Synthesis and Crystal Structure of (Z)-2-(2-oxoacenaphthylen-1(2H)-ylidene)-2-(pyridin-3-yl) Acetonitrile

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Abstract. In this paper, a new phenalenone derivative (Compound 1) was synthesized. Compound 1 was characterized by ^{1}H NMR and their structures determined by single crystal X-ray diffraction. Single crystal X-ray diffraction (SCXRD) analysis revealed that Compound 1 crystallized in the monoclinic space group $P2_1/c$. There is one ketone carbonyl, one double bond and pyridine ring in this structure. CCDC no.: 2394066.

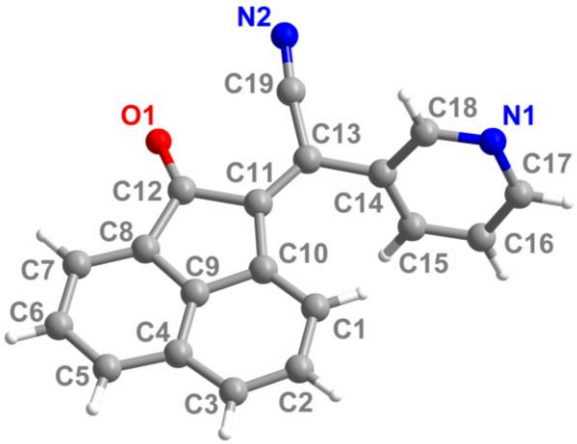

Figure 1. The crystal structure of Compound 1

Keywords: Crystal structure, Molecular design, Phenalenone.

1. Introduction

All starting materials and solvents were purchased from commercial sources and used as supplied without additional purification unless otherwise mentioned. Acenthoquinone (1 mmol) and 2-(pyridine-3-yl) acetonitrile (1.3 mmol) were added successively to the round-bottomed flask, followed by acetonitrile, and reflux was carried out at 70ºC for 1 h. After the solvent was removed by vacuum distillation, the crude product was separated and purified by silica gel chromatography with methylene chloride and ethyl acetate (v/v = 100/1) as eluent. We obtained the yellow compound with a yield of 75%. Subsequently, Compound 1 was further recrystallized with methylene chloride at room temperature in four days by evaporation (Figure 2).

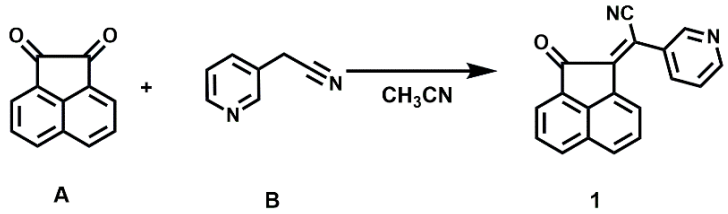

Figure 2. Synthesis of Compound 1

2. Experimental

Table 1. Data collection and handling

Crystal:	light yellow needle
Size:	0.1×0.01×0.001 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	0.091 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture, φ and ω
θ_{max}, completeness:	25.025°, 75%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	36446, 4634, 0.1019
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma (I_{obs})$, 3323
$N(param)_{refined}$:	397
Programs:	Olex2 [1], Bruker [2], SHELX [3], Diamond [4]

Single-crystal X-ray diffraction data for Compound 1 were obtained directly from the above preparations. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

3. Comment

Phenalenone-based compounds are a class of molecules with large planar structure and multiple substitution sites. It is used in used for fluorescence detection of target analytes (glutathione, cysteine, etc.) as a fluorophore [5-7] and the design and synthesis of targeted antitumor lead compounds [8-9], such as Mcl-1/Bcl-2 protein inhibitors. In order to better study and utilize these molecules, we try to structurally modify different substituents at different sites, and obtain the intermediate compounds, the title Compound 1.

In this paper, we reported the synthesis and crystal structure of Compound 1. Single crystal X-ray diffraction (SCXRD) analysis revealed that Compound 1 crystallized in the monoclinic space group P21/c. There is one ketone carbonyl and one double bond in this structure. The ketone bonds were determined by the distance of 1.217 Å (C12-O1). [10] The double bond was identified by the distance of 1.342 Å (C11-C13). The dihedral angle of the pyridine ring and acenaphthenone ring is 67.74°. In general, all bond lengths and angles are in the expected ranges.

Table 2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$).

