Electronic Supplementary Information

$C_{10}H_{10}ClNO_3$: Exploration of Birefringent Crystal in Isoquinoline System

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Contents

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Reagents

$C_{10}H_7NO_2$ (97%) and HCl (98%) were purchased from Aladdin and used as received.

Synthesis of $C_{10}H_{10}ClNO_3$ (1)

The crystal of **1** was synthesized by a simple solution evaporation technique. Mix $C_{10}H_7NO_2$ (0.126g, 1mmol) raw material reactant with hydrochloric acid (10 mL) in a glass beaker. The solution was stirred with a magnetic stirrer for 30 minutes to obtain a transparent liquid. The beaker is sealed with perforated plastic packaging and placed at room temperature for about 3 days. The purity of the obtained product was confirmed by powder X-ray diffraction (XRD), which was measured by Rigaku MiniFlex II diffractometer (Cu $K\alpha$ radiation), the range is $2\theta = 7°-70°$, step size 0.01°, sampling rate 1° min^{-1}. The results are consistent with the XRD spectra calculated in the single crystal XRD analysis (Fig. 2a).

Single-Crystal Structure Determination

A colorless **1** crystal was selected using an optical microscope for single-crystal XRD analysis. The diffraction data were collected at 293(2) K on an an XtaLAB Pro II AFC12 equipped with a Hybrid Pixel Array Detector and Rigaku Mo X-ray Source. The collection of the intensity data, cell refinement, and data reduction were carried out with the program CrysAlisPro.[1] Using Olex2,[2] the structure was solved with the olex2.solve[3] structure solution program using Charge Flipping and refined with the SHELXL[4] refinement package using Least Squares minimisation. Details of crystal parameters, data collection, and structure refinement are summarized in Table S1. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table S2, and the anisotropic displacement parameters are listed in Table S3. The selected bond distances and angles are presented in Table S4−S5.

Thermal Stability Analysis

The thermogravimetric (TG) and differential thermal analysis (DTA) of **1** was carried out on a NETZSCH STA 449C simultaneous analyzer. About 7.5 mg of **1** was placed in Al_2O_3 crucibles, heated at a rate of 20 °C min^{-1} from room temperature to 600 °C under flowing nitrogen.

UV-Vis-NIR Diffuse Reflectance Spectroscopy

The UV/Vis/NIR diffuse reflection data were collected on a PerkinElmer Lamda-1050 UV/vis/NIR spectrophotometer. A whiteboard provided by the merchant was used as a reference (100% reflectance) in the range from 220 nm to 800 nm.

Infrared Spectroscopy

Infrared spectrum was measured on a Nicolet iS50FT-IR spectrometer with KBr pellets as a standard in the range of 4000~400 cm^{-1}. The mixture of **1** and dried KBr (mass ratio = 1:100) was ground thoroughly in an agate mortar, and then pressed into a thin slice for measurement.

Birefringence Measurements

The Birefringence of **1** was obtained through a polarizing microscope (Nikon LV1000) equipped with a Berek compensator at a wavelength of 550 nm. Small crystal was chose for the measurement. The following formula was listed

to calculate birefringence: $R = |N_e - N_o| = \Delta n \times T$, where R denotes the optical path difference, Δn represents birefringence, and T denotes the thickness of the crystal.

Computational Methods

The first-principles calculations for **1** were performed by CASTEP[5] on a plane-wave pseudopotential total energy package based density functional theory (DFT).[6] The functional developed by Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA)[7−8] form was adopted to describe the exchange-correlation energy. The ultrasoft pseudopotentials were used to model the effective interaction between atom cores and valence electrons. H $1s^1$, C $2s^2 2p^2$, N $2s^2 2p^3$, O $2s^2 2p^4$ and Cl $3s^2 3p^5$ electrons were treated as valence electrons. The kinetic energy cutoff of 380 eV and dense $2 \times 2 \times 1$ Monkhorst-Pack[9] k-point meshes in the Brillouin zones were chosen. The linear optical properties were examined based on the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of dielectric function ε_2 can be calculated based on the electronic structures and the real part is obtained by the Kramers-Kronig transformation, accordingly the refractive indices and the birefringence (Δn) can be calculated. The frequency-dependent refractive indices were calculated to demonstrate the validity of birefringence measurements.
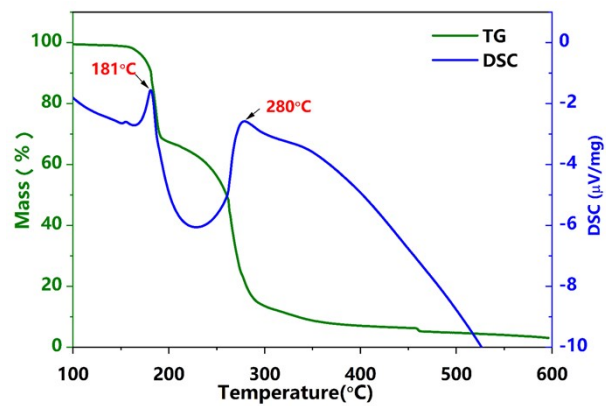
Fig. S1 Thermal stability analysis for **1**.

