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Crystal structure of (*E*)-*N'*-((1,8-dihydropyren-1-yl)-methylene)picolinohydrazide, C₂₃H₁₅N₃O

<https://doi.org/10.1515/ncrs-2019-0297>

Received April 24, 2019; accepted June 24, 2019; available online July 18, 2019

Abstract

C₂₃H₁₅N₃O, monoclinic, *P*₂₁/*c* (no. 14), *a* = 14.4372(3) Å, *b* = 11.9366(2) Å, *c* = 10.23409(19) Å, β = 106.963(2)°, *V* = 1686.92(6) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0380, *wR*_{ref}(*F*²) = 0.1055, *T* = 115.2(3) K.

CCDC no.: 1909229

The asymmetric unit of the title structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals purchased were used without further purification. The title compound was synthesized from pyrene-1-carbaldehyde by condensation reaction [5].

To a 100 mL flask, pyrene-1-carbaldehyde (1 mmol, 230 mg) was dispersed in 30 mL absolute ethanol. Under vigorously stirring, 20 mL colorless clarified solution containing picolinohydrazide (1 mmol, 137 mg) was added to the above, two drops of acetic acid were also added as catalyst. After the addition, the stirred mixture was refluxed for 4 h. At the beginning of stirring, a pale yellow clear solution formed. About one hour later, yellow precipitate appeared. The precipitate was filtered, washed 3 times with

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.20 × 0.10 × 0.10 mm
Wavelength:	Cu Kα radiation (1.54184 Å)
μ:	0.69 mm ^{−1}
Diffractometer, scan mode:	SuperNova, ω
θ _{max} , completeness:	71.4°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	6586, 3193, 0.019
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 2887
<i>N</i> (<i>param</i>) _{refined} :	244
Programs:	CrysAlis ^{PRO} [1], Olex2 [2], SHELX [3, 4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
O1	0.84562(6)	0.28316(8)	0.07460(8)	0.0270(2)
N1	0.99204(8)	0.16827(10)	0.38576(11)	0.0292(3)
N2	0.83471(7)	0.29280(9)	0.29246(10)	0.0226(2)
H2	0.8614	0.2780	0.3774	0.027*
N3	0.74812(7)	0.35073(9)	0.25153(10)	0.0228(2)
C1	1.06772(10)	0.10087(13)	0.43467(14)	0.0344(3)
H1	1.0874	0.0865	0.5280	0.041*
C2	1.11881(10)	0.05097(12)	0.35510(15)	0.0337(3)
H2A	1.1711	0.0041	0.3938	0.040*
C3	1.09007(11)	0.07274(13)	0.21693(15)	0.0389(4)
H3	1.1225	0.0402	0.1602	0.047*
C4	1.01222(10)	0.14368(13)	0.16336(14)	0.0341(3)
H4	0.9923	0.1609	0.0707	0.041*
C5	0.96500(8)	0.18814(10)	0.25122(12)	0.0230(3)
C6	0.87669(8)	0.25982(10)	0.19658(12)	0.0216(3)
C7	0.70558(9)	0.36353(10)	0.34455(12)	0.0229(3)
H7	0.7343	0.3375	0.4328	0.028*
C8	0.61136(8)	0.41954(10)	0.31002(11)	0.0212(3)
C9	0.58717(10)	0.49575(11)	0.20178(12)	0.0259(3)
H9	0.6337	0.5164	0.1599	0.031*
C10	0.49550(10)	0.54092(10)	0.15602(12)	0.0275(3)
H10	0.4817	0.5928	0.0851	0.033*
C11	0.42331(9)	0.51012(10)	0.21417(12)	0.0250(3)
C12	0.32611(10)	0.55182(11)	0.16378(14)	0.0320(3)
H12	0.3107	0.6017	0.0908	0.038*
C13	0.25685(10)	0.52004(12)	0.22011(15)	0.0362(3)
H13	0.1946	0.5488	0.1854	0.043*
C14	0.27669(9)	0.44313(12)	0.33208(15)	0.0326(3)
C15	0.20523(11)	0.40585(14)	0.39038(19)	0.0450(4)

