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Synthesis, Crystal Structure and Fluorescent Property of 2-(2-(Diphenylamino)-2-oxoethoxy)-*N*-(pyridin-2-ylmethyl)benzamide

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The crystal structure of 2-(2-(diphenylamino)-2-oxoethoxy)-*N*-(pyridin-2-ylmethyl)benzamide has been determined by single crystal X-ray diffraction method. The crystal belongs to triclinic system, space group P-1 with unit cell constants a = 9.6256(6), b = 10.3653(7), c = 12.0927(8) Å, α = 94.7570(10), β = 91.2490(10), γ = 108.4670(10), V = 1138.97(13) Å^3, Z = 2, D_c = 1.276 g/cm^3, μ = 0.084 mm^{-1}, F(000) = 460, R and wR are 0.0551 and 0.1504, respectively for 4386 unique reflections with 3137 observed reflections ($I > 2\sigma(I)$). Molecules of the compound are linked into ribbons along the b axis, *via* C17-H17A···O3 and C26-H26A···N1 intermolecular interactions. The packing is further stabilized by Van der Waals forces. The fluorescent property of compound was also reported.

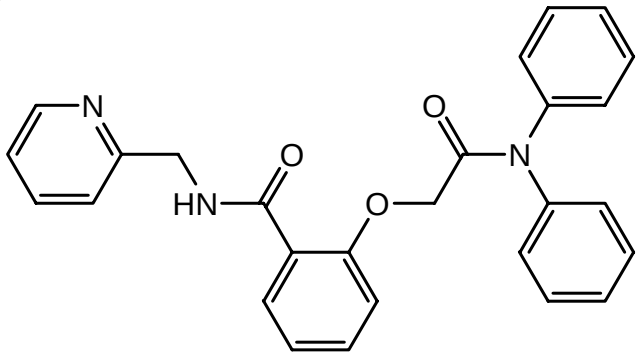
Key Words: Synthesis, Crystal structure, Salicylic acid derivative.

INTRODUCTION

Salicylic acid and its derivatives have been finding wide application in the pesticide, pharmaceutical, dyes, rubber and other regions because their such biological acticity as killing or inhibition to bacterium and fungus[1-3]. The studies of the new synthetic method and the biological acticity for the amide-type compound based on salicylic acid are a significant subject. In the present paper, a new salicylic acid derivative with two amide bonds, 2-(2-(diphenylamino)-2-oxoethoxy)-*N*-(pyridin-2-ylmethyl)benzamide (**I**), was synthesized and its structure was characterized by EA, IR, ^{1}H NMR and X-ray crystallographic analysis.

EXPERIMENTAL

All chemicals were of analytical reagent grade and used directly without further purification. ^{1}H NMR spectrum was recorded by Bruker AC-500 with TMS as an internal standard. IR spectrum was taken by Nicolet



2-(2-(Diphenylamino)-2-oxoethoxy)-N-(pyridin-2-ylmethyl)benzamide (**I**)

510P FT-IR spectrometer (KBr). Elemental analysis was performed by Perkin-Elmer 240.

2-Hydroxy-*N*-(pyridin-2-ylmethyl)benzamide was prepared by the reaction of salicylic acid and 2-aminomethylpyridine according to the literature method[4]. To a solution of 2-hydroxy-*N*-(pyridin-2-ylmethyl)-benzamide (2.28 g, 10 mmol) in acetone (30 mL) were added 2-chloro-*N*,*N*-diphenyl-acetamide (2.45 g, 10 mmol), K_2CO_3 (1.52 g, 11 mmol) and KI (0.5 g), respectively and the mixture was stirred at 56ºC for 5 h. The mixture was washed three times with water (50 mL) and then filtered. The filter cake was washed with a small amount of acetone and water. 2-Hydroxy-*N*-(pyridin-2-ylmethyl)benzamide (4 g) was obtained after dryness of the resulting yellow powders at room-temperature for 48 h. Yellow rhombic single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation at room-temperature from ethyl acetate after 7 d. ^{1}H NMR (500 MHz, $CDCl_3$): 9.47 (s, 1H), 8.54 (d, 1H), 8.23 (d, 1H), 7.65 ~ 6.70 (16H), 4.82 (d, 2H), 4.70 (s, 2H). IR (KBr, cm^{-1}): 1596 (s), 1484 (s), 1431 (s), (Ar); 1686 (vs), ν(C=O); 1298 (s), ν(C–N); 1239(s), 1069(w), ν(Ar–O–C); 3357(s), ν(N–H); 3052(w), ν(Ar–H). Anal. Calcd. (%) for $C_{27}H_{23}N_3O_3$: C, 74.12; H, 5.30; N, 9.60. Found (%): C, 73.82; H, 5.38; N, 9.56.

