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Synthesis and Crystal Structure of 1,4-Di(1-naphthyl)-2,5-piperazinedione

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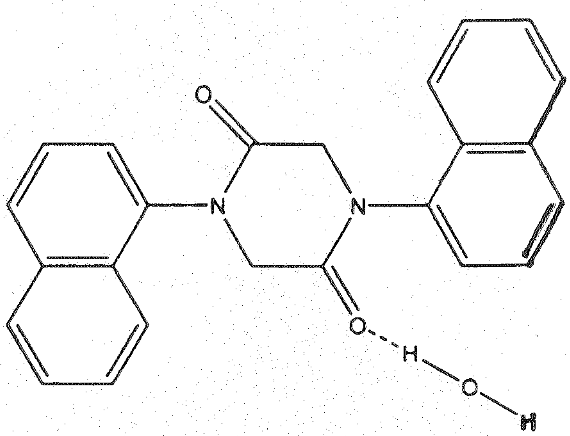
The crystal structure of 1,4-di(1-naphthyl)-2,5-piperazinedione has been determined by single crystal X-ray diffraction method. The crystal belongs to monoclinic system, space group C2/c with unit cell constants $a = 28.71$ (2), $b = 5.721$ (4), $c = 11.451$ (9) Å, $V = 1847$ (2) Å^3, $Z = 8$, $D_c = 1.368$ g/cm^3, $\mu = 0.092$ mm^{-1}, F(000) = 792, R and wR are 0.0871 and 0.2836, respectively for 1601 unique reflections with 998 observed reflections ($I > 2\sigma(I)$). The molecules are interconnected into three-dimensional network by O1W-H1W1···O1 & C8-H8···O1W intermolecular interactions.

Key Words: Synthesis, Crystal structure, Piperazinedione.

INTRODUCTION

Piperazinedione and its derivatives are the smallest structural cyclodipeptides and are regarded as a by-product in the synthesis, especially in the solid-phase synthesis of peptides[1-3]. The hydrogen bonds are one of the main modes for the interaction between drug and acceptor, and two donors and two acceptors to form hydrogen bonds are present in the molecule of piperazinedione; so its derivatives have been used widely in pharmaceutical chemistry, *e.g.*, the inhibition of the cell growth cycles of the mammals[4, 5], the inhibition of glutathion-S-transferase[6] and the inhibition of the activated factor of thrombocytes[7]. In recent years, piperazinedione and its derivatives have received considerable attention due to such properties as the stable six-membered cyclic structure and molecular diversity. In the present paper, a new piperazinedione derivative, 1,4-bis(naphthalen-1-yl)piperazine-2,5-dione (I), was synthesized by the cyclocondensation reaction of N-naphthalen-1-yl chloroacetamide and its structure was characterized by EA, IR, ^{1}H NMR, TG and X-ray crystallographic analysis.



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EXPERIMENTAL

All chemicals were of analytical reagent grade and used directly without further purification. ^1H NMR spectrum was recorded by Bruker AC-300 with TMS as an internal standard. IR spectrum was taken by Nicolet 510P FTIR spectrometer (KBr). Elemental analysis was performed by Perkin-Elmer 240.

N-naphthalen-1-yl chloroacetamide was prepared by the reaction of 1-naphthylamine and chloroacetyl chloride in the presence of triethylamine according to the literature method[8]. To a solution of N-naphthalen-1-yl chloroacetamide (4.39 g, 20 mmol) in acetone (30 mL) were added K_2CO_3 (3.04 g, 22 mmol) and NaI (0.5 g), respectively, and the mixture was stirred at 56°C 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. The title compound was obtained after dryness of the resulting white powders at room temperature for 48 h. Colourless prismatic single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation at room temperature from $CHCl_3 : CH_3CH_2OH$ (1 : 1) after 10 days. ^1H NMR (400 MHz, DMSO): 4.25 (s, 4H), 7.28 (t, 2H), 7.47 (t, 2H), 7.80 (t, 2H), 7.90 (d, 2H), 8.08 (d, 2H), 8.20 (d, 2H), 8.40 (d, 2H), IR (KBr, cm^{-1}): 1597 (w), 1574 (w), 1480 (s) (Ar); 1643 (*vs*), ν(C═O); 1274 (w), ν(C—N). Anal., Calcd. for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65%; Found: C, 78.69; H, 5.00; N, 7.56%.

