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Structure and spectral property of 8-(2-(5-(4-methylphenyl)-2-thienyl)vinyl)-10,10-dimethyl-10*H*-pyrido[1,2-*a*]indolium perchlorate

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Abstract The title compound 8-(2-(5-(4-methylphenyl)-2-thienyl)vinyl)l-10,10-dimethyl-10*H*-pyrido[1,2-*a*]indolium perchlorate (**3**) has been synthesized by cycloaddition and condensation reactions, and characterized by elemental analysis, IR, ^{1}H NMR, and single-crystal X-ray diffraction. The crystal structure analysis exhibits that the molecule of **3** possesses good coplanarity, and the three rings (10*H*-pyrido[1,2-*a*]indolium, thienyl and phenyl) and vinyl moiety can make up a large conjugated system. Its UV-Vis and fluorescence spectra were measured, and found that it displays larger maximum absorptions and emission wavelengths in comparison with 8-(4-methylphenyl)vinyl analogue.

Keywords Synthesis · 10*H*-pyrido[1,2-*a*]indolium perchlorate · Crystal structure · Spectral property

Introduction

Substituted 10*H*-pyrido[1,2-*a*]indolium perchlorates can be used as photosensitive dyes, fluorescent whiteners, and organic light-guide sensitizers [1–3]. Since the first substituted 10*H*-pyrido[1,2-*a*]indolium perchlorate was prepared by Chapman in 1974, many of these types of compounds, such as methyl, phenyl, styryl or furyl-substituted 10*H*-pyrido[1,2-*a*]indolium perchlorates, have been synthesized [4–8]. On the basis of synthesis and spectral property study of this class of compounds, Liu

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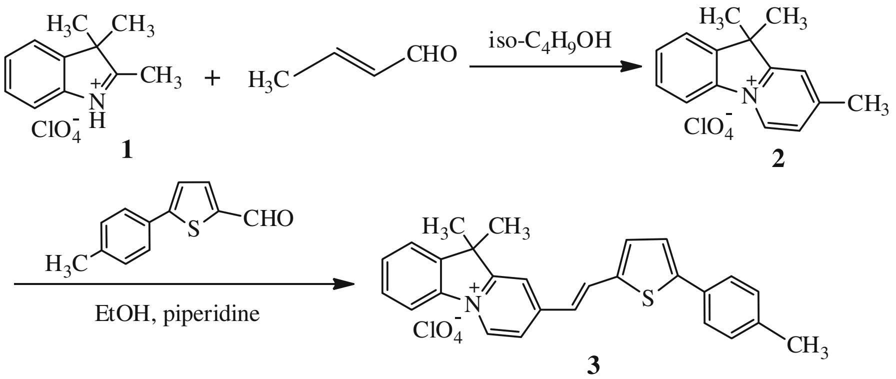


Scheme 1 Synthetic route for the target compound

et al. [9] found that the introduction of a conjugated substituent at the 8-position of 10*H*-pyrido[1,2-*a*]indolium ring can yield a significant red shift of the maximum absorption and maximum emission, and no remarkable change was observed while the introduction was at the 6-position.

In order to further study the relationship between the structure and maximum absorption, the crystal structures of three compounds in this family were determined by single-crystal X-ray diffraction [10–12], and found that the dihedral angle between 10*H*-pyrido[1,2-*a*]indolium and substituted phenyl at the 8-position is small, ranging from 27.2° to 29.8°. Therefore, the two groups are able to make up a conjugated system, and this is the reason for a significant red shift when a conjugated substituent was introduced at the 8-position. Considering that thiophene possesses unique optical properties, and electronic transmission capability [13], herein, we introduced 5-[(4-methyphenyl)-2-thienyl] vinyl onto the 8-position of 10*H*-pyrido[1,2-*a*]indolium and synthesized the target compound **3**, obtaining a compound with large maximum absorption and maximum emission. The structure was confirmed by elemental analysis, IR, ^{1}H NMR. The synthetic route is shown in Scheme 1.

Experimental

General

2,3,3-Trimethyl-3*H*-indolium perchlorate (**1**) [14] and 8,10,10-trimethyl-10*H*-pyrido[1,2-*a*]indolium perchlorate (**2**) [5] were prepared in our laboratory, respectively. 5-(4-Methylphenyl)-2-thiophene-carbaldehyde was prepared by the application of Vilsmeier formylation to 5-(4-methyphenyl)-2-thiophene [15, 16]. The other chemicals were of analytical grade and were distilled before use.

