ORIGINAL PAPER

Synthesis, Characterization and Crystal Structure of N,N'-di[(E)-1-(2-hydoxyphenyl)methylidene]-2,6-naphthalenedicarbohydrazide

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Abstract A new bishydrazone compound, N,N'-di[(E)-1-(2-hydoxyphenyl)methylidene]-2,6-naphthalenedicarbohydrazide (1), has been prepared by condensation reaction of 2.6-naphthalenedicarbohydrazide with salicylaldehyde in ethanol, and characterized by elemental analysis, FT-IR, ¹H- and ¹³C-NMR, ESI–MS and single-crystal X-ray diffraction analysis. The crystal of 1.2DMF belongs to monoclinic, space group P2(1)/n with a = 10.454(1), b =7.711(1), c = 18.801(2) Å, $\beta = 93.364(1)^{\circ}$, V = 1512.9(3)Å³, Z = 2, $D_c = 1.314$ g cm⁻³, $\mu = 0.093$ mm⁻¹, F(000) =632, Mr = 598.65, the final $R_1 = 0.0861$ and $wR_2 =$ 0.2279 for 7243 observed reflections with $I > 2\sigma(I)$. The structural analysis reveals that compound 1.2DMF contains one N, N'-di[(E)-1-(2-hydoxyphenyl)methylidene]-2,6-naphthalenedicarbohydrazide molecule and two N,N-dimethylformamide solvent molecules. A 2D supramolecular structure of 1.2DMF was constructed by multiple intermolecular N-H···O and C-H···O hydrogen bonds.

Keywords Hydrazone compound · Synthesis · Characterization · Crystal structure

Introduction

Currently, hydrazone compounds have been intensively investigated because they possess widely antimicrobial, anticonvulsant, antitubercular, analgesic, antiinflammatory, antiplatelet and antitumoral activities [1-3], and also because some of them have been successfully employed in the self-assembly of several intriguing molecular architectures, such as metallacrown, macrocycle, nanocage, inorganic [2]-catenane and $[n \times n]$ grid etc. [4–10]. Thompson and coworkers [5, 6] have carried out a series of wonderful work on the construction of functional molecules using hydrazone ligands. He and coworkers have also reported some interesting artificial chemosensors with multidentate hydrazone ligands [7, 8]. In our previous article, we also successfully prepared enneanuclear nanocage and trinuclear macrocycle using asymmetric tritopic hydrazone ligands [9, 10]. To continue our research in this area, we designed and successfully prepared a new functional aroyl hydrazone compound, N,N'-di[(E)-1-(2-hydoxyphenyl)methylidene]-2,6-naphthalenedicarbohydrazide (1), which was completely characterized by elemental analysis, FT-IR, ¹H- and ¹³C-NMR, ESI-MS and singlecrystal X-ray diffraction analysis.

Experimental Section

Materials and Method

All chemicals were of reagent grade obtained from commercial sources and used without further purification. The elemental analyses of C, H and N were performed on a PE-2400 II elemental analyzer. The melting point was obtained with SRS OptiMelt-100 melting point apparatus and is uncorrected. IR spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs. ¹H- and ¹³C-NMR spectra were measured on a Bruker AVANCE III 400 MHz FT-NMR spectrometer using tetramethylsilane (TMS) as the internal reference. ESI–MS spectra were recorded on a

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Finnigan DE-CAX-30000 LCQ Deca XP ion trap mass spectrometer.

