ellipsoids shown at the 50% probability level.

2. Structural commentary

As shown in Fig. 1, the isatin unit of the molecule is essentially planar, with a mean deviation of 0.009 (2) Å and a maximum deviation of 0.0870 (8) Å (for atom O1) from the mean plane of the indoline core (C1–C8/N1). As a result of the short intramolecular contacts (C10···C7, C14···O1) and the H7···H10 steric hindrance, there is a dihedral angle of 51.8 (1)° between the phenyl ring and the mean plane of the indoline core. As a comparison, the dihedral angle of the DFT/b3lyp/6-311++g(2d,p) optimized (see below) title molecule is 60.0°. The sum of the angles surrounding N1 is 359.96°,

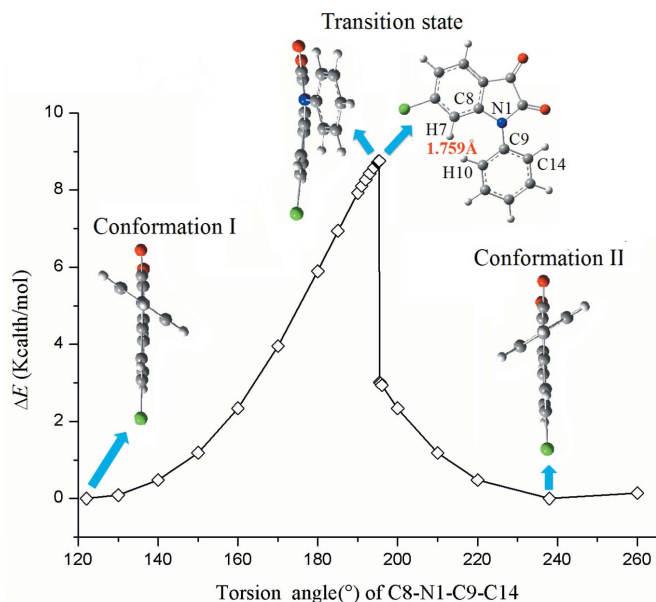


Figure 2
DFT/b3lyp/6-311++g(2 d,p) optimization of series of relaxed conformation with different C8–N1–C9–C14 torsion angles for the title molecule.

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C10–H10···O1 ⁱ	0.956 (17)	2.572 (18)	3.2063 (16)	124.0 (13)

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

suggesting that this atom is sp^2 hybridized. The C9–N1 bond length [1.4279 (14) Å] is slightly shorter than that [1.436 (2) Å] in the similar compound 1-phenylindoline-2,3-dione (Shukla & Rajeswaran, 2011). The C1–C2 [1.557 (2) Å] bond length is longer than a typical Csp^2 – Csp^2 bond but it is notable that the geometry optimization gave a length of 1.568 Å for this bond. The C1–C2 length [1.545 (3) Å] in 1-phenylindoline-2,3-dione is somewhat shorter (Shukla & Rajeswaran, 2011).

As a result of the $P2_12_12_1$ space group of the crystal, all molecules have the same ‘frozen chiral’ conformation (defined as conformation I). The single conformation of these molecules in this as-tested crystal is confirmed by a Flack parameter $x = 0.03$ (5) and R_1 factor of 0.0317. By comparison, an inversion operation to the present structure resulted in an incorrect structure of conformation II with $x = 0.97$ (5) and $R_1 = 0.0336$. 1-Phenylindoline-2,3-dione also crystallized in $P2_12_12_1$ (Shukla & Rajeswaran, 2011) and this space group may be well suited to accommodate this class of molecules.

As shown in Figs. 1 and 2, the isoenergetic conformations I and II are mirror images and non-superposable one another. The calculated rotation barrier (rotating around the N1–C9 bond to transform from I to II) is 8.74 kcal mol^{−1}, which is much higher than the thermal energy $k_B T = 0.596$ kcal mol^{−1} at 300 K. The main hindrance from free rotation may be the H7···H10 steric repulsion with a calculated distance of 1.759 Å at the transition state (see Fig. 2).

