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ORIGINAL PAPER

Synthesis, Characterization, Crystal Structure and Fluorescence Property of Tetramethyl 5,5′-(Terephthaloylbis(azanediyl))-Diisophthalate

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Abstract An aroyl acylamide compound, tetramethyl 5,5′-(terephthaloylbis(azanediyl))-diisophthalate (**1**), has been prepared by nucleophilic substitution reaction of dimethyl 5-aminoisophthalate and terephthaloyl chloride, and characterized by elemental analysis, FT-IR, ^{1}H-NMR, ESI–MS and single-crystal X-ray diffraction. The crystal of **1**·2DMF belongs to monoclinic space group *P*2/*c* with $a = 21.609(2)$ Å, $b = 4.060(1)$ Å, $c = 21.606(2)$ Å, $\beta = 112.805(1)°$, $V = 1747.4(3)$ Å^3, $Z = 2$, $D_c = 1.320$ Mg m^{-3}, $\mu = 0.101$ mm^{-1}, $F(000) = 732$, $M_r = 694.68$, the final $R_1 = 0.0879$ and $wR_2 = 0.1872$ for 8091 observed reflections with $I > 2\sigma(I)$. The structural analysis reveals that compound **1**·2DMF contains one tetramethyl 5,5′-(terephthaloylbis-(azanediyl))-diisophthalate and two *N,N*-dimethylformamide solvent molecules. A 3D supramolecular structure of **1**·2DMF is constructed by multiply intermolecular C–H···O H-bonds and π–π stacking interactions. In addition, compound **1** exhibits a strong blue fluorescence at 413 nm in the solid state at room temperature.

Keywords Acylamide compound · Synthesis · Crystal structure · Fluorescence

Introduction

Acylamide compounds have attracted considerable attention due to their wide applications in chemistry, biology, medicine and materials science along with their fascinating molecular and supramolecular structures [1–4]. Acylamides are particularly of high interest because some of them have been successfully employed in the self-assembly of several intriguing molecular architectures, such as nanotube, macrocycle and porous metal–organic frameworks, etc. [5–10]. Sun and coworkers have carried out a series of wonderful work on the construction of MOFs using acylamide ligands [6, 8]. Bai et al. [10] have also reported some interesting luminescent complexes assembled from acylamide ligands. To explore in this area, we designed and successfully prepared a novel aroyl acylamide compound, tetramethyl 5,5′-(terephthaloylbis(azanediyl))-diisophthalate (**1**). Herein, we reported the detailed synthesis, characterization and crystal structure of compound **1**, which exhibits a strong blue emission at 413 nm in the solid state at room temperature.

Experimental Section

Materials and Method

All chemicals and solvents used for synthesis were obtained from commercial sources. Elemental analyses for C, H and N were carried out with a Perkin-Elmer 2400 II elemental analyzer. The ^{1}H-NMR spectra were recorded on a Mercury Plus 400 MHz FT-NMR spectrometer using tetramethylsilane (TMS) as an internal reference. IR spectra were measured on a Nicolet-5700

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FT-IR spectrophotometer using KBr discs. ESI–MS spectra were performed on a Finnigan DE-CAX-30000 LCQ Deca XP ion trap mass spectrometer. Fluorescence spectra of the solid samples were recorded on a Hitachi F-7000FL fluorescence spectrophotometer.

Synthesis of Compound **1**

Dimethyl 5-aminoisophthalate (1.32 g, 6.33 mmol) and triethylamine (1.50 ml, 9.50 mmol) were reacted with terephthaloyl chloride (0.58 g, 2.86 mmol) in anhydrous dichloromethane (20 mL) for 10 h at room temperature. The solvent was removed by rotary evaporation, and the solid was washed three times with dichloromethane. The white product was dried under vacuum overnight. Yield: 1.43 g, 91.30 %. Anal. Calcd. for $C_{28}H_{24}N_2O_{10}$ (548.50): C, 61.31; H, 4.41; N, 5.11. Found: C, 61.27; H, 4.35; N, 5.14 %. ^{1}H-NMR (DMSO-d$_6$, ppm): δ 10.82 (s, 2H, –CONH–), 8.75 (s, 4H, Ar–H), 8.23 (s, 2H, Ar–H), 8.16 (s, 4H, Ar–H), 3.91 (s, 12H, –CH_3). ^{13}C-NMR could not be done because of the insolubility of the compound. Selected IR spectrum (KBr, cm^{-1}): 3346, 2955, 1720, 1555, 1263, 865, 758, 671. ESI–MS: *m/z* 549.3 [M + H$^+$]. The colorless crystals of **1**·2DMF suitable for X-ray diffraction were obtained by recrystallization from *N,N*-dimethylformamide (DMF).