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H15	0.1422	0.4324	0.3564	0.054*
C16	0.22718(12)	0.33066(14)	0.4969(2)	0.0485(4)
H16	0.1786	0.3063	0.5330	0.058*
C17	0.32056(12)	0.29072(13)	0.55126(17)	0.0401(4)
H17	0.3342	0.2406	0.6240	0.048*
C18	0.39448(10)	0.32521(11)	0.49746(13)	0.0279(3)
C19	0.49203(10)	0.28662(10)	0.55046(13)	0.0277(3)
H19	0.5078	0.2395	0.6261	0.033*
C20	0.56213(9)	0.31664(10)	0.49373(12)	0.0232(3)
H20	0.6245	0.2888	0.5303	0.028*
C21	0.54220(8)	0.39069(10)	0.37808(11)	0.0197(2)
C22	0.44645(8)	0.43457(10)	0.32701(12)	0.0212(3)
C23	0.37259(9)	0.40128(10)	0.38578(13)	0.0248(3)

ethanol/water (1:1) to obtain yellow powder. Yield: *ca* 85%. The yellow powder (0.05 mmol, 17.5 mg) was dissolved in methanol/dichloromethane (1:1) (10 mL) under stirring to give a pale yellow solution to evaporate slowly at room temperature. After three days, yellow plate crystals appeared. Yield: *ca* 70%.

Experimental details

The H atoms were added geometrically using riding models and refined isotropically. Their *U*_{iso} values were set to 1.2*U*_{eq} of the parent C and N atoms, and 1.5*U*_{eq} of the parent O atoms.

Comment

Various transition-metal ions are important for the life of organisms [6]. Fluorescent probe and chemosensors have been widely focused to detect transition-metal ions, especially in living cells and *in vivo* [7–9]. To our knowledge, the fluorescent probes based on pyrene derivatives have not been widely reported [5, 10, 11]. Herein, we report a new pyrene-derived compound that contains an amide functional group, a pyridine ring and a carbon-nitrogen double bond moiety that can coordinate to metal ions. The title compound may be the potential probe for certain metal ion.

The asymmetric unit of the title compound contains a neutral molecule (see the figure). The amide C=O bond length is 1.2291(15) Å. The bond length of C7–N3 is 1.2837(15) Å, which showed that the form of a double-bond between C7 and N3 [12]. The dihedral angle between pyrene moiety and pyridine ring is 42.66°. There are obvious intermolecular

hydrogen bonds between imine and carbonyl oxygen (D···A: 2.986 Å), which link adjacent molecules into a one-dimensional supramolecular chain structure.

Acknowledgements: This work was supported by the project of scientific and technological in Henan Province (Project No. 172102310433).

References

1. Rigaku. CrysAlis PRO Software system, version 1. 171. 38. 43f. Rigaku Oxford Diffraction (2015).
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42** (2009) 339–341.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Sheldrick, G. M.: SHELXT-integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
5. Zhou, Y.; Wang, F.; Kim, Y.; Kim, S.; Yoon, J.: Cu²⁺-selective ratiometric and “off-on” sensor based on the rhodamine derivative bearing pyrene group. *Org. Lett.* **11** (2009) 4442–4445.
6. Lippard, S. J.; Berg, J. M.: Principles of bioinorganic chemistry. University science books, Mill Valley, CA (1994).
7. Xi, P.; Dou, J.; Huang, L.; Xu, M.; Chen, F.; Wu, Y.; Bai, D.; Li, W.; Zeng, Z.: A selective turn-on fluorescent sensor for Cu(II) and its application in imaging in living cells. *Sens. Actuators, B* **148** (2010) 337–341.
8. Yang, H.; Zhou, Z.; Huang, K.; Yu, M.; Li, F.; Yi, T.; Huang, C.: Multisignaling optical-electrochemical sensor for Hg²⁺ based on a rhodamine derivative with a ferrocene unit. *Org. Lett.* **9** (2007) 4729–4732.
9. Diao, Q.; Ma, P.; Lv, L.; Li, T.; Sun, Y.; Wang, X.; Song, D.: A water-soluble and reversible fluorescent probe for Al³⁺ and F[−] in living cells. *Sens. Actuators B* **229** (2016) 138–144.
10. Wang, F.; Nandhakumar, R.; Moon, J. H.; Kim, K. M.; Lee, J. Y.; Yoon, J.: Ratiometric fluorescent chemosensor for silver ion at physiological pH. *Inorg. Chem.* **50** (2011) 2240–2245.
11. Manandhar, E.; Broome, J. H.; Myrick, J.; Lagrone, W.; Cragg, P. J.; Wallace, K. J.: A pyrene-based fluorescent sensor for Zn²⁺ ions: a molecular ‘butterfly’. *Chem. Commun.* **47** (2011) 8796–8798.
12. Saravanan, A.; Shyamsivappan, S.; Suresh, T.; Subashini, G.; Kadirvelu, K.; Bhuvanesh, N.; Nandhakumar, R.; Mohan, P. S.: An efficient new dual fluorescent pyrene based chemosensor for the detection of bismuth(III) and aluminium(III) ions and its applications in bio-imaging. *Talanta* **198** (2019) 249–256.