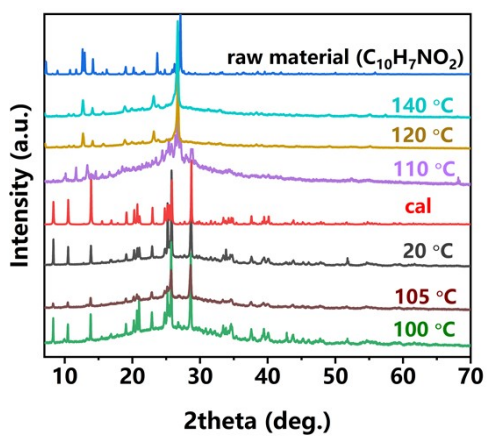**Fig. S2** XRD of **1** at different temperatures.
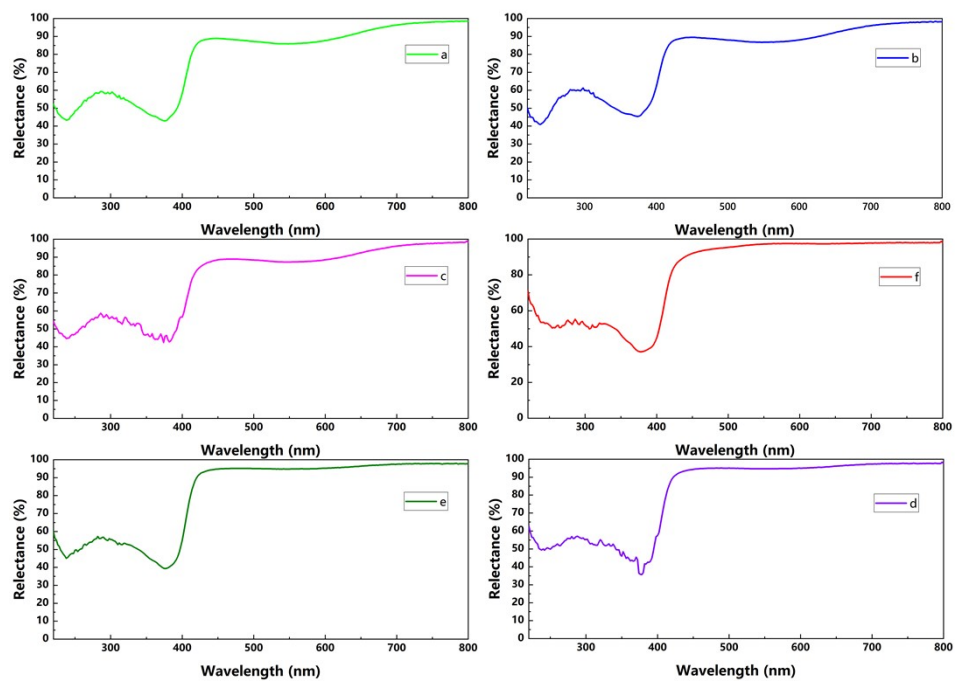
Fig. S3 UV-Vis-NIR diffuse reflection spectra of **1.**
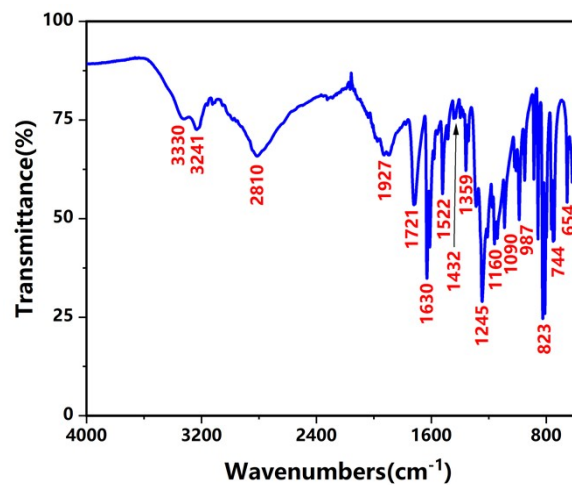
Fig. S4 Infrared spectrum of **1.**
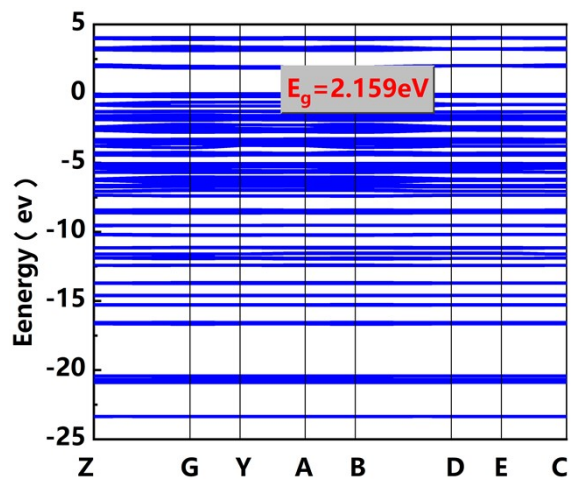
Fig. S5 Electronic band structure of **1** (GGA).
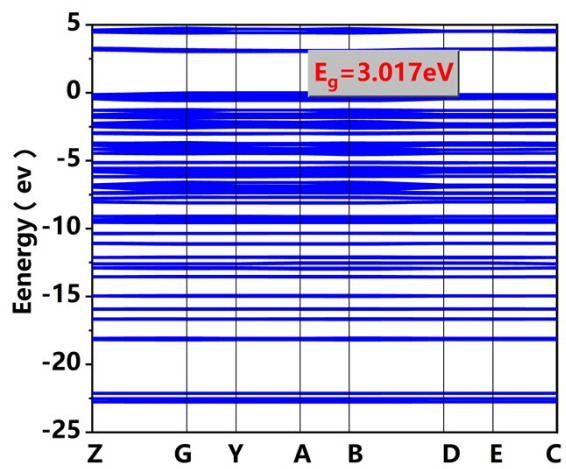
Fig. S6 Electronic band structure of **1** (HSE06).