3. Supramolecular features

As shown in Fig. 3, the intermolecular interactions in the *a*-axis direction are characterized by a C10–H10···O1 hydrogen bond (Table 1) and an O1···H11($x - 1, y, z$) [2.63 (2) Å] short contact between two side-by-side molecules. The strength of the hydrogen bond can be scaled by the electronic transfer integral (t) between two molecules and it was calculated by equation (3). The t value between the above two adjacent molecules is maximal ($t_1 = 0.196$ eV), indicating that a kind of side-by-side one-dimensional chain has formed along the *a*-axis direction. We believe that this *a*-directional chain plays an important role in guiding the crystal growth, for the long axis of the bar-shaped crystal was indexed to be in the [100] direction.

By the 2_1 [010] screw operation, molecules are packed into columns along the *b*-axis direction involving C2···C12($2 - x, \frac{1}{2} + y, \frac{3}{2} - z$) [3.280 (2) Å] and H10···C14($2 - x, \frac{1}{2} + y, \frac{3}{2} - z$) [2.50 (3) Å] short intermolecular contacts between two neighboring molecules (see Fig. 4). The transfer integral

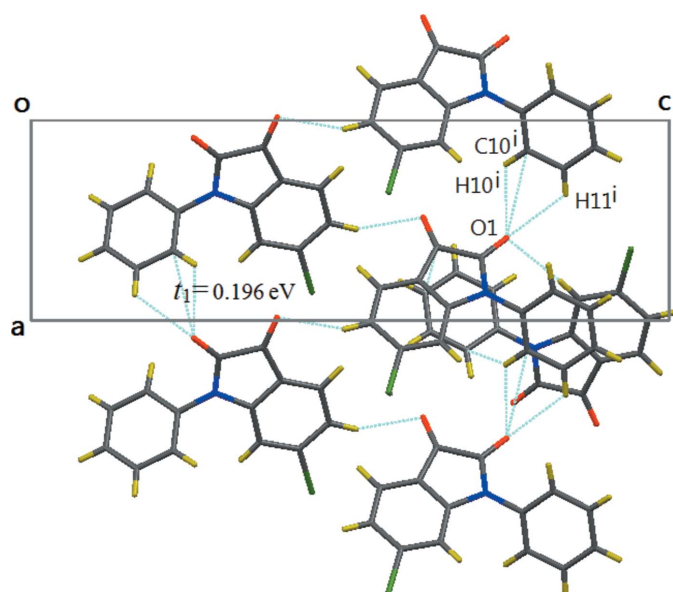


Figure 3
The view along the *b* axis, showing the chain linkage by the $C10^i-H10^i \cdots O1$ hydrogen bond and the $O1 \cdots H11^i$ short intermolecular contacts along the *a*-axis direction. [Symmetry code: (i) $-1 + x, y, z$.]

between such two face-to-face molecules is somewhat smaller ($t_2 = 0.116$ eV) in this direction.

Along the *c*-axis direction, there is a $H5 \cdots O2(\frac{1}{2} + x, \frac{3}{2} - y, 1 - z)$ [2.69 (2) Å] short intermolecular contact and the *t* value between the two molecules is a minimum ($t_3 = 0.0794$ eV, see Fig. 4): thus the intermolecular interactions in this direction are relatively weak.

4. Calculation and opto-electronic properties

It is well known that the necessary structural condition for second-order non-linear optical response is non-centrosymmetry, both for molecules and crystals. The $P2_12_12_1$ space group of the crystal prompted us to make a SHG (second harmonic generation) test. When the sample of crystalline