Preparation of Compound 1

2,6-naphthalene-dicarbohydrazide (3 mmol, 0.732 g) was added to EtOH solution (60 mL) containing salicylaldehyde (6 mmol, 0.732 g). After 3 drops of acetic acid were added, the yellow mixture was heated at boiling temperature under magnetic stirring for 24 h. During the reaction, a yellow precipitate was formed, which was collected by filtration. Yield: 1.085 g, 80%. M.p.: 326-328 °C. Anal. calc. For C₂₆H₂₀N₄O₄ (%): C, 69.02; H, 4.46; N, 12.38. Found (%): C, 68.95; H, 4.50; N, 12.30. IR (KBr, cm⁻¹): 3450, 3208, 1665, 1608, 1445, 1410, 1285, 1028, 875, 465. ¹H-NMR (400 MHz, DMSO-d₆, ppm): 12.365 (s, 2H, -NH), 11.264 (s, 2H, -OH), 8.717 (s, 2H, -CH=N-), 8.649 (s, 2H, Ar-H), 8.250 (d, 2H, J = 8.4 Hz, Ar-H), 8.101 (d, 2H, J = 8.4 Hz)Ar–H), 7.605 (d, 2H, J = 6.8 Hz, Ar–H), 7.349 (m, 2H, Ar-H), 6.954 (m, 4H, Ar-H). ¹³C-NMR (100 MHz, DMSO-d₆, ppm): 183.76 (-C(O)NH-), 168.11 (Ph-C-OH), 162.91 (-CH=N-), 153.85 (Ar-C), 138.98(Ar-C), 137.43 (Ar-C), 136.95(Ar-C), 134.86(Ar-C), 133.34(Ar-C), 130.67(Ar-C), 124.84(Ar-C), 124.18(Ar-C), 121.88(Ar-C). ESI-MS: m/z 453.4 [M + H⁺]. The high-quality yellow single crystals of 1.2DMF suitable for X-ray diffraction were obtained by recrystallization from N,N-dimethylformamide (DMF).

X-Ray Crystallography

A suitable yellow single-crystal with dimensions of $0.30 \times 0.20 \times 0.15$ mm was selected for indexing and intensity data collection on a Bruker smart-1000 CCD diffractometer at 298(2) K using MoK_{α} radiations (0.71073 Å). Multi-scan absorption corrections based on symmetry equivalents were applied to the 7243 reflections collected $(2\theta_{\text{max}} = 50.04)$, 2675 unique reflections were observed $(R_{\rm int} = 0.0496)$ after data reduction. The structure was solved by direct methods and refined by full-matrix leastsquares on F^2 using SHELXL-97 program [11]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically. The final refinement by full-matrix least squares method was converged at $R_1 = 0.0861$, and $wR_2 = 0.2279$ $(R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|, wR = [\Sigma w (F_o^2 - V_o) / \Sigma |F_o|]$ $F_c^2/\Sigma w(F_o^2)^2]^{1/2}$, S = 1.025, $(\Delta/\sigma)_{\rm max} = 0.000$. The largest peak in the final difference Fourier map is 0.847 $e \text{\AA}^{-3}$ and the minimum peak is $-0.333 \text{ e}\text{\AA}^{-3}$.

The crystallography details for the structure determination and refinement for 1.2DMF are summarized in Table 1, selected bond lengths and bond angles for compound 1.2DMF are listed in Table 2, and hydrogen bond

Table 1	Crystal	data	and	structure	refinement	for	1.2DMF
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C ₃₂ H ₃₄ N ₆ O ₆
598.65
298(2)
0.71073
Monoclinic
<i>P</i> 2(1)/ <i>n</i>
a = 10.454(1) Å
b = 7.711(9) Å
c = 18.801(2) Å
$\beta = 93.364(1)^{\circ}$
1512.9(3)
2
1.314
0.093
632
$0.30\times0.20\times0.15$
2.17-25.02
$\begin{array}{l} -12 \leq h \leq 8, -9 \leq k \leq 9, \\ -22 \leq l \leq 22 \end{array}$
7243/2675 ($R_{\rm int} = 0.0496$)
99.9%
Multi-scan
0.9862 and 0.9727
Full-matrix least-squares on F^2
2675/0/201
1.025
$R_1 = 0.0861, wR_2 = 0.2279$
$R_1 = 0.1620, wR_2 = 0.2980$
0.847 and -0.333

parameters are given in Table 3. The molecular structure of compound 1.2DMF is shown in Fig. 1, and the supramolecular structure including the H-bonding interactions is illustrated in Fig. 2.

Results and Discussion

Synthesis and Spectral Characterization of Compound 1

As shown in Scheme 1, compound 1 was prepared by Schiff base reaction of 2,6-naphthalene-dicarbohydrazide and salicylaldehyde in ethanol with 3 drops of acetic acid. The molecular formula of 1 is determined to be $C_{26}H_{20}N_4O_4$ according to elementary analysis and ESI–MS spectrum.

