

Electronic Supplementary Information

C₈H₆IN₃O₄: A birefringent crystal induced by the uniformly aligned hybrid groups†

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Reagents

$C_8H_5IN_2O$ (97%) and HNO_3 (65%) were purchased from Aladdin and used as received.

Synthesis of $C_8H_6IN_3O_4$ (**1**)

Crystals of **1** were synthesized by a simple evaporation technique of aqueous solution. The raw reactants of $C_8H_5IN_2O$ (0.223 g, 1 mmol) and HNO_3 (0.630g, 10 mmol) were mixed together in a glass beaker. The solution was stirred with a magnetic mixer for 30 minutes, and then filtered through a filter paper to obtain a clear, transparent liquid. The solution was then left to stand at room temperature for crystal growth. After several days of growth, colourless block crystals of **1** were obtained, with dimensions reaching $2 \times 1 \times 1$ mm³ (Figure S1). The purity of the obtained product is confirmed by the powder X-ray diffraction (XRD) patterns, which were taken on a Rigaku MiniFlex II diffractometer (Cu $K\alpha$ radiation) in the range of $2\theta = 7^\circ$ – 60° with a step width of 0.01° and a sampling rate of 1° min^{-1} . The results agree well with the calculated XRD patterns from single-crystal XRD analyses (Figure 1a).

Single-Crystal Structure Determination

Colorless block crystals of **1** was selected using an optical microscope for single-crystal XRD analysis. The diffraction data were collected by using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K on the XtaLAB Pro II AFC12 instrument 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.solve³ structure solution program using Charge Flipping and refined with the SHELXL⁴ 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. The torsion angles and hydrogen atom coordinates and isotropic displacement parameters are shown in Tables S6 and S7, respectively.

Thermal Stability Analysis

The thermogravimetric (TG) and differential thermal analysis (DTA) of **1** was carried out on a NETZSCH STA 449F3 simultaneous analyzer. About 6.372 mg of **1** was placed in Al_2O_3 crucibles, heated at a rate of $15 \text{ }^\circ\text{C min}^{-1}$ from room temperature to $900 \text{ }^\circ\text{C}$ 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.

Computational Methods

The first-principles calculations for **1** were performed by CASTEP⁵ 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 1s¹, C 2s²2p², N 2s²2p³, O 2s²2p⁴ and I 5s²5p⁵ electrons were treated as valence electrons. The kinetic energy cutoff of 630 eV and dense 1 × 2 × 1 Monkhorst-Pack⁹ k-point meshes in the Brillouin zones were chosen. The linear optical properties were examined based on the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. 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.

To explore the polarizability anisotropy and electronic structure of [C₈H₆IN₂O]⁺ and [NO₃]⁻ systematic calculations were implemented via the Gaussian 09 package¹⁰ with the hybrid B3LYP functional at 3-21G level. After that, the calculation results were analyzed by the Multiwfn 3.8 code.¹¹ The polarizability anisotropy was defined by the static polarizability, according to the following Eq (1). Detailed static polarizability has been shown in the Table S8. It is clear that the polarizability is highly anisotropic.

$$\delta = \sqrt{[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2)]/2} \quad \text{Eq (1)}$$

where α represents the static polarizability, and δ is the polarizability anisotropy.

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.



Figure S1. Single crystals photo of 1.

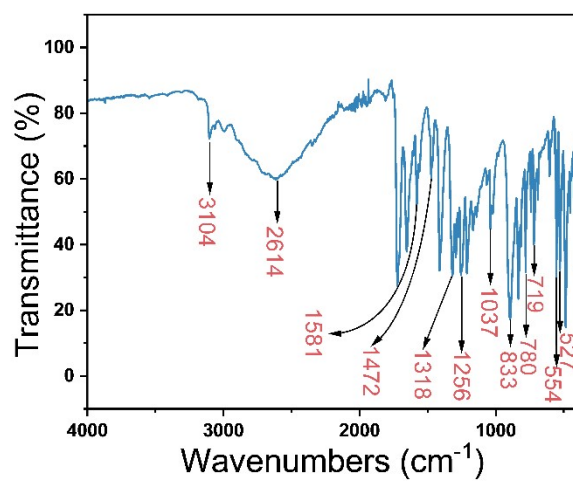


Figure S2. Infrared spectrum of 1.