X-Ray Crystallography

A colorless needle single-crystal with dimensions of 0.44 × 0.11 × 0.09 mm^3 was selected for indexing and intensity data collection on a Bruker smart-1000 CCD diffractometer at 298(2) K using graphite monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Multi-scan absorption corrections based on symmetry equivalents were applied to the 8091 reflections collected ($2\theta_{\max} = 50.02$), 3061 unique reflections were observed [$R_{int} = 0.0837$] after data reduction. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELX-97 program package [11]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions and refined isotropically. The refinement converged to a final $R_1 = 0.0879$, and $wR_2 = 0.1872$ of $I > 2\sigma(I)$, $S = 1.065$, $(\Delta/\sigma)_{\max} = 0.000$. The largest peak in the final difference Fourier map is 0.687 e Å^{-3} and the minimum peak is −0.243 e Å^{-3}. The details of the crystal parameters, data collection and refinements for the **1**·2DMF are summarized in Table 1, selected bond lengths and angles are listed in Table 2, the geometric parameters of H-bonds and π–π stacking interactions for **1**·2DMF are given in Table 3.

Table 1 Crystal data and structure refinement for **1**·2DMF

Empirical formula	$C_{34}H_{38}N_4O_{12}$
Formula weight	694.68
Crystal system	Monoclinic
Space group	*P*2/*c*
Unit cell dimensions	$a = 21.609(2)$ Å
	$b = 4.060(1)$ Å
	$c = 21.606(2)$ Å
	$\beta = 112.805(1)°$
Volume(Å^3)	1747.4(3)
Z	2
Calculated density(Mg m^{-3})	1.320
Absorption coefficient(mm^{-1})	0.101
F(000)	732
Crystal size(mm^3)	0.44 × 0.11 × 0.09
Theta range for data collection(°)	2.26 to 25.01
Limiting indices	$-17 \le h \le 25$, $-4 \le k \le 4$, $-25 \le l \le 25$
Reflections collected/Unique	8091/3061 [$R_{int} = 0.0837$]
Completeness to $\theta = 25.01°$	99.6 %
Max. and min. transmission	0.9910 and 0.9569
Data/Restraints/Parameters	3061/0/230
Goodness-of-fit on F^2	1.065
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0879$, $wR_2 = 0.1872$
R indices (all data)	$R_1 = 0.1641$, $wR_2 = 0.2115$
Largest diff. peak and hole(e.Å^{-3})	0.687 and −0.243

Results and Discussion

Synthesis and Spectral Characterization of Compound **1**

As shown in Scheme 1, compound **1** was obtained from the nucleophilic substitution reaction of dimethyl 5-aminoisophthalate and terephthaloyl chloride in dichloromethane with triethylamine. The molecular formula of compound **1** is determined to be $C_{28}H_{24}N_2O_{10}$ according to elemental analysis and ESI–MS spectrum.

The number of hydrogen atoms observed in the ^{1}H-NMR spectrum is in agreement with the molecular formula. The downfield signal at 10.82 is ascribed to –C(O)NH and the signal at 3.91 is assigned to the –CH_3. The other three signals at 8.75, 8.23 and 8.16 are ascribed to the hydrogen atoms on the phenyl ring.

In the IR spectrum, the broad adsorption band at 3346 cm^{-1} characterizes the –NH– stretching vibration of the acylamide group in compound **1**. The peak at 2955 cm^{-1} is assigned to the Ar–H stretching vibration adsorption, and the peak at 1720 cm^{-1} is ascribed to the –C=O adsorption of –Ar(C=O)OCH_3 group. The absorption peaks at 1555 cm^{-1} and 1263 cm^{-1} are ascribed to the