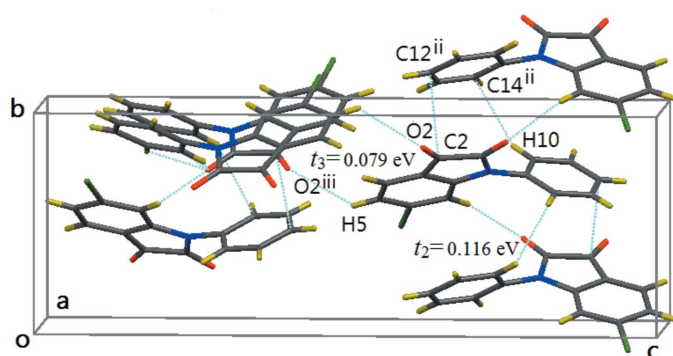


Figure 4
The view along the *a* axis, showing the columnar structure and short contacts of $C2 \cdots C12^{ii}$ and $H10 \cdots C14^{ii}$ along the *b*-axis direction, also showing the short contact of $H5 \cdots O2^{iii}$ along the *c* direction. [Symmetry codes: (ii) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$.]

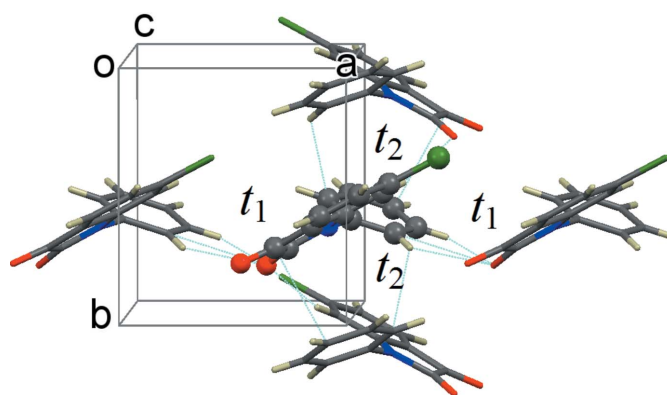
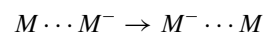
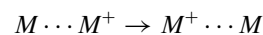


Figure 5
The view along the *c* axis, showing the cage-model for the DFT geometry optimization with one host molecule being surrounded by four guest molecules.

powder was irradiated with infrared laser pulses (1064 nm), green light pulses (532 nm) could be observed.

Density functional theory (DFT) calculations for the electronic transfer integral *t* and the reorganization energy λ , were carried out using the *GAUSSIAN03* program (Frisch *et al.*, 2003) within the framework of b3lyp/6-311g(d).

The charge transport in organic semiconductors can be described by the hopping of an electron between a molecule and a neighbouring cation (hole) or anion shown below



Based on the Marcus electron-transfer theory (Marcus, 1993), the mobility (μ) in a one-dimensional uniform structure, can be expressed as (Sakanoue *et al.*, 1999; Fang *et al.*, 2015)

$$\mu = \frac{e}{2k_B T \hbar} \left(\frac{\pi}{\lambda k_B T} \right)^{1/2} d^2 t^2 \exp\left(-\frac{\lambda}{4k_B T}\right) \quad (1)$$

where *d* is the distance between two neighbouring molecules and λ is reorganization energy. For the hole transport, λ can be expressed by (Berlin *et al.*, 2003)

$$\lambda = \lambda_1 + \lambda_2 = (E_+^0 - E_+^0) + (E_+^0 - E_+^+). \quad (2)$$

Thus, λ_1 measures the energy difference between the stable molecule and the molecule with the cation geometry and λ_2 measures the energy difference between the stable cation and the cation with the molecule geometry.

The *t* in equation (1) is the electronic transfer integral, which measures the intermolecular interactions between two neighbouring molecules and can be calculated by (Deng & Goddard, 2004)

$$t = (E_{\text{HOMO}} - E_{\text{HOMO}-1})/2 \quad (3)$$

where E_{HOMO} and $E_{\text{HOMO}-1}$ are the energy levels of the HOMO (highest occupied molecular orbital) and the HOMO-1 orbital of a two-molecule pair, respectively.

The molecular geometry for the *t* calculation is based on this X-ray structure without optimization, while the geometries of

Table 2

 Charge-transport properties (eV , $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) of the title crystal.

	t	λ_{h} (λ_{e})	μ_{h} (μ_{e})
side-by-side [100]	0.196	0.319 (0.520)	4.67 (0.524)
face-to-face [010]	0.116	0.319 (0.520)	0.518 (0.058)

the molecule and the cation/anion have been optimized for the λ calculation. Since the molecule in the crystal is different from the free molecule, we adopted the cage model (Fang *et al.*, 2015) in the course of geometry optimization, in which the host (molecule or cation or anion) being optimized is constrained by four guest molecules with fixed X-ray structures (see Fig. 5).