Figure S3. Crystal used for birefringence measurements with thickness of 20.4 μm .

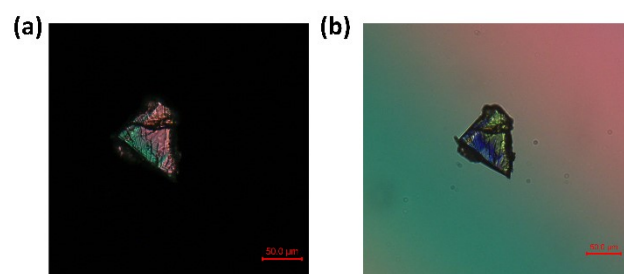


Figure S4. The Original (a) and completely extinct (b) crystal of 1.

Table S1. Crystal Data and Structural Refinement for C₈H₆IN₃O₄.

Empirical formula	C ₈ H ₆ IN ₃ O ₄
Formula weight	335.06
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	<i>Pnma</i>
a/Å	11.3638(4)
b/Å	6.3747(3)
c/Å	15.1177(5)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	1095.14(7)
Z	4
ρ_{calc} g/cm ³	2.032
μ /mm ⁻¹	2.927
F(000)	640.0
Crystal size/mm ³	0.06 × 0.05 × 0.05
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	4.484 to 54.076
Index ranges	-13 ≤ h ≤ 14, -8 ≤ k ≤ 7, -17 ≤ l ≤ 18
Reflections collected	6145
Independent reflections	1260 [R _{int} = 0.0428, R _{sigma} = 0.0277]
Data/restraints/parameters	1260/0/98
Goodness-of-fit on F ²	1.051
Final R indexes [I >= 2 σ (I)]	R ₁ = 0.0294, wR ₂ = 0.0707
Final R indexes [all data]	R ₁ = 0.0470, wR ₂ = 0.0800

Table S2. The Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_8\text{H}_6\text{IN}_3\text{O}_4$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	$U(\text{eq})$	BVS
I1	5082.1(3)	7500	7120.9(2)	76.2(2)	1.067
O1	431(3)	7500	5827(2)	83.0(12)	
N2	2273(3)	7500	3580(2)	50.0(9)	2.826
N3	529(3)	7500	4338(2)	55.9(9)	2.701
C1	4172(4)	7500	5915(3)	53.5(10)	
C2	4764(4)	7500	5115(3)	52.7(11)	
C3	4149(3)	7500	4331(3)	50.8(10)	
C4	2933(3)	7500	4355(2)	44.3(9)	
C5	1131(4)	7500	3591(2)	54.8(11)	
C6	1052(4)	7500	5177(3)	56.3(11)	
C7	2331(3)	7500	5157(2)	46.3(9)	
C8	2971(4)	7500	5944(3)	55.1(11)	
O2	1947(3)	2500	5607.0(18)	64.5(8)	
O3	3321(2)	2500	6589(2)	70.9(10)	
O4	1513(2)	2500	6992.8(18)	75.5(11)	
N1	2275(3)	2500	6398(2)	52.0(9)	5.026

Table S3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_8\text{H}_6\text{IN}_3\text{O}_4$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	87.8(3)	86.7(4)	54.1(3)	0	-34.27(16)	0
O1	59.8(18)	146(4)	42.7(18)	0	11.7(16)	0
N2	42.7(18)	78(3)	29.0(17)	0	-1.9(14)	0
N3	40.9(18)	84(3)	43(2)	0	1.4(16)	0
C1	63(3)	60(3)	37(2)	0	-14.9(19)	0
C2	45(2)	59(3)	55(3)	0	-7.6(19)	0
C3	46(2)	65(3)	42(2)	0	0.4(18)	0
C4	45(2)	55(2)	33.7(19)	0	-4.3(16)	0
C5	47(2)	84(3)	33(2)	0	-4.3(17)	0
C6	52(2)	80(3)	37(2)	0	5.5(18)	0
C7	50(2)	57(3)	32(2)	0	-2.4(17)	0
C8	65(3)	67(3)	33(2)	0	-1.5(18)	0
O2	57.0(17)	99(2)	37.4(16)	0	-4.1(13)	0
O3	37.0(16)	117(3)	58.7(19)	0	-1.6(14)	0
O4	43.9(16)	144(3)	38.8(16)	0	6.3(13)	0
N1	43(2)	71(3)	42(2)	0	1.7(15)	0