Table 1. Crystal Data and Structural Refinement for $C_{10}H_{10}ClNO_3$.

Empirical formula	$C_{10}H_{10}ClNO_3$
Formula weight	227.64
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.6630(10)
b/Å	13.7778(16)
c/Å	7.2187(8)
α/°	90
β/°	96.204(10)
γ/°	90
Volume/Å^3	1054.31(19)
Z	4
ρ_{calc}/cm^3	1.434
μ/mm^{-1}	0.348
F(000)	472.0
Crystal size/mm^3	$0.4 \times 0.3 \times 0.2$
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.842 to 54.034
Index ranges	$-13 \leq h \leq 12, -12 \leq k \leq 17, -9 \leq l \leq 9$
Reflections collected	6769
Independent reflections	2185 [R_{int} = 0.0385, R_{sigma} = 0.0346]
Data/restraints/parameters	2185/3/148
Goodness-of-fit on F^2	1.115
Final R indexes [I>=2σ (I)]	R1 = 0.0398, wR2 = 0.1046
Final R indexes [all data]	R1 = 0.0515, wR2 = 0.1124

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for $C_{10}H_{10}ClNO_3$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Cl1	6701.2(4)	4156.1(3)	−2070.8(6)	51.1(2)
O1	3468.6(12)	3083.3(10)	1921.2(17)	58.0(4)
O2	5111.4(11)	3716.1(10)	3702.5(17)	54.6(4)
N1	3836.2(15)	4093.2(10)	6410(2)	40.7(4)
C1	3159.6(15)	3797.5(11)	4855(2)	37.0(4)
C2	1830.1(15)	3747.2(11)	4796(2)	40.0(4)
C3	1022.3(16)	3460.2(13)	3190(3)	52.1(5)
C4	-250.2(18)	3436.1(15)	3249(3)	62.8(6)
C5	-787.4(18)	3681.8(14)	4870(3)	61.3(6)
C6	-52.2(18)	3963.2(14)	6429(3)	55.6(5)
C7	1281.2(16)	4009.7(12)	6442(3)	45.1(4)
C8	2067.6(19)	4311.0(13)	8018(3)	52.6(5)
C9	3335.0(18)	4349.0(13)	7985(3)	49.3(5)
C10	3914.3(16)	3491.1(12)	3303(2)	41.7(4)
O3	6655.1(13)	3032.0(10)	1642.9(19)	55.2(4)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for $C_{10}H_{10}ClNO_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	51.8(3)	56.6(4)	44.7(3)	−4.0(2)	4.4(2)	−3.52(19)
O1	60.4(8)	63.2(9)	50.0(8)	−23.3(6)	3.5(7)	−2.6(6)
O2	44.6(7)	73.4(10)	46.5(8)	−14.5(7)	8.6(6)	0.5(6)
N1	44.1(8)	39.4(9)	38.7(8)	−1.5(6)	4.3(7)	−2.9(6)
C1	45.7(9)	26.5(9)	38.8(9)	0.0(7)	4.5(7)	−0.1(6)
C2	44.3(9)	27.5(9)	47.8(10)	2.1(7)	3.6(8)	−0.5(7)
C3	51.1(10)	43.9(11)	59.8(12)	−10.9(9)	−0.7(9)	−0.1(8)
C4	49.6(10)	51.5(13)	83.9(15)	−9.5(11)	−7.8(11)	−1.9(9)
C5	43.1(10)	47.7(12)	93.3(17)	7.7(11)	8.7(11)	−1.4(8)
C6	52.1(11)	48.6(12)	69.4(14)	9.3(10)	21.8(10)	2.4(9)
C7	49.8(9)	33.1(10)	53.9(11)	5.3(8)	12.2(9)	2.3(7)
C8	61.4(11)	55.6(12)	43.6(11)	0.4(9)	18.1(9)	3.8(9)
C9	59.5(11)	53.4(12)	35.2(10)	−2.3(8)	6.3(9)	−1.8(9)
C10	47.9(9)	33.7(10)	43.1(10)	−1.7(8)	2.8(8)	2.5(7)
O3	61.7(8)	56.1(9)	49.7(8)	0.6(7)	15.3(7)	4.7(7)