Table 2 Selected bond lengths [Å] and angles [°] for **1**·2DMF

Lengths(Å)			
O1–C1	1.229(4)	N1–C5	1.433(5)
O2–C11	1.346(5)	N2–C15	1.335(6)
O2–C12	1.437(5)	N2–C16	1.446(6)
O3–C11	1.221(4)	N2–C17	1.440(7)
O4–C13	1.355(5)	C1–C2	1.505(6)
O4–C14	1.459(5)	C3–C4^{a}	1.400(6)
O5–C13	1.212(5)	C4–C3^{a}	1.400(6)
O6–C15	1.242(6)	C7–C11	1.515(6)
N1–C1	1.383(5)	C9–C13	1.508(5)
Angles(°)			
O1–C1–N1	123.0(4)	C1–N1–C5	127.2(3)
O1–C1–C2	121.7(4)	C1–C2–C3	117.2(4)
O2–C11–O3	123.4(4)	C1–C2–C4	124.4(4)
O2–C11–C7	112.1(4)	C2–C3–C4^{a}	120.2(4)
O3–C11–C7	124.4(4)	C2–C4–C3^{a}	121.6(4)
O4–C13–O5	124.1(4)	C3–C2–C4	118.2(4)
O4–C13–C9	112.5(4)	C11–O2–C12	116.8(3)
O5–C13–C9	123.4(4)	C13–O4–C14	115.0(3)
O6–C15–N2	127.3(5)	C15–N2–C16	122.0(5)
N1–C1–C2	115.2(4)	C15–N2–C17	120.5(5)
N1–C5–C6	117.7(4)	C16–N2–C17	117.5(5)
N1–C5–C10	122.1(4)		

Symmetry code: ^{a}−x,−y−1,−z

vibrations of acylamide II band and acylamide III band, respectively. In addition, the adsorption bands at 865, 758 and 671 cm^{-1} are ascribed to the Ar–H out-of-plane ring deformation vibrations in compound **1**. All the above IR attribution is consistent with structural determination.

Structural Description of Compound **1**·2DMF

Single-crystal X-ray diffraction analysis reveals that compound **1**·2DMF crystallizes in monoclinic space group *P*2/*c* and consists of one tetramethyl 5,5′-(terephthaloylbis(azanediyl))-diisophthalate molecule and two DMF solvent molecules. As shown in Fig. 1, the –CH group of terminal phenyl ring and amide O atom are linked by intramolecular C–H···O (Table 3, C10–H10···O1) H-bonds to form a six-member-ring structure, thus the plane containing terminal phenyl ring group and C1, N1, O1 atoms is almost coplanar. However, the whole tetramethyl 5,5′-(terephthaloylbis(azanediyl))-diisophthalate in **1**·2DMF adopts a non-planar conformation, and the dihedral angle between the central phenyl ring and the above mentioned plane containing C1, N1, O1 atoms and phenyl ring group is about 34.91(14)°. This non-planar conformation of tetramethyl 5,5′-(terephthaloylbis(azanediyl))-diisophthalate should root from the C–C (C1–C2) single bond rotation between the central phenyl ring and acylamide group, and be stabilized by the N–H···O (Table 3, N1–H1···O6) and C–H···O (Table 3, C4–H4···O6 and C6–H6···O6) H-bonds. Two new C–N bonds in **1**·2DMF formed by the nucleophilic substitution reaction represent the typical acylamide bonds. The bond lengths of C–N (C1–N1 1.383(5) Å) and C=O (C1–O1 1.229(4) Å) suggest the C(O)NH group adopts usually ketonic form in **1**·2DMF, which are in the normal range of acylamide compounds [12–14].

As shown in Fig. 2, the non-planar molecules of tetramethyl 5,5′-(terephthaloylbis(azanediyl))-diisophthalate are linked by intermolecular C–H···O (Table 3, C14–H14B···O3^{b}) H-bonds to form a 1D double chain structure along the *c*-axis. The resulting chains are further connected through intermolecular π-π stacking interactions (Table 3)

Table 3 The geometric parameters of H-bonds and π-π stacking interactions for **1**·2DMF

H-bonds

	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N1–H1···O6	0.86	2.18	3.019(5)	163.9(3)
C4–H4···O6	0.93	2.62	3.354(6)	136.7(3)
C6–H6···O6	0.93	2.62	3.351(7)	136.5(3)
C10–H10···O1	0.93	2.30	2.875(5)	119.5(3)
C12–H12B···O5^{a}	0.96	2.78	3.168(5)	105.1(3)
C14–H14B···O3^{b}	0.96	2.57	3.467(5)	154.9(3)
C15–H15···O3^{c}	0.93	2.63	3.406(8)	141.9(4)

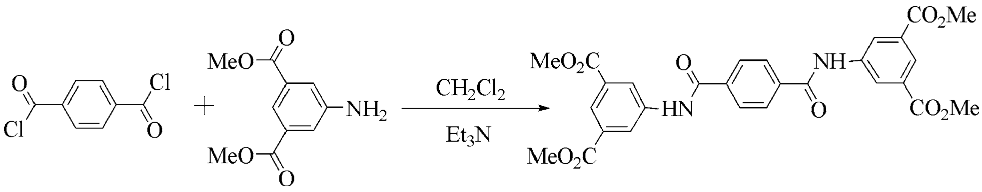
π-π stacking interactions

	Centroid–Centroid (Å)	Interplanar separation (Å)	Dihedral angle (°)	Slip angle (°)
Cg1···Cg1^{c}	4.060	3.491	0.00	30.7
Cg2···Cg2^{c}	4.060	3.623	0.00	26.8
Cg1^{d}···Cg1^{e}	4.060	3.491	0.00	30.7