Melting point was determined with an X-5 microscopic melting-point apparatus and uncorrected. Elemental analyses were performed with a Vario EL III Elemental Analyzer. IR spectra were recorded in KBr pellet on a Nicolet-6700 infrared spectrophotometer. ^{1}H NMR spectra were carried out on a Varian Mercury Plus 400 spectrometer in DMSO-d_6 with TMS as internal standard. UV-Vis and fluorescence spectra were measured using acetonitrile as solvent (2×10^{-5} M) on a Shimdazu 2450PC UV-Vis a spectrophotometer and RF-5301PC fluorophotometer, respectively. X-ray data were collected on a Bruker Smart APEX CCD diffractometer.

Synthesis

A mixture of **2** (0.37 g, 1.2 mmol) and 5-(4-methyphenyl)-2-thiophenecarbaldehyde (0.24 g, 1.2 mmol) in anhydrous ethanol (10 mL) was added five drops of piperidine and was heated to refluxing temperature with stirring. After refluxing for 5 h, the resulting mixture was cooled to room temperature. Then the mixture was filtered under reduced pressure and the solid residue was recrystallized from ethanol-acetonitrile (V:V = 2:1), affording compound **3** as a red needle (0.46 g, yield 78.5%), m.p. 259.1–260.8 °C. Anal. Calcd. (%) for $C_{27}H_{24}ClNO_4S$: C 65.65, H 4.90, N 2.84; found: C 65.42, H 4.83, N 2.79. IR (KBr pellet, cm^{-1}), 1640.9 (m), 1362.2 (w), 1101.6 (s), 957.3 (s), 620.7 (m). ^{1}H NMR (DMSO-d_6, 400 MHz), δ1.78 [s, 6H, $C(CH_3)_2$], 2.39 (s, 3H, CH_3), 7.16 [d, $J = 16$ Hz, 1H, –CH=CH– (*E*)], 7.25–7.59 (m, 4H, Ph-H), 7.45–7.50 (m, 2H, thiophene-H), 7.66–8.21 (m, 4H, indole-H), 8.30 [d, $J = 16$ Hz, 1H, –CH=CH–(*E*)], 8.32 (d, $J = 6.8$ Hz, 1H, pyridinum-7-H), 8.65 (s, 1H, pyridinum-9-H), 9.66 (d, $J = 6.8$ Hz, 1H, pyridinum-6-H). The red single crystal was cultured from a mixture solution of ethanol and acetonitrile by slow evaporation at room temperature.

Crystal structure determination

A red crystal of the target compound with dimensions of $0.21 \times 0.14 \times 0.12$ mm^3 was selected for X-ray diffraction analysis. The data were collected by a Bruker Smart APEX CCD diffractometer equipped with a graphite-monochromated Mo*Kα* radiation ($\lambda = 0.71073$ Å) at 298(2) K. A total of 12,381 reflections were collected in the range of $1.65° \leq \theta \leq 25.05°$ by using a φ-ω scan mode, among which 4,262 ($R_{\text{int}} = 0.0279$) were unique ones. The structure was solved by direct methods and expanded by using difference Fourier techniques with SHELXS-97 [17]. All the non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located geometrically and refined isotropically. The final full-matrix least-squares refinement gave the final $R = 0.0488$, and $wR = 0.1257$ ($w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 1.3404P]$, where $P = (F_o^2 + 2F_c^2)/3$), $(\Delta\rho)_{\max} = 0.449$, $(\Delta\rho)_{\min} = -0.312$ e/Å^3. The molecular structure and the packing diagram in a unit-cell of compound **3** are shown in Figs. 1 and 2, respectively. The selected bond lengths, bond angles, and torsion angles are listed in Tables 1 and 2.

