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Synthesis, characterization, crystal structure and DFT studies on 1′,3′-dihydrospiro[fluorene-9,2′-perimidine]

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ABSTRACT

The title compound, 1′,3′-dihydrospiro[fluorene-9,2′-perimidine] has been synthesized and characterized by NMR, ESI-MS, IR, elemental analysis, UV–vis and fluorescence spectroscopy. The crystal structures of the title compound and its co-crsytal with 9-fluorenone have also been determined by X-ray single crystal diffraction. Density functional theory (DFT) calculations and vibrational frequencies have been performed at B3LYP/6-31G* level. The comparisons between the experimental vibrational frequencies and the predicted data show that B3LYP/6-31G* method can simulate the IR of the title compound on the whole. The theoretical electronic absorption spectra have been calculated by using TD-DFT method and compared with the experimental result. The solid-fluorescence determination of the title compound reveals two emission bans at 430 and 590 nm while its co-crystal reveals only one emission band at 590 nm.

1. Introduction

During the past twenty years, organic light-emitting diodes (OLEDs) have received much attention owing to their promising display applications. However, one of the main drawbacks of OLED technology is the shorter lifetime of blue emitting materials compared to the green and red materials. Therefore, materials with stable blue emission within an electroluminescent device continue to hold the attention of number of research groups [1]. Oligofluorenes (OF) and polyfluorenes (PF) have been recognized as potential blue light-emitting materials because of their good charge transport properties, high luminescence efficiency, and excellent processibility [2–11]. Many groups reported the synthesis and properties of molecular systems having fluorene unit, such as spirofluorenes [12–17], terfluorenes [18–20], oligofluorenes [21,22], and polyfluorenes [23–25]. The electronic and photophysical properties exhibited by these systems have made them important in organic light-emitting diodes [26–30], organic field effect transistors [31,32], organic photovoltaic cells [9,33] and organic nonlinear optical applications [34,35].

Perimidines are of interest because they constitute an important class of natural and non-natural products, many of which exhibit useful biological activity [36]. Recently, it was found that the dihydroperimidine system was very effective as aromatic electron donor groups [37]. In this work, we are motivated to introduce the dihydroperimidine group to the 9 position of fluorene which could form the spiro structrue. Herein, we report the facile synthesis on the title compound of 1′,3′-dihydrospiro[fluorene-9,2′-perimidine]. The crystal structures of the title compound and its co-crsytal with 9-fluorenone have also been determined by X-ray single crystal diffraction. Density functional theory (DFT) calculational results are obtained and compared with the experimental ones.

2. Experimental details

2.1. Physical measurements

Melting points were recorded with a BÜCHI B-500 melting point apparatus and uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AVANCE Digital 400 spectrometer. MS measurements were performed on a Bruker Esquire HCT PLUS spectrometer. Elemental analyses for carbon, hydrogen and nitrogen were carried out on an Elementar Vario EL elemental analyzer. IR spectra (4000–500 cm^{-1}), as KBr pellets, were recorded on a SP2000 FT-IR spectrophotometer (Pye Unicam Ltd., England). Electronic absorption spectra were recorded on a HITACHI 3010 UV–vis spectrophotometer and solid state fluorescence spectra were measured on a F96-fluorospectrophotometer. Thermal gravimetric analysis was carried out on a TA Instruments DTG60 TGA. A heating rate of 10 °C min^{-1} under flowing N_2 was used with runs being conducted from room temperature 25 °C to high temperature 700 °C.

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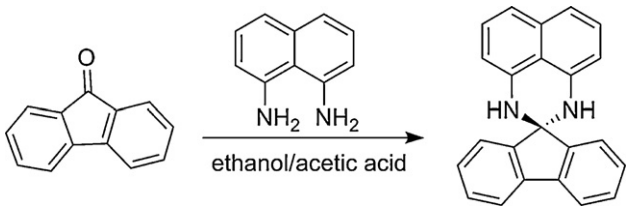

Scheme 1. Synthetic route of compound **1**.

2.2. Synthesis of 1′,3′-dihydrospiro [fluorene-9,2′-perimidine] (*1*)

All chemicals were obtained from a commercial source and used without further purification. The synthetic route is shown in Scheme 1.

To an oven dried 100 ml three necked round bottom flask, 9-fluorenone (1.8 g, 10 mmol) and naphthalane-1,8-diamine (1.58 g, 10 mmol) were dissolved in ethanol (40 ml). Then a few drops of acetic acid were added. The reaction mixture was heated with refluxing for 24 h. After then, the mixture was cool to room temperature and was filtrated to produce a brown solid. The crude product was purified by recrystallization with a mixture of chloroform/hexane (1:1/v:v) (yield: 65%). Single crystals of **1** suitable for X-ray diffraction were grown by solvent evaporation of chloroform solution for a few days. MP: 255–256 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 4.25 (br s, 2H), 6.43–6.48 (m, 2H), 7.13 (t, J = 7.2 Hz, 2H), 7.24–7.29 (m, 6H), 7.36 (t, J = 7.2 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 107.02, 112.82, 117.85, 119.92, 123.93, 127.25, 128.56, 129.81, 134.35, 138.90, 140.14. ESI-MS (M^+): 320. Elemental analysis calculated (%): C 86.22, H 5.03, N 8.74; found: C 86.15, H 4.96, N 8.89.

