Crystal Structure of 2,5-Bis(1-butyl-benzimidazol-2-yl)thiophene

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The title compound, 2,5-bis(1-butyl-benzimidazol-2-yl)thiophene ($C_{26}H_{32}N_4O_2S$, $M_r = 464.62$), was synthesized and its crystal structure determined by single-crystal X-ray diffraction. The crystal is of monoclinic, space group $P2_1/n$ with $a = 8.7215(8)$, $b = 18.9156(18)$, $c = 14.7475(14)$ Å, $\beta = 96.696(2)^\circ$, $V = 2416.3(4)$ Å³, $Z = 4$; the final $R = 0.0426$ and $wR = 0.1064$. The molecules are linked by intermolecular hydrogen bonds (O–H...O, and O–H...N) to form a parallel dimer structure, which stabilizes the crystal structure.

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Recently, heterocyclic imidazole derivatives have attracted considerable attention because of their unique optical properties. It was reported that 2,5-bis(benzimidazol-2-yl)thiophenes and their homologues are useful as optical brighteners for synthetic fibers and plastics, as clearing agents for organic materials, as optical bleaches for resins, cellulosic fibers, nylon and polyvinyls or as dye intermediates,^{1–3} or a fabric softening agent. Also some of them could exhibit bio-activity, such as against triochophyton rubrum and fungicide activity. Therefore, it is very important to investigate the synthetic method and the optical spectral behaviors of this kind of compound. We hope to report a good method to introduce some alkyl groups into a molecule of 2,5-bis(benzimidazol-2-yl)thiophene to obtain 2,5-bis(1-alkyl-benzimidazol-2-yl)thiophene compounds to improve the solubility in common organic solvents.

2,5-Bis(benzimidazol-2-yl)thiophene was prepared as a reference.^{1–3} 2,5-Bis(1-butylbenzimidazol-2-yl)thiophene was synthesized according to as the following procedure: a mixture of 0.63 g (2.0 mmol) of 2,5-bis(benzimidazol-2-yl)thiophene, 0.60 g (4.4 mmol) of 1-bromobutane, 0.30 g of tetrabutylammonium bromide and 10 mL of 50% NaOH in 10 mL of butanone was refluxed for 4 h. The mixture was cooled to room temperature and then poured into 200 mL of water. When butanone evaporated a crude product, 2,5-bis(1-butylbenzimidazol-2-yl)thiophene, was obtained; the crude product was recrystallized from ethanol to yield pure 2,5-bis(1-butylbenzimidazol-2-yl)thiophene products. Yield: 71.0%, m.p. 104–105°C. ¹H-NMR (300 MHz, DMSO, δ): 0.95 (t, $J = 7.3$ Hz, 6H), 1.44 (m, 4H), 1.89 (m, 4H), 4.41 (t, $J = 7.5$ Hz, 4H), 7.27 (m, 4H), 7.34 (m, 2H), 7.66 (s, 2H), 7.80 (m, 4H). ¹³C-NMR (DMSO, δ): 14.0, 20.5, 32.5, 45.1, 110.2, 120.3, 123.1, 123.6, 129.0, 135.2, 136.5, 143.5, 146.9. MS(m/z): 429.3(M + H⁺). A colorless single crystal suitable for an X-ray structural analysis was obtained by slowly evaporating from ethanol at room temperature.

A single crystal of the title compound having dimensions of 0.50 × 0.40 × 0.20 mm was chosen for X-ray diffraction studies.

The measurements were made on a Bruker SMART CCD diffractometer with graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å) at 293(2)K. The structure was solved by direct methods using SHELXS-97, and refined by full-matrix least-squares techniques anisotropically for all non-H atoms.

The hydrogen atoms of water molecules were located in a difference Fourier map; the remaining hydrogen atoms were added according to a theoretical model. The crystal data and experimental parameters are listed in Table 1. The chemical diagram of the title compound is shown in Fig. 1, and the crystal structure is shown in Fig. 2. The selected bond lengths and bond angles are summarized in Table 2. The hydrogen-bonding distances and angles are presented in Table 3.

Table 1 Crystal and experimental data

Formula	$C_{26}H_{32}N_4O_2S$
Formula weight	464.62
Crystal system	monoclinic
Space group	$P2_1/n$, $Z = 4$
a	8.7215(8) Å
b	18.9156(18) Å
c	14.7475(14) Å
β	96.696(2)°
V	2416.3(4) Å ³
D_x	1.277 Mg/m ³
Absorption coefficient	0.165 mm ^{−1}
$F(0\ 0\ 0)$	992
θ range for data collection	1.76 to 27.05° with Mo K_α
Reflections collected/unique	16278/5231 [$R(\text{int}) = 0.0330$]
Data/restraints/parameters	5231/0/300
Goodness-of-fit on F^2	1.042
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0426$, $wR2 = 0.1064$
$(\Delta/\sigma)_{\text{max}}$	0.000
$(\Delta\rho)_{\text{max}}$	0.372 e. Å ^{−3}
$(\Delta\rho)_{\text{min}}$	−0.348 e. Å ^{−3}
Measurement	Bruker SMART CCD area detector
Structure determination	Direct method
Refinement	full-matrix least-squares on F^2
CCDC No	636369

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Fig. 1 Structural chemical diagram.

Fig. 2 Molecular structure along with atom labeling.