Results and discussion

Crystal structure

In the crystal structure of compound **3** (Fig. 1), the 10*H*-pyrido[1,2-*a*]indolium ring and a thiophene ring are connected with an *E*-type C=C bond, which is also

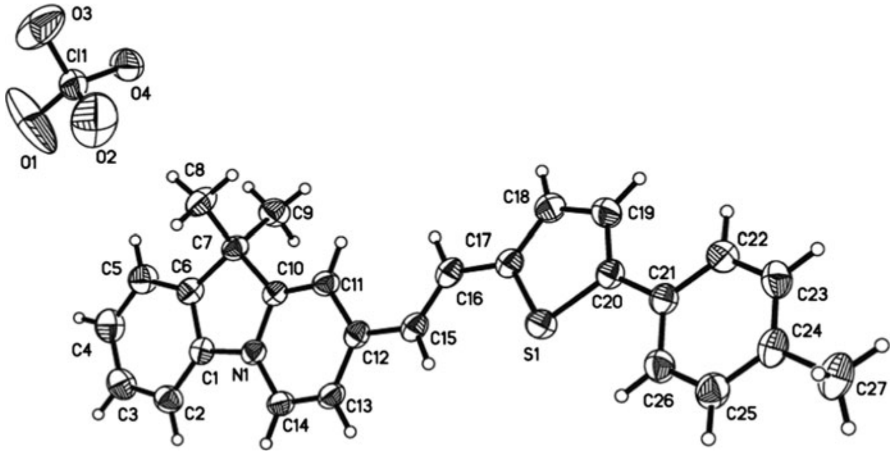


Fig. 1 Molecular structure of compound 3

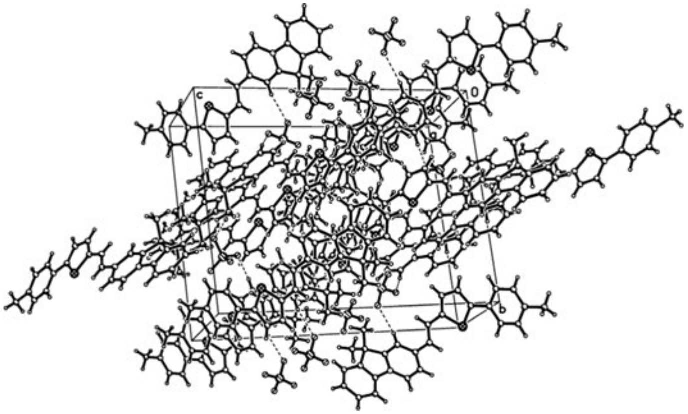


Fig. 2 Packing diagram in unit-cell of compound 3

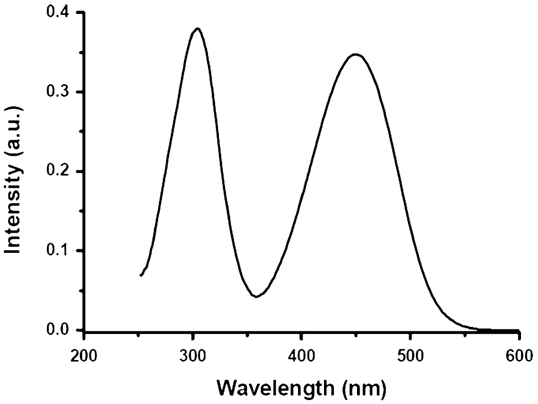
Table 1 Selected bond lengths (Å) and bond angles (°) of compound **3**

Bond	Dist.	Bond	Dist.	Bond	Dist.
N1–C1	1.431(3)	C12–C15	1.447(4)	S1–C17	1.719(3)
N1–C10	1.364(3)	C15–C16	1.328(4)	C19–C20	1.363(4)
N1–C14	1.361(3)	C16–C17	1.441(4)	C20–C21	1.468(4)
C12–C13	1.402(4)	C17–C18	1.363(4)	S1–C20	1.719(3)
Angle	(°)	Angle	(°)	Angle	(°)
C10–N1–C1	110.6(2)	C16–C15–C12	124.9(3)	C19–C20–S1	109.6(2)
C14–N1–C10	121.6(2)	C15–C16–C17	125.6(3)	C19–C20–C21	129.5(3)
C11–C12–C13	117.2(3)	C16–C17–S1	122.2(2)	C22–C21–C20	121.1(3)
C11–C12–C15	123.0(3)	C18–C17–S1	110.0(2)	C26–C21–C22	116.8(3)