2.3. Synthesis of co-crystal (*2*)

The purified compound **1** (1.6 g, 5 mmol) and fluorenone (0.9 g, 5 mmol) were dissolved in ethanol and stirred at room temperature for 1 h. The undissolved solids were removed by filtration. The resulting solution was set aside to evaporate slowly. After a few days, red crystals (0.9 g) of **2** suitable for X-ray diffraction were obtained. Elemental analysis found (%): C 86.52, H 4.63, N 5.68, which is consistent with the calculated result (C 86.38, H 4.83, N 5.60).

2.4. Crystal structure determination

X-ray crystallographic data were collected with a Bruker AXS SMART CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were collected at 173 K and the structure was resolved by direct methods and refined by full-matrix least-squares on F^2. The computation was performed with the SHELXL-97 program [38]. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were located by difference synthesis and refined isotropically. The key crystallographic data are given in Table 1. CCDC-768329 for compound **1** and CCDC-768330 for co-crsytal **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 33; email: deposit@ccdc.cam.ac.uk.

3. Computational methods

DFT calculations with a hybrid functional B3LYP (Becke's three parameter hybrid functional using the LYP correlation functional) at basis set 6-31G* by the Berny method [39] were performed with the Gaussian 03 software package [40]. Vibrational frequencies calculated ascertain the structure was stable (no imaginary frequencies). Time-dependent density functional theory (TD-DFT) [41–43] calculations of electronic absorption spectra were performed on the optimized structure.

Table 1
Crystal data and structure refinement.

Crystal	**1**	**2**
CCDC No.	768329	768330
Color/shape	Brown/block	Red/block
Chemical formula	$C_{23}H_{16}N_2$	$C_{36}H_{24}N_2O$
Formula weight	320.38	500.57
Temperature (K)	173(2)	173(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pca2(1)*
Unit cell dimension		
a (Å)	14.914(9)	18.0732(9)
b (Å)	16.2126(8)	7.7216(4)
c (Å)	26.4850(14)	17.8262(9)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å^3)	6404(4)	2487.7(2)
Z	16	4
Density (calculated) (g/cm^3)	1.329	1.337
Absorption coefficient (mm^{-1})	0.078	0.081
Diffractometer/scan	Bruker AXS SMART 1000 CCD diffractometer	Bruker AXS SMART 1000 CCD diffractometer
θ range for data collection (°)	2.01–27.07	2.25–27.04
Reflections measured	32,682	12,502
Independent/observed reflections	7013 (R_{int} = 0.0353)/4771 [$I > 2\sigma(I)$]	2800 (R_{int} = 0.0266)/2436 [$I > 2\sigma(I)$]
Data/restraints/parameters	4349/0/345	2800/1/352
Goodness of fit on F^2	1.047	1.170
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0513, wR_2 = 0.1371	R_1 = 0.0386, wR_2 = 0.0967
R indices (all data)	R_1 = 0.0826, wR_2 = 0.1612	R_1 = 0.0482, wR_2 = 0.1026

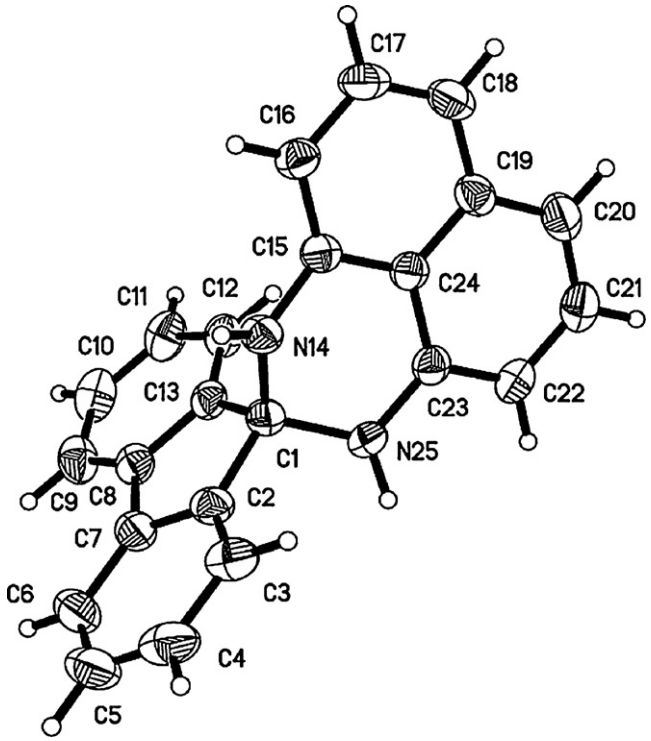

Fig. 1. Molecular structure of compound **1** with the atomic numbering scheme.