Crystal data and structure determination: A yellow single crystal with a dimension of 0.11 × 0.17 × 0.34 mm was mounted on a glass fiber in a random orientation. The data were collected by Bruker Smart 1000 CCD diffactometer with graphite monochromated MoKα radiation (λ = 0.71073 Å) using ω scan mode in the range of $1.7 \leq \theta \geq 26.0^o$ at temperature 293 ± 2 K. A total of 6493 reflections were collected with 4386 unique ones, of which 3137 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinements. Intensity data were corrected for Lp factors and empirical absorption. The structure was solved by direct methods and expanded by using Fourier differential techniques with

SHELXL-97[5]. All non-hydrogen atoms were located with successive difference Fourier syntheses. The structure was refined by full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added according to the theoretical models. Full matrix least-squares refinement gave the final R = 0.0551 and wR = 0.1504, $W = 1/[\sigma^2(F_0)^2 + (0.0647P)^2 + 0.2999P]$ where $P = (F_0^2 + 2F_c^2)/3$. Software used to prepare material for publication: SHELXTL, PARST[6] and PLATON[7].

RESULTS AND DISCUSSION

Selected bond lengths and bond angles are illustrated in Tables 1 and 2, respectively. The hydrogen bonding geometries are shown in Table-3. Fig. 1 shows the molecular structure of the compound.

TABLE-1
SELECTED BOND LENGTHS (Å)

Bond	Distance	Bond	Distance
O1-C7	1.226(3)	C1-C2	1.371(13)
O2-C13	1.368(2)	C1B-C2	1.71(2)
O2-C14	1.415(2)	C2-C3	1.224(11)
N1-C1	1.308(10)	C3-C4	1.393(6)
N1-C5	1.377(7)	C4-C5	1.308(4)
N1B-C5	1.465(12)	C5-C6	1.505(3)
N2-C6	1.447(3)	C7-C8	1.507(3)
N2-C7	1.340(3)	C8-C9	1.387(4)
N3-C16	1.445(2)	C9-C10	1.371(4)
N3-C22	1.441(3)	C10-C11	1.364(4)
C8-C13	1.402(3)	C11-C12	1.376(3)
C14-C15	1.514(3)	C12-C13	1.383(3)
N3-C15	1.362(2)	C16-C21	1.373(3)

The bond lengths and angles in 2-(2-(diphenylamino)-2-oxoethoxy)-*N*-(pyridin-2-ylmethyl)benzamide are within normal ranges[8] and are comparable with those in the related structure[9]. The N3 atom shows a •planar configuration, to which the two benzene rings (C16-C21 and C22-C27) attached making a dihedral angle of 77.3(1)°. While these two rings twist 88.5(1) and 45.9(1)°, respectively, from the central C8-C13 ring. The pyridine ring shows positional disorder, with occupancy of 0.57 for the main compounent.

There exists an intramolecular hydrogen bond, *via* N2–H2A···2, forming a six-membered ring. Molecules of the 2-(2-(diphenylamino)-2-oxoethoxy)-*N*-(pyridin-2-ylmethyl)benzamide are linked into ribbons along the b axis, *via* C17–H17A···O3 and C26–H26A···N1 intermolecular

TABLE-2
SELECTED BOND ANGLES (°)