The number of hydrogen atoms observed in the ¹H-NMR spectrum of compound **1** is in agreement with this molecular formula. In the ¹H-NMR spectrum, two down-field signals at 12.365 and 11.264 are ascribed to -C(O)NH- and -OH, respectively. The signal at 8.717 is

Table 2 Selected bond lengths(Å) and angles (°) for 1.2DMF

Bond lengths (Å)	
O1–C6	1.221(6)
O2-C13	1.353(6)
O3–C19	1.194(8)
N1-C6	1.347(6)
N1-N2	1.371(5)
N2-C7	1.282(6)
N3-C19	1.277(8)
N3-C21	1.410(8)
N3-C22	1.452(9)
C1-C5#1	1.368(6)
C1–C2	1.407(6)
C2–C3	1.412(6)
C2–C2#1	1.414(9)
C3–C4	1.367(6)
C4–C5	1.410(7)
C4–C6	1.487(7)
C5-C1#1	1.368(7)
C7–C8	1.446(6)
C8-C13	1.391(7)
C8–C9	1.395(7)
C9–C10	1.371(7)
C10-C11	1.369(8)
C11-C12	1.367(7)
C12-C13	1.393(7)
Bond angles (°)	
C6-N1-N2	117.8(4)
C7-N2-N1	117.4(4)
C19-N3-C21	123.5(7)
C19–N3–C22	118.8(7)
C21-N3-C22	117.6(7)
C5#1-C1-C2	120.6(5)
C1 - C2 - C3	122.1(4)
C1 - C2 - C2 = C2	119 6(5)
$C_{3}-C_{2}-C_{2}\#1$	118 4(5)
$C_{2} C_{2} C_{2} C_{2} C_{2}$	121 4(4)
$C_{3}-C_{4}-C_{5}$	119 8(4)
$C_{3}-C_{4}-C_{6}$	116 9(4)
C5-C4-C6	123 3(4)
$C_{1}=C_{1$	120.3(4)
01_C6_N1	120.3(4)
01 - C6 - C4	121.3(3) 121.7(5)
N1 C6 C4	121.7(5) 117.0(5)
$N_{1} = C_{0} = C_{4}$	117.0(3) 120.1(5)
$N_2 = C_7 = C_8$	110.1(3)
$C_{13} = C_{0} = C_{7}$	122 2(4)
$C_{13} - C_{0} - C_{1}$	122.3(4)
$C_{2} - C_{3} - C_{1}$	119.5(5)
C_{10} $-C_{9}$ $-C_{8}$	121.3(5)
	119.3(5)
C12-C11-C10	121.5(5)
CHI-C12-C13	119.3(5)

Table 2 continued	O2-C13-C8	122.7(4)	
	O2-C13-C12	117.0(5)	
Symmetry transformations used	C8-C13-C12	120.4(5)	
to generate equivalent atoms: #1 -r + 1 - y + 1 - z	O3-C19-N3	131.6(9)	
$\lambda + 1, y + 1, -\zeta$			

Table 3 Hydrogen bond lengths (Å) and angles (°) for 1.2DMF

	D–H	Н…А	D····A	D–H…A
N1–H1A…O3	0.79	2.09(5)	2.835(6)	158.8(3)
O2-H2A…N2	0.81	1.93(6)	2.610(5)	144.3(2)
С5-Н5…О3	0.93	2.40	3.299(6)	161.8(3)
С7-Н7…О3	0.93	2.53	3.291(3)	139.1(3)
C16-H16A…O#1	0.96	2.71	3.574(2)	150.3(1)
C16-H16C…O2#1	0.96	2.70	3.349(2)	125.3(2)

Symmetry transformations used to generate the equivalent atoms: #1 x - 1/2, 3/2 - y, z - 1/2

ascribed to the proton on the -CH=N- group, and the other signals from 8.649 to 6.954 can be ascribed to the hydrogen atoms on the phenyl and naphthyl rings. Additional support for the structure of the compound **1** was provided by ¹³C-NMR spectra. The chemical shift values (ppm) at 183.76, 168.11 and 162.91 are tentatively ascribed to the carbon atoms in -C(O)NH-, Ph-C–OH and -CH=N- groups, respectively. And the other ten signals from 153.85 to 121.88 could be ascribed to the aromatic carbon atoms on the phenyl and naphthyl rings.