Cg1 and Cg2 are the centroids of the rings defined by C5–C6–C7–C8–C9–C10, C2–C3–C4–C2^{d}–C3^{d}–C4^{d}, respectively

Symmetry codes: ^{a}1 − x, 1 + y, ½ − z; ^{b}x, −y, z − 1/2; ^{c}x, y−1, z; ^{d}−x, −y − 1, −z; ^{e}−x, −y − 2, −z

Scheme 1 Synthesis of compound **1**



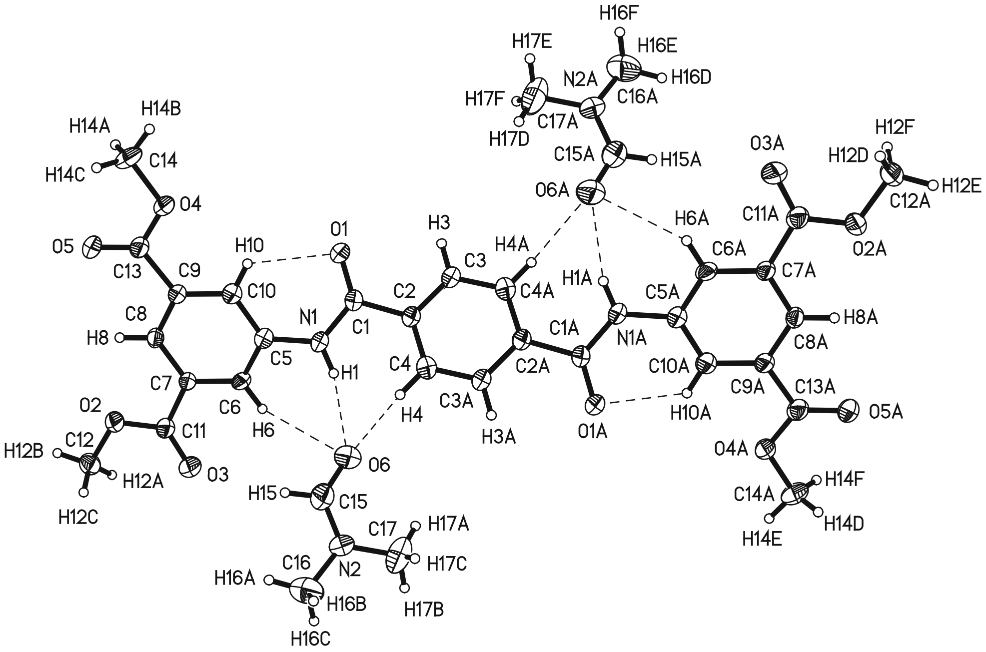
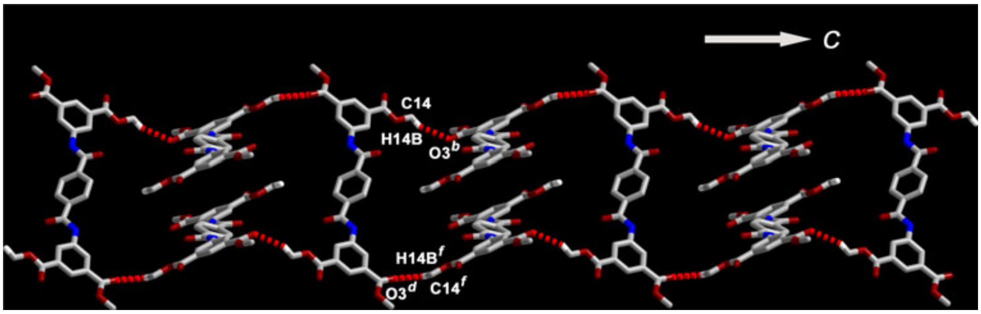


Fig. 1 Molecular structure of **1**·2DMF. Dotted lines indicate the N–H···O and C–H···O H-bonds

Fig. 2 A 1D double chain structure of **1**·2DMF linked by intermolecular C–H···O H-bonds along *c*-axis (solvent DMF molecules and H atoms except for H14B are omitted for clarity). Symmetry codes: (*b*) x, −y, z − 1/2; (*d*) −x, −y − 1, −z; (*f*) −x, y − 1, −z−1/2



and another intermolecular C–H···O H-bonds (Table 3, C12–H12B···O5^a) along two different directions, yielding a 3D supramolecular framework with large rectangle channels. Interestingly, the guest DMF molecules are found in these 1D channels (Fig. 3). In consideration of the H-bonds (Table 3, N1–H1···O6, C4–H4···O6, C6–H6···O6 and C15–H15···O3^c) between the host framework and guest molecules, the DMF molecules can be considered as supramolecular templates and are beneficial to the stability of this 3D framework.