Angle	(°)	Angle	(°)
C13-O2-C14	118.70(15)	N1B-C5-C4	117.3(4)
C1-N1-C5	116.9(7)	N1B-C5-C6	106.3(4)
C1B-N1B-C5	112.2(10)	N2-C6-C5	114.34(19)
C6-N2-C7	120.76(17)	O1-C7-N2	121.24(19)
C15-N3-C16	122.70(17)	O1-C7-C8	119.99(19)
C16-N3-C22	116.84(15)	N2-C7-C8	118.72(18)
C15-N3-C22	120.06(16)	O2-C13-C8	116.44(17)
N1-C1-C2	122.1(9)	O2-C13-C12	122.87(17)
N1B-C1B-C2	107.8(11)	C8-C13-C12	120.69(19)
C1B-C2-C3	104.5(8)	O2-C14-C15	106.39(16)
C1-C2-C3	119.7(6)	O3-C15-C14	121.84(17)
C2-C3-C4	118.8(5)	N3-C15-C14	114.96(17)
C3-C4-C5	121.3(4)	O3-C15-N3	123.19(19)
N1-C5-C4	115.8(3)	N3-C16-C17	120.48(17)
N1-C5-C6	112.7(3)	N3-C16-C21	119.4(2)
C4-C5-C6	127.4(3)	C17-C16-C21	120.1(2)

TABLE-3
THE HYDROGEN BOND LENGTHS (Å) AND BONG ANGLE (°)
FOR THE TITLE COMPOND

Donor-H···Acceptor	D-H	H···A	D···A	D-H···A
N2--H2A···O2	0.8599	1.9662	2.637(2)	134.00
C9--H9A···O1	0.9308	2.4222	2.759(3)	101.21
C17--H17A···O3^{i}	0.9309	2.5745	3.458(3)	158.67
C26--H26A···N1^{ii}	0.9297	2.5163	3.441(6)	173.02

Symmetry codes: i = -x, 2-y, -z; ii = -1-x, 1-y, -z

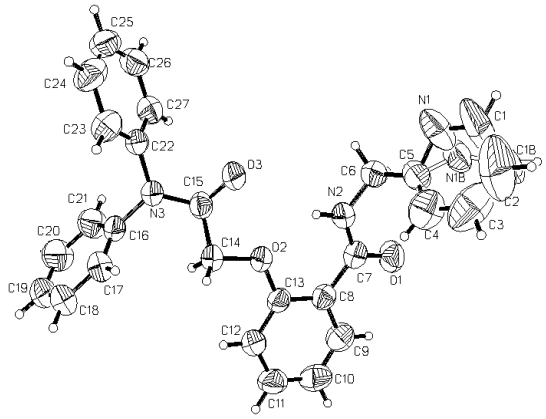


Fig. 1. Molecular structure of the 2-(2-(diphenylamino)-2-oxoethoxy)-*N*-(pyridin-2-ylmethyl)benzamide with the atomic numbering scheme

interactions (Table-4). The packing is further stabilized by Van der Waals forces. Packing diagram of the title compound in a unit cell is shown in Fig. 2.

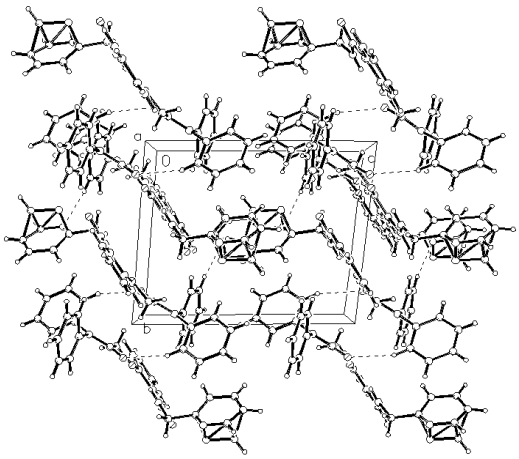


Fig. 2. A view of the crystal packing of 2-(2-(diphenylamino)-2-oxoethoxy)-*N*-(pyridin-2-ylmethyl)benzamide

Fluorescent property: The fluorescent spectrum of 2-(2-(diphenylamino)-2-oxoethoxy)-*N*-(pyridin-2-ylmethyl)benzamide was detected and shows very strong fluorescent property, when Ex_{max} = 333 nm, Em_{max} = 393 nm.

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