As shown in Table 2, (i) the hole mobility (μ_{h}) is one order of magnitude larger than the electron mobility (μ_{e}), indicating that the title crystal could be used as a hole-transport material rather than an electron-transport material and (ii) both the hole mobility (μ_{h}) and the electron mobility (μ_{e}) in the [100] direction (the side-by-side chain direction) are an order of magnitude larger than those in the [010] direction (the face-to-face column direction).

In summary, the side-by-side hydrogen bonding in the one-dimensional chain in the [100] direction is stronger than the face-to-face π - π interactions in the [010] direction for this crystal, which relates to the non-linear optical and electronic transport properties of the crystal.

5. Database survey

A search in the Cambridge Structural Database (WebCSD, Version 1.1.2; last update November 2016), for indoline-2,3-dione derivatives gave 137 hits. Among them, there are nine hits for halogen 6-substituted indoline-2,3-dione derivatives and two hits which contain the substructure of the 1-phenylindoline-2,3-dione skeleton. There are four non-centrosymmetric structures and seven centrosymmetric structures among these eleven crystal structures.

6. Synthesis and crystallization

We synthesized the title compound by the reaction of 6-chloroindoline-2-one and phenylboronic acid (see Fig. 6). 6-Chloroindoline-2-one (0.168 g, 1.00 mmol) was dissolved in DMF (18 ml). Then pyridine (0.05 mL), phenylboronic acid (0.244 g, 2.00 mmol) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.197 g, 0.99 mmol) were sequentially added into the flask. The mixture was stirred

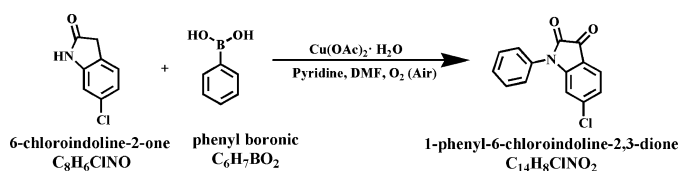

Figure 6
Reaction scheme.

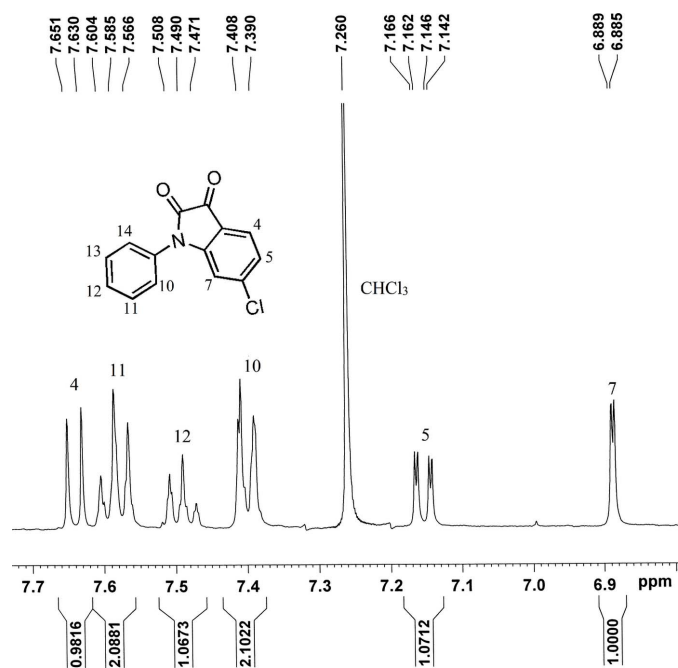
Table 3

Experimental details.