Table S4. Bond Lengths for C₈H₆IN₃O₄.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C1	2.096(4)	C2	C3	1.375(6)
O1	C6	1.210(5)	C3	C4	1.382(5)
N2	C4	1.392(4)	C4	C7	1.393(5)
N2	C5	1.298(5)	C6	C7	1.454(6)
N3	C5	1.321(5)	C7	C8	1.394(5)
N3	C6	1.401(5)	O2	N1	1.252(4)
C1	C2	1.384(6)	O3	N1	1.223(4)
C1	C8	1.365(6)	O4	N1	1.249(4)

Table S5. Bond Angles for C₈H₆IN₃O₄.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	N2	C4	121.9(3)	O1	C6	N3	119.2(4)
C5	N3	C6	123.7(3)	O1	C6	C7	126.9(4)
C2	C1	I1	121.4(3)	N3	C6	C7	113.9(3)
C8	C1	I1	117.7(3)	C4	C7	C6	120.6(3)
C8	C1	C2	120.9(4)	C4	C7	C8	119.1(4)
C3	C2	C1	120.4(4)	C8	C7	C6	120.3(3)
C2	C3	C4	119.1(4)	C1	C8	C7	119.6(4)
N2	C4	C7	118.0(4)	O3	N1	O2	121.0(3)
C3	C4	N2	121.1(3)	O3	N1	O4	120.2(3)
C3	C4	C7	120.9(3)	O4	N1	O2	118.8(3)
N2	C5	N3	121.9(4)				

Table S6 Torsion Angles for C₈H₆IN₃O₄.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
I1	C1	C2	C3	180.000(1)	C3	C4	C7	C6	180.000(1)
I1	C1	C8	C7	180.000(1)	C3	C4	C7	C8	0.000(1)
O1	C6	C7	C4	180.000(1)	C4	N2	C5	N3	0.000(1)
O1	C6	C7	C8	0.000(1)	C4	C7	C8	C1	0.000(1)
N2	C4	C7	C6	0.000(1)	C5	N2	C4	C3	180.000(1)
N2	C4	C7	C8	180.000(1)	C5	N2	C4	C7	0.000(1)
N3	C6	C7	C4	0.000(1)	C5	N3	C6	O1	180.000(1)
N3	C6	C7	C8	180.000(1)	C5	N3	C6	C7	0.000(1)
C1	C2	C3	C4	0.000(1)	C6	N3	C5	N2	0.000(1)
C2	C1	C8	C7	0.000(1)	C6	C7	C8	C1	180.000(1)
C2	C3	C4	N2	180.000(1)	C8	C1	C2	C3	0.000(1)
C2	C3	C4	C7	0.000(1)					

Table S7. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for C₈H₆IN₃O₄.

Atom	x	y	z	U(eq)
H2	2632.14	7500	3078.73	60
H3	-226.25	7500	4307.9	67
H2A	5581.86	7500	5106.53	63
H3A	4545.12	7500	3793.3	61
H5	724.83	7500	3056.85	66
H8	2582.87	7500	6485.64	66

Table S8. Static polarizability of different units.

Units	Static polarizability					
	xx	xy	yy	xz	yz	zz
[C ₈ H ₆ IN ₂ O] ⁺	189.67	28.82	126.75	0.00	0.00	31.58
[NO ₃] ⁻ ,	21.04	0.00	21.05	0.00	0.00	4.34

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