In the IR spectrum, the absorption bands at 3,450– 3,208 cm⁻¹ characterize the –OH and –NH groups in compound **1**. The two strong peaks at 1,665 and 1,410 cm⁻¹ are assigned to the –C=O and –C=N absorption of the hydrazone group according to the literature [12]. The absorption peak at 1,285 cm⁻¹ is ascribed to the vibration of amide III band, and the absorption peak at 1,028 cm⁻¹ is ascribed to the C–O stretching vibration of Ph-OH group. In addition, the absorption peak at 875 cm⁻¹ is ascribed to the C–H bending vibration of *E*-(–CH=N–) group. And the absorption band at 465 cm⁻¹ is 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 P2(1)/n space group and consists of one N,N'-di[(E)-1-(2-hydoxyphenyl)methylidene]-2,6-naphthalenedicarbohydrazide molecule and two DMF solvent molecules. As shown in Fig. 1, the hydroxyl group and imine N atom are linked by intramolecular O–H…N (O2–H2A…N2: O2…N2 2.610(5) **Fig. 1** The molecular structure of 1.2DMF. *Dotted lines* indicate the O–H…N, N–H…O and C–H…O H-bonding interactions





Fig. 2 The suparmolecular structure of 1·2DMF linked by intermolecular O–H…N, N– H…O and C–H…O H-bonding interactions: **a** 1D supramolecular chain, **b** 2D supramolecular network

Å, O2–H2A···N2 144.3(2)°) H-bonding interactions to form a six-member-ring structure, thus the plane containing iminosalicylidene group and C6, N1, O1 atoms is almost coplanar with the maximum deviation 0.087 Å for O1 atom in the acyl group. However, to our surprise, the whole N,N'-di[(*E*)-1-(2-hydoxyphenyl)methylidene]-2,6-naphthalenedicarbohydrazide in 1·2DMF adopts a non-planar conformation, and the dihedral angle between the central naphthyl ring and the above mentioned plane containing C6, N1, O1 atoms and iminosalicylidene group is about 11.94°. This non-planar conformation of N,N'-di[(E)-1-(2-hydoxyphenyl)methylidene]-2,6-naphthalenedicarbohydrazide should root from the C–C (C4–C6) single bond rotation between the central naphthyl ring and acyl



Scheme 1 Synthesis of compound 1

group, and be stabilized by the intermolecular N–H···O (N1–H1A···O3: N1···O3 2.835 (6) Å, N1–H1A···O3 158.8(3)°) and C–H···O (C5–H5···O3: C5···O3 3.299 (6) Å, C5–H5···O3 161.8(3)° and C7–H7···O3: C7···O3 3.291 (3) Å, C7–H7···O3 139.1(3)°) H-bonding interactions. Two new C=N bonds in 1·2DMF formed by the condensation reaction represent the typical double bonds with distances of 1.282(6) (C7–N2 and C7A–N2A) Å. The bond lengths of C=O (C6–O1 1.221(6) Å) and C–N (C6–N1 1.347(6) Å) suggest the C(O)NH group adopts usually ketonic form in 1·2DMF, which are in the normal range of carbohydrazone compounds [12–14].

In the crystal structure of 1.2DMF, the non-planar molecules of 1.2DMF and solvent DMF molecules are connected by intermolecular N–H…O and C–H…O H-bonding interactions to form a 1D supramolecular chain (Fig. 2a). Interestingly, these 1D supramolecular chains are further linked to form a 2D extended supramolecular network through intermolecular N–H…O and C–H…O H-bonding interactions along another direction (Fig. 2b).

In conclusion, a new bishydrazone compound, N,N'di[(*E*)-1-(2-hydoxyphenyl)methylidene]-2,6-naphthalenedicarbohydrazide, has been successfully prepared and characterized by elemental analysis, FT-IR, ¹H- and ¹³C-NMR, ESI–MS and single-crystal X-ray diffraction analysis. The structural analysis reveals that the N,N'di[(*E*)-1-(2-hydoxyphenyl)methylidene]-2,6-naphthalenedicarbohydrazide molecule adopts a non-planar conformation by the solvent-assisted C–C single bond rotation. Besides, a 2D supramolecular network structure was constructed by intermolecular multiple N–H···O and C–H···O H-bonding interactions.

Supplementary Material

CCDC 780563 contains the supplementary crystallographic data for the compound. These data can be obtained free of charge via http://www.ccdc.cam.ac.Uk/deposit, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail:deposit@ccdc.cam.ac.uk.

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