Fluorescence Property of **1**

The fluorescence emission spectrum of tetramethyl 5,5′-(terephthaloylbis(azanediyl))-diisophthalate was investigated in the solid state at room temperature, with the result shown in Fig. 4. Upon excitation at 270 nm, compound **1** exhibits a strong blue emission with the main peak (λ_{max}) appearing at 413 nm, indicating that **1** is a good molecule-based solid fluorescent material. Besides, considering that compound **1** could easily form H-bonds with guest

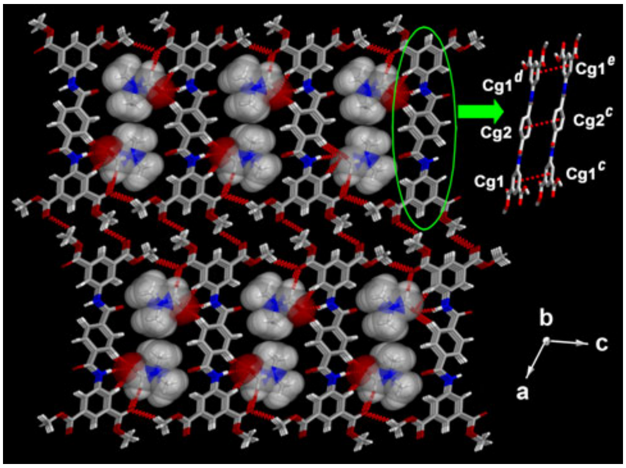


Fig. 3 A 3D supramolecular framework structure of **1**·2DMF constructed by intermolecular C–H···O H-bonds and π–π stacking interactions, the guest DMF molecules (space-filling mode) occupy in the 1D channels. Symmetry codes: (*c*) x, y − 1, z; (*d*) −x, −y − 1, −z; (*e*) −x, −y − 2, −z

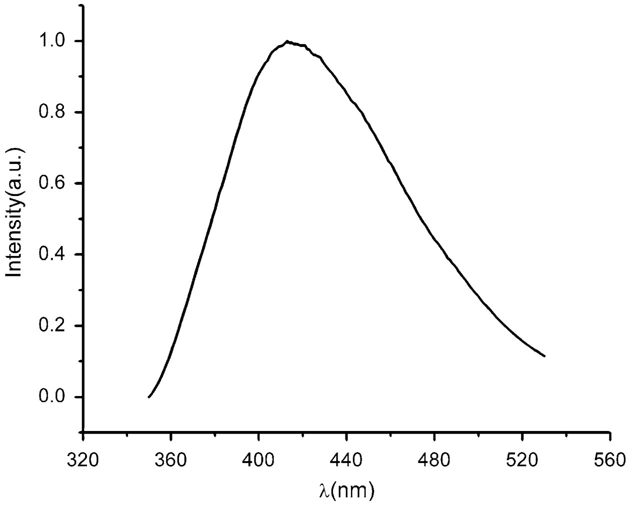


Fig. 4 Solid-state emission spectrum of compound **1** (λ_{ex} = 270 nm) at room temperature

molecules, it may be further used as a prospected photosensor in detecting small organic molecules or biologic macromolecules [15].

Conclusions

In summary, an acylamide compound, tetramethyl 5,5′-(terephthaloylbis(azanediyl))-diisophthalate (**1**), has been prepared and characterized by elemental analysis, FT-IR, ^{1}H-NMR, ESI–MS and single-crystal X-ray diffraction analysis. The structural analysis reveals that the tetramethyl 5,5′-(terephthaloylbis(azanediyl))-diisophthalate molecule adopts a non-planar conformation by the solvent-assisted C–C single bond rotation, and a 3D supramolecular framework structure is constructed by multiply intermolecular C–H···O H-bonds and π–π stacking interactions. Moreover, compound **1** exhibits a strong blue fluorescence at 413 nm in the solid state at room temperature.

Supplementary Material

CCDC 857994 contains the supplementary crystallographic data for the compound. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail:deposit@ccdc.cam.ac.uk.

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