Crystal data and structure determination

A colourless single crystal with approximate dimension of 0.40 × 0.37 × 0.03 mm was mounted on glass fibre in a random orientation. The data were collected by Bruker Smart 1000 CCD diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) using ω scan mode in the range of $1.44 \le \theta \le 25.00°$ at temperature 293(2) K. A total of 4123 reflections were collected with 1601 unique ones ($R_{int} = 0.0661$), of which 998 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinements. Intensity data were corrected for L_p factors and empirical absorption. The structure was solved by direct methods and expanded by using Fourier differential techniques with SHELXL-97[9]. 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 $R = 0.0871$ and $wR = 0.2836$, $W = 1/[\sigma^2(F_0)^2 + (0.1327P)^2 + 0.5336P]$ where $P = (F_0^2 + 2F_c^2)/3$.

RESULTS AND DISCUSSION

The final atomic parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table-1. Selected bond lengths and bond angles are illustrated in Tables 2 and 3, respectively. The hydrogen bonding geometries are shown in Table-4. Fig. 1 shows the molecular structure of the compound.

TABLE-1

ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}
O1W	0.0000	–0.7337(11)	1/4	0.0728(16)
O1	0.03729(10)	0.3542(7)	0.6406(3)	0.0627(11)
N1	0.04935(10)	0.0398(6)	0.5331(3)	0.0391(10)
C1	0.12098(15)	–0.0937(11)	0.6628(4)	0.0552(14)
C2	0.17047(16)	–0.0772(12)	0.7099(4)	0.0619(16)
C3	0.19709(15)	0.0841(10)	0.6700(4)	0.0551(15)
C4	0.17706(13)	0.2412(9)	0.5792(4)	0.0472(13)
C5	0.20384(15)	0.4175(10)	0.5363(4)	0.0532(14)
C6	0.18406(17)	0.5647(11)	0.4476(4)	0.0588(15)
C7	0.13563(16)	0.5370(10)	0.3945(4)	0.0528(13)
C8	0.10837(14)	0.3811(9)	0.4349(4)	0.0467(12)
C9	0.12735(12)	0.2215(8)	0.5289(3)	0.0405(12)
C10	0.10071(12)	0.0530(8)	0.5758(3)	0.0423(12)
C11	0.02158(13)	0.1898(9)	0.5753(3)	0.0443(12)
C12	0.03219(13)	–0.1595(9)	0.4556(4)	0.0498(13)

TABLE-2

SELECTED BOND LENGTHS (Å)

Bond	Dist.	Bond	Dist.
O1-C11	1.233(5)	C4-C9	1.439(5)
N1-C11	1.323(5)	C5-C6	1.358(7)
N1-C10	1.465(5)	C6-C7	1.418(7)
N1-C12	1.471(6)	C7-C8	1.327(7)
C1-C10	1.348(7)	C8-C9	1.438(6)
C1-C2	1.425(6)	C9-C10	1.399(6)
C2-C3	1.333(7)	C11-C12A	1.527(5)
C3-C4	1.412(7)	C12-C11A	1.527(5)
C4-C5	1.411(7)		

TABLE-3
SELECTED BOND ANGLES (°)

Angle	(°)	Angle	(°)
C11-N1-C10	118.3(3)	C7-C8-C9	121.5(4)
C11-N1-C12	124.5(3)	C10-C9-C8	124.6(3)
C10-N1-C12	116.3(3)	C10-C9-C4	118.3(4)
C10-C1-C2	119.9(5)	C8-C9-C4	117.2(4)
C3-C2-C1	120.8(5)	C1-C10-C9	121.5(4)
C2-C3-C4	120.9(4)	C1-C10-N1	118.8(4)
C5-C4-C3	122.6(4)	C9-C10-N1	119.7(4)
C5-C4-C9	118.8(4)	O1-C11-N1	122.6(3)
C3-C4-C9	118.7(4)	O1-C11-C12A	117.7(4)
C6-C5-C4	121.6(4)	N1-C11-C12A	119.6(4)
C5-C6-C7	119.3(5)	N1-C12-C11A	115.9(3)
C8-C7-C6	121.4(5)		