Table 2 Selected bond lengths [Å] and bond angles [°]

Atoms	Length	Atoms	Length
S(1)-C(11)	1.726(17)	N(4)-C(18)	1.380(2)
S(1)-C(8)	1.7275(18)	N(4)-C(23)	1.464(2)
N(1)-C(7)	1.319(2)	C(7)-C(8)	1.460(2)
N(1)-C(1)	1.383(2)	C(8)-C(9)	1.368(2)
N(2)-C(7)	1.373(2)	C(9)-C(10)	1.404(3)
N(2)-C(6)	1.389(2)	C(10)-C(11)	1.371(2)
N(2)-C(19)	1.463(2)	C(11)-C(12)	1.455(2)
N(3)-C(12)	1.326(2)	C(19)-C(20)	1.524(2)
N(3)-C(13)	1.383(2)	C(23)-C(24)	1.521(2)
N(4)-C(12)	1.371(2)		
Atom	Angle	Atoms	Angle
C(11)-S(1)-C(8)	92.14(8)	C(9)-C(8)-S(1)	110.73(13)
C(7)-N(1)-C(1)	105.40(14)	C(7)-C(8)-S(1)	115.30(13)
C(7)-N(2)-C(6)	105.95(15)	C(8)-C(9)-C(10)	113.20(16)
C(7)-N(2)-C(19)	128.31(15)	C(11)-C(10)-C(9)	113.38(16)
C(6)-N(2)-C(19)	125.65(15)	C(10)-C(11)-C(12)	133.49(16)
C(12)-N(3)-C(13)	105.19(14)	C(10)-C(11)-S(1)	110.54(13)
C(12)-N(4)-C(18)	106.31(15)	C(12)-C(11)-S(1)	115.90(13)
C(18)-N(4)-C(23)	129.12(15)	N(3)-C(12)-N(4)	112.81(15)
N(1)-C(1)-C(2)	129.89(18)	N(3)-C(12)-C(11)	121.37(15)
N(1)-C(1)-C(6)	109.69(15)	N(4)-C(12)-C(11)	125.80(16)
N(2)-C(6)-C(5)	132.10(18)	N(3)-C(13)-C(14)	130.22(17)
N(2)-C(6)-C(1)	105.89(15)	N(4)-C(18)-C(17)	131.85(18)
N(1)-C(7)-N(2)	113.07(15)	N(4)-C(18)-C(13)	106.03(15)
N(1)-C(7)-C(8)	121.09(15)	N(2)-C(19)-C(20)	113.26(15)
N(2)-C(7)-C(8)	125.84(16)	N(4)-C(23)-C(24)	110.90(15)
C(9)-C(8)-C(7)	133.96(16)		

A structure analysis reveals that each unit cell consists of one 2,5-bis(benzimidazol-2-yl)thiophene neutral molecule and two waters. As can be seen from Fig. 2, the two benzimidazol and thiophene rings are essentially planar with maximum deviations of 0.0083, 0.0253, and 0.0026 Å for atoms N2, N4 and S1, respectively. The dihedral angles between the thiophene ring

Table 3 Geometries of hydrogen-bonds [Å, °]

D-H...A	D-H	H...A	D...A	D-H...A
OW1-H1A ... N3	0.893	2.003	2.890	172.15
OW1-H1B ... OW2 ⁱ	0.921	1.872	2.783	169.48
OW2-H2A ... N1	0.911	1.980	2.889	175.00
OW2-H2B ... OW1	0.922	1.946	2.840	162.86

Symmetry transformations used to generate equivalent atoms: (i) $-x + 1, -y + 1, -z + 1$.

plane and the ring planes of benzimidazol (C1-C7, N1, N2) and (C12-C18, N3, N4) are 2.8 and 4.8°, respectively; the two benzimidazole moieties form a dihedral angle of 2.9°, which indicates that the 2,5-bis(benzimidazol-2-yl)thiophene molecule is nearly coplanar (with maximum deviation of -0.1356 Å for atom S1). However, the butyl atoms (C20-C22, C24-C26) deviate from the molecule mean plane on the same side. As a result, the whole compound is not a planar molecule.

This is evident from the observed distances of N1-C7(1.319(2)Å) and N3-C12(1.326(3)Å), which are consistent with carbon-nitrogen double bonds; similarly, the bond lengths of N2-C7(1.373(2)Å), and N4-C12(1.371(2)Å) are also consistent with typical carbon-nitrogen single bonds. The C7-C8 and C11-C12 bond lengths (1.460(2) and 1.455(2)Å, respectively) are shorter than that of normal C-C single bond, suggesting that the two benzimidazole moieties are conjugated with a thiophene unit. These characteristics are in good agreement with those of 1,2-di(4-methoxybenzyl)-benzimidazole and 2,6-bis(benzo[1,2-d:4,5-d']diimidazole-2'-yl)pyridine.^{4,5}

The water molecules have a particularly significant role in the structure of 2,5-bis(1-butylbenzimidazol-2-yl)thiophene, owing to the participation of hydrogen-bonds. There are four intermolecular hydrogen bonds that are observed in the crystal lattice, two each of the O-H...O and O-H...N types (Table 4), thus generating a parallel dimer structure around the inversion center, which stabilizes the crystal structure.

Because two benzimidazole ring planes and the thiophene ring plane of the 2,5-bis(1-butylbenzimidazol-2-yl)thiophene molecule are nearly coplanar, the two benzimidazole moieties are conjugated with the thiophene unit; 2,5-bis(1-butylbenzimidazol-2-yl) thiophene is thus expected to have a strong fluorescence-emitting ability, and the presence of two butyl groups in this molecule is expected to enhance the solubility of 2,5-bis(benzimidazol-2-yl)thiophene in many kinds of solvents, and almost does not twist the plane of the whole conjugated system.

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