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The title compound, $C_{16}H_{12}N_2S_2$, crystallizes in the monoclinic space group $P2_1/n$ with Z = 4, a = 8.950 (5) Å, b = 9.141 (5) Å, c = 17.429 (5) Å and β = 93.638 (5)°. The benzimidazole ring is essentially planar. The crystal structure is stabilized by intermolecular C—H···N and C—H···π contacts.

Introduction

The benzimidazole ring is a crucial pharmacophore in drug discovery. Benzimidazoles show different biological activities, such as anticancer, antimicrobial, or anthelmintic activities[1]. Benzimidazole derivatives are a unique broad-spectrum class of antirhino/enteroviral agents. Benzimidazoles exhibit significant activities against several viruses including HIV, herpes (HSV-1), RNA, influenza and human cytomegalovirus (HCMV)[2]. The synthesis of benzimidazoles has received much attention owing to the varied biological activity exhibited by a number of these compounds. The synthesis of heteroaryl substituted- 1H benzimidazoles has become of recent interest to medicinal chemists owing to the pharmacophoric properties of the heteroaromatic rings. A number of synthetic methods have been developed in recent years to uncover a variety of new reagents for the synthesis of 2-substituted benzimidazoles[3−8]. Benzimidazoles can be synthesized by a number of methods, usually involving formation of the N—C—N unit as the key step. One of the formerly utilized general routes to benzimidazoles involves the reaction of aldehydes and ketones with *o*-phenylenediamine. Although there are several routes leading to 2-substituted benzimidazoles, a typical procedure involves heating *o*-phenylenediamine with a substituted carboxylic acid in the presence of a mineral acid[9−10]. In this context, we have synthesized several new aryl substituted benzimidazoles, including the title compound.

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Experimental

Instrumentation

Single-crystal X-ray data were collected on a Stoe X-AREA single crystal diffractometer using monochromated MoKα radiation at 296 K. Semi-empirical absorption corrections were made from equivalents. The structure was solved by direct and conventional Fourier methods. H atoms were placed geometrically [0.93 Å (C—H)] and allowed to ride on their parent atoms, with Uiso(H) = 1.2 Ueq(C). The program used for cell refinement: Stoe X-AREA[11]. Program used to solve structure: SHELXS-97[12]. Molecular graphics: ORTEP-3 for Windows[13] and PLATON[14]. Software used to prepare material for publication: WinGX[15] publication routines. Further details concerning data collection and refinement are given in Table 1.

Table 1. Crystal data and structure refinement.

Formula	$C_{16}H_{12}N_2S_2$
Crystal system	Monoclinic
Color/shape	Colorless/Stick
Temperature	296 K
Space group	$P2_1/n$
Unit cell dimensions	a = 8.950 (5) Å
	b = 9.141 (5) Å
	c = 17.429 (5) Å
	β = 93.638 (5)°
Volume	1423.0 (12) Å^3
Z	4
Density (calculated)	1.383 Mg m^{-3}
Wavelength	0.71069 Å
Reflections collected	32082
Independent reflections	3309 [R(int) = 0.0480]
Absorption coefficient (μ)	0.364 mm^{-1}
Crystal size/mm	0.500 × 0.313 × 0.140
Absorption correction	integration X-RED
Data/parameters	3309 / 181
Goodness-of-fit on F^2	1.089
θ ranges / (°)	2.23– 27.93
h / k / l	-11,11 / -11,11 / -22,22
Final R indices [I > 2σ(I)]	R1 = 0.0515, wR2 = 0.1521
Largest diff. peak and hole	0.555 e. Å^{-3} and -0.414 e. Å^{-3}

Synthesis

A solution of 1,2-diaminobenzene (0.01 mol) in absolute ethanol (20 mL) was added in small portions to a solution of thiophen-2-carbaldehyde (0.02 mol) in absolute ethanol (30 mL). The reaction mixture was maintained at 70 °C for 4 h, cooled and then added to ice-cold water. The resulting solid was washed with water, dried and recrystallized from ethanol (yield: 70%; m.p. 424 K). IR (cm^{-1}): 3063 (Ar H), 1589 (C=C), 1568 (C=N), 1159 (C—N); ^{1}H-NMR: δ 5.62 (s, 2H, NH_2), 6.83–7.78 (m, 10H, Ar H); ^{13}C-NMR: δ 45.7, 111.7, 121.8, 124.7, 125.7, 127.2, 129,130, 130.6, 164.8.