Table 2 Selected torsion angles (°) of compound **3**

Angle	(°)	Angle	(°)
C1–N1–C10–C11	179.1(2)	C14–N1–C1–C2	−1.0(4)
C2–C1–C6–C7	179.7(3)	C15–C16–C17–C18	175.9(3)
C7–C10–C11–C12	177.3(3)	C15–C16–C17–S1	−5.6(4)
C11–C12–C15–C16	−11.2(4)	C19–C20–C21–C22	0.1(5)
C12–C15–C16–C17	−179.9(3)	S1–C20–C21–C22	−179.3(2)
C13–C12–C15–C16	168.8(3)	S1–C20–C21–C26	−0.5(4)

Fig. 3 UV-Vis spectrum of compound **3**



confirmed by a coupling constant of 16 Hz for the hydrogen atoms attached to the double bond in ^{1}H NMR spectrum. The single bond lengths of C12–C15 and C16–C17 are 1.447(4) and 1.441(4) Å, respectively, both shorter than the normal C–C bond (1.540 Å) [18], which means both the two single bonds possess a partial double bond character and the electron density was delocalized among C12, C15, C16, and C17 atoms. On the other hand, the torsion angles from C15 to C26, S1 are all near to 0.0° or −180°/180° (Table 2), indicating small dihedral angles between the rings and vinyl moiety. It is estimated that the dihedral angles between 10*H*-pyrido[1,2-*a*]indolium and vinyl, thiophene and vinyl, thiophene and methylbenzene moiety are 11.52°, 5.25°, and 2.65°, respectively. Therefore, it is deduced that the three rings and vinyl moiety in **3** can make up a large conjugated system.

UV-Vis spectral property

There are two absorption bands in compound **3** (Fig. 3), of which $\lambda_{\max}^{1}$ and $\lambda_{\max}^{2}$ are 305.5 and 449.5 nm, respectively. According to the method of Ref. [19], it is deduced that $\lambda_{\max}^{2}$ might be attributed to the $\pi \rightarrow \pi^*$ transition of the whole conjugated system in the molecule, while $\lambda_{\max}^{1}$ may be assigned to the $\pi \rightarrow \pi^*$ transition of the partial conjugated system related to 10*H*-pyrido[1,2-*a*]indolium moiety. Moreover, $\lambda_{\max}^{2}$ undergoes a significant red shift (77.0 nm) in comparison to

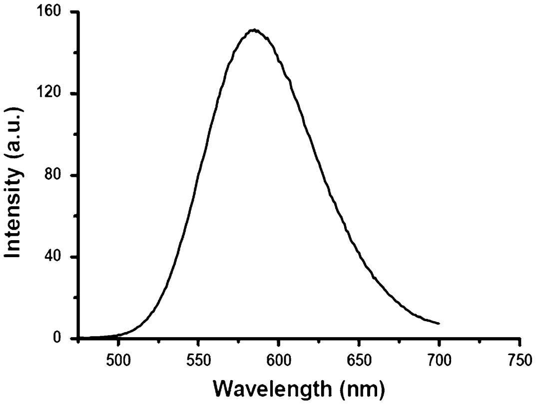


Fig. 4 Fluorescence spectrum of compound **3**

8-(4-methylphenyl)vinyl analogue ($\lambda_{\max} = 372.5$ nm) [7], resulting from the introduction of a thiophene ring in compound **3**.

Fluorescent spectral property

As shown in Fig. 4, the maximum emission of **3** is 567.0 nm, which also exhibits a remarkable red shift (99.0 nm) in comparison with 8-(4-methylphenyl)vinyl analogue ($\lambda_{\mathrm{em}} = 468.0$ nm) [7]. In addition, the fluorescence quantum yield of the title compound was measured according to Ref. [20], and the value is 0.065.

Conclusions

In conclusion, a novel substituted 10*H*-pyrido[1,2-*a*]indolium perchlorate has been synthesized and characterized by elemental analysis, IR, ^{1}H NMR, and single-crystal X-ray diffraction. The target compound exhibits good coplanarity, and as a result, rings and vinyl can make up a large conjugated system. Thus, it possesses larger maximum absorptions and emission wavelengths, and undergoes significant red shifts in maximum absorption and emission wavelength in comparison with 8-(4-methylphenyl)vinyl analogue, respectively.

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