TABLE-4
THE HYDROGEN BOND LENGTHS (Å) AND BONG ANGLE (°) FOR THE TITLE COMPOUND

Donor-H···acceptor	D-H	H···A	D···A	D-H···A
O1W-H1W1···O1^{i}	1.19(7)	1.63(7)	2.817(6)	170(5)
C8-H8···O1W	0.97(4)	2.57(4)	3.479(5)	156(3)

Symmetry code: i = −x, −y, 1 − z; ii = x, 1 + y, z

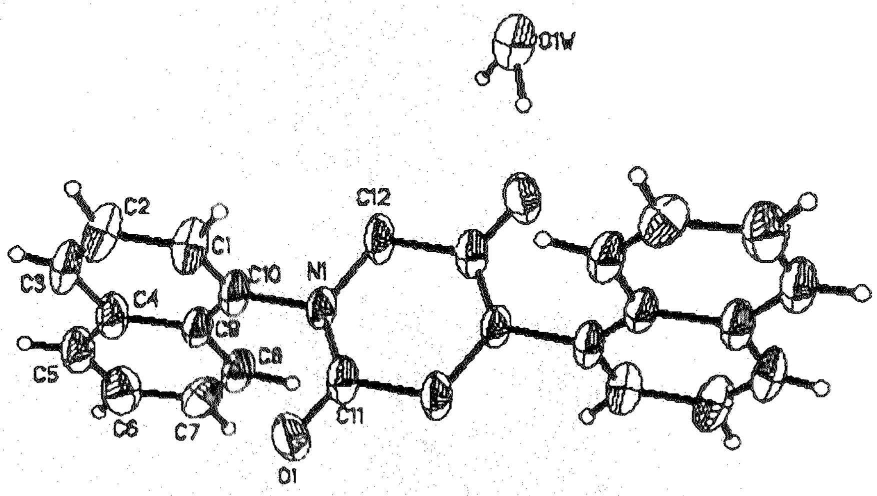

Fig. 1. The molecular structure of the title compound with the atomic numbering scheme

The asymmetric unit of (1) contains half of the molecule and one free water, the other half being related by a crystallographic centre of symmetry at the centroid of the piperazinedione ring (N1/C11/C12/N1^i/C11^i/C12^i) [symmetry code: –x, –y, 1 – z]. The bond lengths and angles are within normal ranges[10], and are comparable with the related structure, 1,4-bis(4-methoxyphenyl)piperazine-2,5-dione, (II)[11]. Compared with the structure of (II), the whole molecule of (I) is not planar, with dihedral angles of 77.7(1)° between the piperazinedione and the two aromatic rings, while the two naphthalene planes are parallel to each other. The sum of the bond angles around atom N1 [359.6(3)°] indicates a planar configuration because of the π conjugation effects arising from the presence of the two carbonyl groups. These two carbonyl groups also cause the decrease of the N1-C11 bond length to 1.323(5) Å, between single and double C—N bonds.

The water molecules act as both donors and acceptors *via* O1W-H1W1· · ·O1 and C8-H8· · ·O1W interactions, connecting the molecules into a three-dimensional network. 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.