Crystal data	
Chemical formula	$\text{C}_{14}\text{H}_8\text{ClNO}_2$
M_r	257.66
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	294
a, b, c (\AA)	6.8190 (3), 7.7062 (3), 21.7492 (9)
V (\AA^3)	1142.89 (8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.33
Crystal size (mm)	$0.58 \times 0.24 \times 0.18$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2005)
$T_{\text{min}}, T_{\text{max}}$	0.834, 0.943
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21380, 3784, 3513
R_{int}	0.021
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.741
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.032, 0.090, 1.04
No. of reflections	3784
No. of parameters	191
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	0.21, -0.23
Absolute structure	Flack (1983), 1583 Friedel pairs
Absolute structure parameter	0.03 (5)

Computer programs: APEX2 and SAINT (Bruker, 2005), SHELXS97, SHELXL97 and SHELXTL (Sheldrick, 2008).

for two h at room temperature in the presence of air. After filtration, the filtrate was poured into 100 ml water and


Figure 7
The ^1H NMR spectra of the title compound.

extracted with dichloromethane. The organic phase was washed by water and dried by anhydrous Na₂SO₄. The crude product was purified by silica gel chromatography, eluting with a mixture of petroleum ether:ethyl acetate (30:1) to obtain an orange solid (0.096 g, yield 37%). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (*d*, *J* = 8.4 Hz, 1H), 7.59 (*t*, *J* = 7.6 Hz, 2H), 7.49 (*t*, *J* = 7.4 Hz, 1H), 7.40 (*d*, *J* = 7.2 Hz, 2H), 7.15 (*dd*, *J* = 8.0, 1.6 Hz, 1H), 6.89 (*d*, *J* = 1.6 Hz, 1H). As shown in Fig. 7, the ¹H NMR signals of all protons of the compound are well separated and well characterized. Orange bar-shaped crystals were obtained by slow evaporation of a solution of the title compound in mixed solvents of dichloromethane and *n*-hexane.

7. Refinement

Crystal data, diffraction data and structure refinement details are summarized in Table 3. All hydrogen atoms were located from the difference-electron-density maps and refined freely, resulting in C–H lengths ranging from 0.92 (2) to 1.00 (2) Å.

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References

- Abadi, A. H., Abou-Seri, S. M., Abdel-Rahman, D. E., Klein, C., Lozach, O. & Meijer, L. (2006). *Eur. J. Med. Chem.* **41**, 296–305.
- Bal, T. R., Anand, B., Yogeewari, P. & Sriram, D. (2005). *Bioorg. Med. Chem. Lett.* **15**, 4451–4455.
- Bergman, J. & Stensland, B. (2014). *J. Heterocycl. Chem.* **51**, 1–10.
- Berlin, Y. A., Hutchison, G. R., Rempala, P., Ratner, M. A. & Michl, J. (2003). *J. Phys. Chem. A*, **107**, 3970–3980.
- Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Deng, W.-Q. & Goddard, W. A. III (2004). *J. Phys. Chem. B*, **108**, 8614–8621.
- Fang, Q., Chen, H., Lei, H., Xue, G. & Chen, X. (2015). *CrystEngComm*, **17**, 787–796.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Frisch, M. J., *et al.* (2003). *GAUSSIAN03*. Gaussian Inc., Pittsburgh, PA, USA.
- Golen, J. A. & Manke, D. R. (2016). *IUCrData*, **1**, x160690.
- Ji, L., Fang, Q. & Fan, J. (2009). *Acta Cryst.* **E65**, o136.
- Marcus, R. A. (1993). *Rev. Mod. Phys.* **65**, 599–610.
- Prakash, C. R., Raja, S. & Saravanan, G. (2010). *Int. J. Pharm. Pharm. Sci.* **2**, 177–181.
- Sakanoue, K., Motoda, M., Sugimoto, M. & Sakaki, S. (1999). *J. Phys. Chem. A*, **103**, 5551–5556.
- Sharmila, N., Sundar, T. V., Satish, G., Ilangoan, A. & Venkatesan, P. (2015). *Acta Cryst.* **C71**, 975–978.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shukla, D. & Rajeswaran, M. (2011). *Acta Cryst.* **E67**, o2034.
- Wang, L., Shen, Y.-X., Dong, J.-T., Zhang, M. & Fang, Q. (2014). *Acta Cryst.* **E70**, o67.