Atom	x	y	z	U_{iso}*/U_{eq}
O2	0.45539(19)	0.31355(7)	0.80004(7)	0.0228(4)
C21	0.5277(3)	0.37084(10)	0.69131(11)	0.0190(5)
C25	0.5780(3)	0.38659(11)	0.56427(11)	0.0229(5)
C31	0.4675(3)	0.24923(10)	0.68854(10)	0.0165(5)
C32	0.4217(3)	0.18668(10)	0.71257(11)	0.0168(5)
C38	0.3573(3)	0.17849(10)	0.78300(12)	0.0189(5)
C29	0.5079(3)	0.27283(10)	0.61697(11)	0.0178(5)
N4	0.2966(2)	0.16517(9)	0.83551(10)	0.0269(4)
C36	0.5887(3)	0.03993(10)	0.60529(11)	0.0223(5)
H36	0.696057	0.025171	0.584062	0.027
N3	0.2756(2)	0.01650(9)	0.63041(9)	0.0226(4)
C34	0.2788(3)	0.07630(10)	0.66597(11)	0.0198(5)
H34	0.171635	0.088880	0.688507	0.024
C37	0.5880(3)	0.10151(10)	0.64091(11)	0.0225(5)
H37	0.694467	0.130409	0.644340	0.027
C39	0.4309(3)	-0.00041(10)	0.60073(11)	0.0213(5)
H39	0.432331	-0.042621	0.575065	0.026
C33	0.4290(3)	0.12123(10)	0.67207(10)	0.0175(5)
C30	0.5418(3)	0.34474(10)	0.62227(11)	0.0173(5)
C22	0.5545(3)	0.43962(11)	0.70516(12)	0.0248(5)
H22	0.544633	0.457910	0.751738	0.030
C20	0.4796(3)	0.31318(10)	0.73655(11)	0.0170(5)
C24	0.6077(3)	0.45697(11)	0.58019(13)	0.0279(5)
H24	0.635555	0.487568	0.543069	0.034
C23	0.5971(3)	0.48228(11)	0.64832(13)	0.0311(6)
H23	0.619173	0.529926	0.657203	0.037
C28	0.5074(3)	0.24299(11)	0.55037(11)	0.0246(5)
H28	0.485945	0.194945	0.544302	0.030
C26	0.5759(3)	0.35377(12)	0.49697(12)	0.0271(5)
H26	0.600147	0.379610	0.455765	0.032
C27	0.5392(3)	0.28498(12)	0.49097(11)	0.0292(6)
H27	0.534880	0.264297	0.444811	0.035
O1	1.05199(18)	0.70232(7)	0.82024(7)	0.0203(3)
C14	1.0346(3)	0.82741(10)	0.62047(10)	0.0155(4)
N1	1.1762(2)	0.87653(9)	0.52098(9)	0.0253(4)
C10	0.9696(3)	0.87983(10)	0.77552(10)	0.0154(4)
C1	0.9517(3)	0.94333(10)	0.74309(11)	0.0189(5)
H1	0.966509	0.948353	0.693463	0.023
C19	1.1312(3)	0.71801(11)	0.67964(10)	0.0171(5)
C8	0.9775(3)	0.80901(10)	0.87838(10)	0.0161(4)
C2	0.9110(3)	1.00086(10)	0.78473(11)	0.0209(5)
H2	0.897751	1.044616	0.762034	0.025
C12	1.0219(3)	0.76402(10)	0.81913(11)	0.0162(4)
C5	0.8959(3)	0.91818(11)	0.96573(11)	0.0206(5)
H5	0.868577	0.954738	0.996806	0.025
C3	0.8896(3)	0.99646(10)	0.85648(11)	0.0199(5)
H3	0.861046	1.036629	0.882288	0.024
C11	1.0178(3)	0.80975(10)	0.75258(10)	0.0150(4)
C9	0.9497(3)	0.87577(10)	0.85011(10)	0.0148(4)
C4	0.9099(3)	0.93249(10)	0.89225(10)	0.0174(5)
C13	1.0571(3)	0.78661(10)	0.68818(10)	0.0155(4)
C18	1.1854(3)	0.84077(10)	0.58244(10)	0.0194(5)
H18	1.303054	0.823467	0.601129	0.023
C15	0.8626(3)	0.85174(11)	0.59262(11)	0.0236(5)
H15	0.755128	0.842822	0.616575	0.028
C7	0.9634(3)	0.79676(10)	0.94997(11)	0.0194(5)
H7	0.981734	0.751851	0.969633	0.023
C17	1.0079(3)	0.90006(11)	0.49650(11)	0.0240(5)
H17	0.997182	0.926119	0.453315	0.029
C6	0.9209(3)	0.85284(11)	0.99332(11)	0.0223(5)
H6	0.909264	0.845309	1.042856	0.027
C16	0.8496(3)	0.88880(11)	0.53010(11)	0.0243(5)
H16	0.733395	0.906446	0.510248	0.029
N2	1.1980(2)	0.66652(9)	0.66689(9)	0.0243(4)

References

[1] 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, 2009, 42, pp. 339-341.

[2] Bruker. APEX2, SAINT and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2012.

[3] G. M. Sheldrick, Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, pp. 3-8.

[4] Brandenburg, K. DIAMOND. Visual Crystal Structure Information System. Ver. 4.0; Crystal Impact: Bonn, Germany, 2015.

[5] Zhang H., Wang C.X., Wang G., Wang K., Jiang K. Thrombin-mediated ratiometric two-photon fluorescent probe for selective imaging of endogenous ultratrace glutathione in platelet. Biosensors and Bioelectronics, 2016, 78, pp. 344-350.

[6] Zhang X.D., Wang Z.Q., Guo Z.W., He N.Z., Liu P., Xia D.S., Yan X.F. and Zhang Z.C. A novel turn-on fluorescent probe for selective sensing and imaging of glutathione in live cells and organisms. Analyst, 2019, 144, pp. 3260-3266.

[7] Zhang X.D., Wang Z.Q., Guo Z.W., Song T., He N.H., Zhu J.J., Cao K.K., and Zhang Z.C. A "Three-in-One" Multifunctional Probe for Bcl-2/Mcl-1 Profiling and Visualizing in Situ. ChemBioChem, 2021, 22, pp. 326-329.

[8] Song T., Wang Z.Q., Ji F.L., Feng Y.G., Fan Y.D., Chai G.B., Li X.Q., Li Z.Q. and Zhang Z.C. Deactivation of Mcl-1 by dual-function small-molecule inhibitors targeting Bcl-2 homology 3 domain and facilitating Mcl-1 ubiquitination. Angewandte chemie international edition, 2016, 55, pp. 14248-14250.

[9] Zhu J.J., Wang Z.Q., Guo Z.W., Zhang X.D., Song T., Guo Y.F., Ji T., Zhang Z.C. Structure-based design, synthesis, and evaluation of Bcl-2/Mcl-1 dual inhibitors. Arch Pharm, 2020. 353(5), pp. e2000005.

[10] Z. Kristallogr. N. Cryst. Struct. 2024, 239, pp. 855-856.