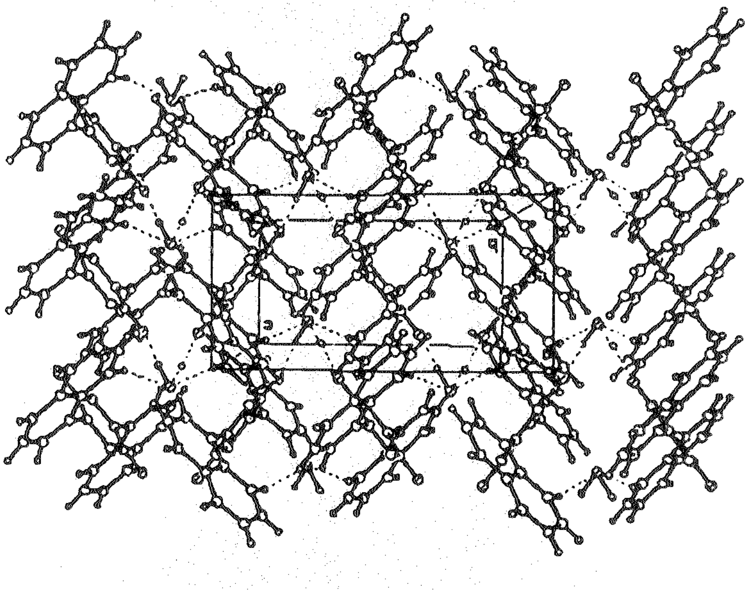

Fig. 2. A view of the crystal packing for the title compound

Thermal analysis

Thermal analysis curves of the title compound are shown in Fig. 3. Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis show that the thermal decomposition of the title compound includes two transitions. There are two peaks corresponding to exothermal processes, *i.e.*, a weak peak at 140.8°C correspoding to removal of free water and a strong peak at 396.6°C implying the decomposition of the title compound.

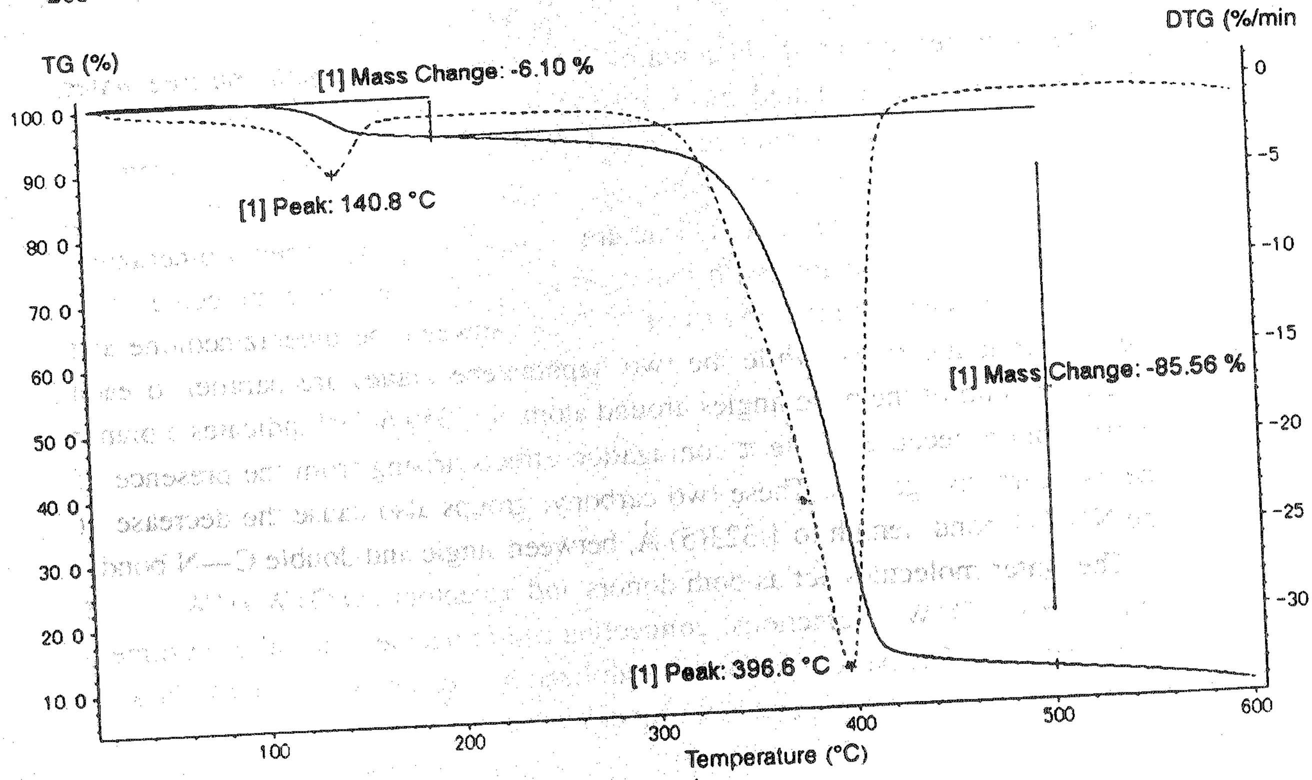

Fig. 3. Thermal anaylsis curves of the title compound

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