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6-Chloro-1-phenylindoline-2,3-dione: absolute structure, non-linear optical and charge-transport properties

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Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINTE* (Bruker, 2005); data reduction: *SAINTE* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

6-Chloro-1-phenylindoline-2,3-dione

Crystal data

$C_{14}H_8ClNO_2$

$M_r = 257.66$

Orthorhombic, $P2_12_12_1$

$a = 6.8190$ (3) Å

$b = 7.7062$ (3) Å

$c = 21.7492$ (9) Å

$V = 1142.89$ (8) Å³

$Z = 4$

$F(000) = 528$

$D_x = 1.497$ Mg m⁻³

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

Cell parameters from 9992 reflections

$\theta = 2.8$ – 31.0°

$\mu = 0.33$ mm⁻¹

$T = 294$ K

Bar, orange

$0.58 \times 0.24 \times 0.18$ mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2005)

$T_{\min} = 0.834$, $T_{\max} = 0.943$

21380 measured reflections

3784 independent reflections

3513 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 31.8^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -9 \rightarrow 9$

$k = -10 \rightarrow 11$

$l = -32 \rightarrow 28$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.090$

$S = 1.04$

3784 reflections

191 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.0865P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.21$ e Å⁻³

$\Delta\rho_{\min} = -0.23$ e Å⁻³

Absolute structure: Flack (1983), 1583 Friedel pairs

Absolute structure parameter: 0.03 (5)

Special details

Experimental. Scan width $0.5^\circ \omega$, Crystal to detector distance 5.96 cm, exposure time 15s, 10 hours and 36 minutes for data collection, with scale. 6-run at 2theta equal -28, -28, -35, -36, -36, -38, respectively.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	1.36000 (5)	0.40110 (5)	0.561115 (17)	0.05229 (11)
C7	1.10733 (16)	0.54301 (15)	0.64149 (5)	0.0323 (2)
O2	0.48463 (15)	0.81725 (15)	0.61436 (5)	0.0514 (3)
O1	0.58784 (14)	0.83661 (15)	0.74488 (5)	0.0466 (2)
C5	1.0114 (2)	0.5438 (2)	0.53283 (6)	0.0423 (3)
C6	1.14176 (18)	0.50392 (15)	0.57981 (5)	0.0355 (2)
C8	0.93314 (16)	0.62745 (14)	0.65401 (5)	0.0298 (2)
N1	0.86151 (14)	0.68187 (13)	0.71209 (4)	0.03287 (18)
C9	0.95746 (17)	0.65986 (15)	0.76993 (5)	0.0309 (2)
C14	0.8529 (2)	0.58710 (17)	0.81830 (6)	0.0400 (3)
C13	0.9437 (3)	0.5724 (2)	0.87499 (6)	0.0502 (3)
H13	0.8757	0.5247	0.9080	0.060*
C12	1.1351 (3)	0.6281 (2)	0.88297 (6)	0.0539 (4)
C3	0.79945 (17)	0.66972 (16)	0.60753 (5)	0.0339 (2)
C4	0.8377 (2)	0.62747 (18)	0.54664 (6)	0.0417 (3)
C2	0.63341 (17)	0.75880 (16)	0.63578 (6)	0.0366 (2)
C1	0.68398 (16)	0.76703 (16)	0.70553 (6)	0.0348 (2)
C11	1.2390 (2)	0.6983 (2)	0.83442 (6)	0.0456 (3)
C10	1.15006 (18)	0.71514 (15)	0.77716 (5)	0.0350 (2)
H5	1.042 (3)	0.510 (2)	0.4916 (9)	0.056 (5)*
H4	0.739 (3)	0.659 (2)	0.5147 (9)	0.050 (5)*
H10	1.219 (3)	0.768 (2)	0.7437 (8)	0.041 (4)*
H11	1.369 (3)	0.735 (2)	0.8379 (9)	0.054 (5)*
H12	1.195 (4)	0.618 (3)	0.9210 (11)	0.081 (7)*
H14	0.724 (3)	0.548 (3)	0.8112 (9)	0.056 (5)*
H7	1.195 (3)	0.509 (2)	0.6711 (8)	0.038 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.04536 (17)	0.0669 (2)	0.04463 (17)	0.01248 (15)	0.01136 (13)	-0.00487 (15)