Table 4 Bond Lengths for C$_{10}$H$_{10}$ClNO$_3$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C10	1.197(2)	C2	C7	1.427(3)
O2	C10	1.315(2)	C3	C4	1.362(3)
N1	C1	1.331(2)	C4	C5	1.399(3)
N1	C9	1.354(2)	C5	C6	1.357(3)
C1	C2	1.415(2)	C6	C7	1.422(2)
C1	C10	1.509(2)	C7	C8	1.401(3)
C2	C3	1.424(2)	C8	C9	1.355(3)

Table 5 Bond Angles for C$_{10}$H$_{10}$ClNO$_3$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C9	124.09(15)	C5	C6	C7	120.41(19)
N1	C1	C2	119.36(16)	C6	C7	C2	118.86(18)
N1	C1	C10	115.34(14)	C8	C7	C2	119.20(16)
C2	C1	C10	125.22(15)	C8	C7	C6	121.94(18)
C1	C2	C3	123.64(17)	C9	C8	C7	120.50(17)
C1	C2	C7	117.53(15)	N1	C9	C8	119.31(18)
C3	C2	C7	118.83(16)	O1	C10	O2	125.60(16)
C4	C3	C2	119.89(19)	O1	C10	C1	123.67(15)
C3	C4	C5	121.3(2)	O2	C10	C1	110.72(15)
C6	C5	C4	120.73(18)				

Table 6 Hydrogen Bonds for C$_{10}$H$_{10}$ClNO$_3$.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O2	H2	O3	0.82	1.71	2.5174(18)	167.6

Table 7 Torsion Angles for $C_{10}H_{10}ClNO_3$.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C1	C2	C3	178.63(15)	C3	C2	C7	C8	−178.78(16)
N1	C1	C2	C7	−0.8(2)	C3	C4	C5	C6	0.8(3)
N1	C1	C10	O1	169.25(16)	C4	C5	C6	C7	−0.2(3)
N1	C1	C10	O2	−9.5(2)	C5	C6	C7	C2	−0.6(3)
C1	N1	C9	C8	−0.2(3)	C5	C6	C7	C8	179.02(18)
C1	C2	C3	C4	−179.67(18)	C6	C7	C8	C9	−179.88(18)
C1	C2	C7	C6	−179.77(15)	C7	C2	C3	C4	−0.3(3)
C1	C2	C7	C8	0.6(2)	C7	C8	C9	N1	0.1(3)
C2	C1	C10	O1	−7.6(3)	C9	N1	C1	C2	0.5(2)
C2	C1	C10	O2	173.66(16)	C9	N1	C1	C10	−176.50(15)
C2	C3	C4	C5	−0.5(3)	C10	C1	C2	C3	−4.6(3)
C2	C7	C8	C9	−0.3(3)	C10	C1	C2	C7	175.98(15)
C3	C2	C7	C6	0.8(2)					

Table 8 Hydrogen Atom Coordinates ($Å×10^4$) and Isotropic Displacement Parameters ($Å^2×10^3$) for $C_{10}H_{10}ClNO_3$.

Atom	x	y	z	U(eq)
H2	5523.49	3474.82	2924.49	82
H1	4660(20)	4052(13)	6420(30)	60(6)
H3	1362.6	3289.37	2102.47	62
H4	−771.86	3252.9	2190.27	75
H5	−1658.04	3651.78	4879.61	74
H6	−422.43	4126.72	7495.55	67
H8	1717.19	4486.26	9094.88	63
H9	3855.08	4548.74	9032.91	59
H3A	6590(20)	3250(16)	550(20)	83
H3B	6650(20)	2422(11)	1650(30)	83

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