C7	0.0316 (5)	0.0373 (5)	0.0281 (4)	0.0001 (4)	0.0017 (4)	0.0021 (4)
O2	0.0373 (4)	0.0633 (6)	0.0536 (6)	0.0104 (4)	-0.0091 (4)	-0.0017 (5)
O1	0.0361 (4)	0.0589 (6)	0.0448 (5)	0.0057 (4)	0.0071 (4)	-0.0055 (4)
C5	0.0491 (7)	0.0514 (7)	0.0263 (5)	0.0011 (5)	0.0025 (4)	-0.0016 (5)
C6	0.0352 (5)	0.0391 (5)	0.0324 (5)	0.0011 (4)	0.0071 (4)	-0.0003 (4)
C8	0.0299 (4)	0.0330 (5)	0.0265 (4)	-0.0031 (4)	0.0022 (3)	0.0008 (4)
N1	0.0281 (4)	0.0435 (5)	0.0270 (4)	0.0015 (4)	0.0026 (3)	-0.0012 (3)
C9	0.0354 (5)	0.0315 (5)	0.0260 (4)	0.0013 (4)	0.0026 (4)	-0.0002 (4)
C14	0.0468 (7)	0.0381 (5)	0.0353 (5)	-0.0017 (5)	0.0102 (5)	0.0016 (4)
C13	0.0712 (9)	0.0490 (7)	0.0305 (6)	0.0122 (7)	0.0121 (6)	0.0080 (5)
C12	0.0714 (9)	0.0600 (8)	0.0303 (5)	0.0256 (8)	-0.0083 (6)	-0.0015 (5)
C3	0.0328 (5)	0.0384 (5)	0.0305 (5)	-0.0006 (4)	-0.0017 (4)	0.0013 (4)
C4	0.0463 (6)	0.0490 (6)	0.0299 (5)	0.0021 (5)	-0.0053 (5)	0.0005 (5)
C2	0.0313 (5)	0.0400 (5)	0.0385 (5)	-0.0019 (4)	-0.0019 (4)	0.0001 (4)
C1	0.0280 (5)	0.0393 (5)	0.0372 (5)	-0.0014 (4)	0.0017 (4)	-0.0001 (4)
C11	0.0453 (7)	0.0527 (7)	0.0388 (6)	0.0106 (6)	-0.0109 (5)	-0.0067 (6)
C10	0.0343 (5)	0.0381 (5)	0.0327 (5)	0.0017 (4)	-0.0004 (4)	-0.0005 (4)

Geometric parameters (Å, °)

C11—C6	1.7343 (12)	C9—C10	1.3896 (16)
C7—C8	1.3815 (16)	C14—C13	1.384 (2)
C7—C6	1.3948 (15)	C14—H14	0.94 (2)
C7—H7	0.916 (17)	C13—C12	1.385 (3)
O2—C2	1.2039 (16)	C13—H13	0.9300
O1—C1	1.2040 (15)	C12—C11	1.382 (2)
C5—C4	1.3816 (19)	C12—H12	0.93 (2)
C5—C6	1.3889 (18)	C3—C4	1.3884 (17)
C5—H5	0.96 (2)	C3—C2	1.4597 (17)
C8—C3	1.3996 (15)	C4—H4	1.00 (2)
C8—N1	1.4179 (13)	C2—C1	1.5570 (17)
N1—C1	1.3844 (14)	C11—C10	1.3916 (17)
N1—C9	1.4279 (14)	C11—H11	0.93 (2)
C9—C14	1.3892 (16)	C10—H10	0.956 (17)
C8—C7—C6	115.85 (11)	C12—C13—H13	119.7
C8—C7—H7	123.8 (11)	C11—C12—C13	120.60 (13)
C6—C7—H7	120.3 (11)	C11—C12—H12	119.1 (16)
C4—C5—C6	119.46 (11)	C13—C12—H12	120.3 (16)
C4—C5—H5	121.2 (12)	C4—C3—C8	120.79 (11)
C6—C5—H5	119.3 (12)	C4—C3—C2	131.11 (11)
C5—C6—C7	123.52 (11)	C8—C3—C2	108.10 (10)
C5—C6—C11	118.54 (9)	C5—C4—C3	118.56 (11)
C7—C6—C11	117.94 (10)	C5—C4—H4	122.6 (11)
C7—C8—C3	121.83 (10)	C3—C4—H4	118.8 (11)
C7—C8—N1	127.67 (10)	O2—C2—C3	131.81 (12)
C3—C8—N1	110.50 (10)	O2—C2—C1	123.27 (12)
C1—N1—C8	110.46 (9)	C3—C2—C1	104.92 (10)

C1—N1—C9	123.21 (9)	O1—C1—N1	127.88 (12)
C8—N1—C9	126.29 (9)	O1—C1—C2	126.16 (11)
C14—C9—C10	121.55 (11)	N1—C1—C2	105.95 (10)
C14—C9—N1	118.68 (11)	C12—C11—C10	119.78 (14)
C10—C9—N1	119.75 (10)	C12—C11—H11	122.9 (12)
C13—C14—C9	118.54 (14)	C10—C11—H11	117.3 (12)
C13—C14—H14	122.6 (12)	C9—C10—C11	119.00 (12)
C9—C14—H14	118.8 (12)	C9—C10—H10	120.5 (10)
C14—C13—C12	120.52 (13)	C11—C10—H10	120.5 (11)
C14—C13—H13	119.7		
C4—C5—C6—C7	0.4 (2)	N1—C8—C3—C2	1.03 (13)
C4—C5—C6—C11	-179.26 (11)	C6—C5—C4—C3	0.2 (2)
C8—C7—C6—C5	-0.69 (19)	C8—C3—C4—C5	-0.45 (19)
C8—C7—C6—C11	178.95 (8)	C2—C3—C4—C5	178.98 (13)
C6—C7—C8—C3	0.44 (17)	C4—C3—C2—O2	1.2 (2)
C6—C7—C8—N1	179.89 (11)	C8—C3—C2—O2	-179.36 (14)
C7—C8—N1—C1	178.11 (11)	C4—C3—C2—C1	-178.96 (13)
C3—C8—N1—C1	-2.38 (13)	C8—C3—C2—C1	0.52 (13)
C7—C8—N1—C9	0.14 (18)	C8—N1—C1—O1	-176.24 (13)
C3—C8—N1—C9	179.64 (11)	C9—N1—C1—O1	1.80 (19)
C1—N1—C9—C14	52.94 (16)	C8—N1—C1—C2	2.58 (12)
C8—N1—C9—C14	-129.33 (12)	C9—N1—C1—C2	-179.37 (10)
C1—N1—C9—C10	-125.42 (12)	O2—C2—C1—O1	-3.1 (2)
C8—N1—C9—C10	52.31 (16)	C3—C2—C1—O1	176.95 (12)
C10—C9—C14—C13	0.92 (19)	O2—C2—C1—N1	178.00 (12)
N1—C9—C14—C13	-177.41 (11)	C3—C2—C1—N1	-1.90 (12)
C9—C14—C13—C12	-0.4 (2)	C13—C12—C11—C10	0.8 (2)
C14—C13—C12—C11	-0.4 (2)	C14—C9—C10—C11	-0.56 (18)
C7—C8—C3—C4	0.11 (18)	N1—C9—C10—C11	177.75 (11)
N1—C8—C3—C4	-179.42 (11)	C12—C11—C10—C9	-0.30 (19)
C7—C8—C3—C2	-179.43 (10)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C10—H10...O1 ⁱ	0.956 (17)	2.572 (18)	3.2063 (16)	124.0 (13)

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