Results and Discussion

The molecular structure of the title compound is depicted in Figure 1. The title compound contains 3 planar rings. One is the benzimidazole ring (N1, N2, C1- C7); the others are the thiophene rings. The benzimidazole ring in Figure 1 is essentially planar, with a maximum deviation of -0.007 (3) Å for atom C6 (Figure 2). Selected bond lengths and angles are given in Table 2. The thiophene group [A (S2,C13—C16)], attached to C1, is planar and forms a dihedral angle of 24.43 (12)° with the benzimidazole plane. This distortion is probably determined by the interaction between the thiophene group and the C8 methylene

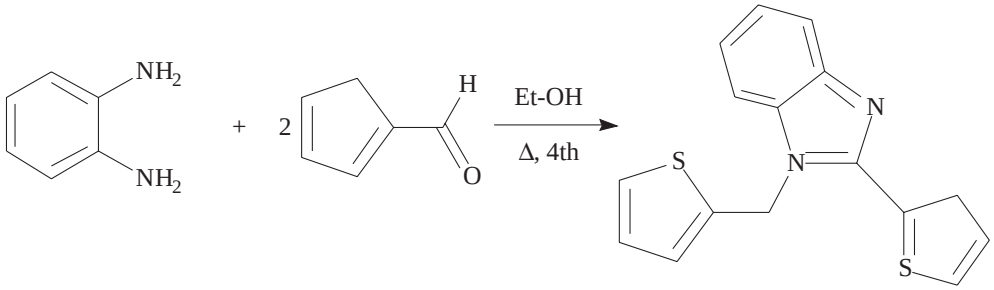

Figure 1. The chemical diagram.

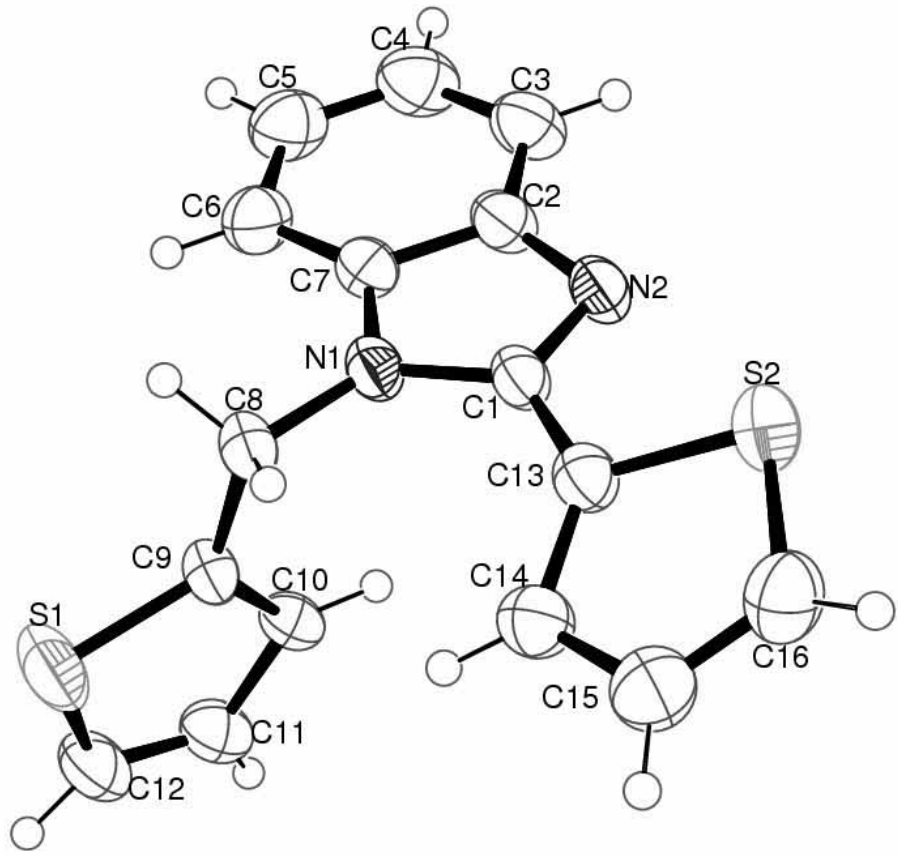

Figure 2. An ORTEP-3[13] drawing of the title compound with atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

group. The thienyl ring [B (S1, C9—C12)] was attached to the C8 methylene group almost perpendicular to the benzimidazole plane (with a dihedral angle of 85.27 (11)°). This ring is disordered (probably swinging about the C8-C9 bond) as is found in other compounds[16,17]. These 2 thienyl rings (A and B) form a dihedral angle of 84.74 (13)°. The C8—C9, N1—C8 and N2—C1 bond distances are 1.501 (3), 1.452 (3) and 1.315(3) Å, respectively, which are similar to the corresponding bond lengths in clemizole [1.492 (6), 1.477(5) and 1.328(5) Å, respectively][18], clemizole hydrochloride [1.491 (10), 1.475(9) and 1.325(8) Å, respectively][19] and clemizoledichlorocobalt(II) [1.521 (8), 1.479(7) and 1.337 (7) Å, respectively][20]. The S1—C9 bond length of 1.706 (2) Å is similar to the corresponding bond lengths in N-benzyl-2,5-bis(2-thienyl)pyrrole [1.7288 (18) Å][21] and 2-[(4-Hydroxyphenyl)iminomethyl]-thiophene [1.712(2) Å][22].

Intermolecular C—H···N close contacts (Table 3) stabilize the crystal structure, forming molecular chains extending approximately parallel to the c axis and stacked along the b axis (Figure 3). The crystal structure also contains C16—H16···π and C10—H10···π interactions with the centroid, CgP, of rings A and B (Figure 3, Table 3).

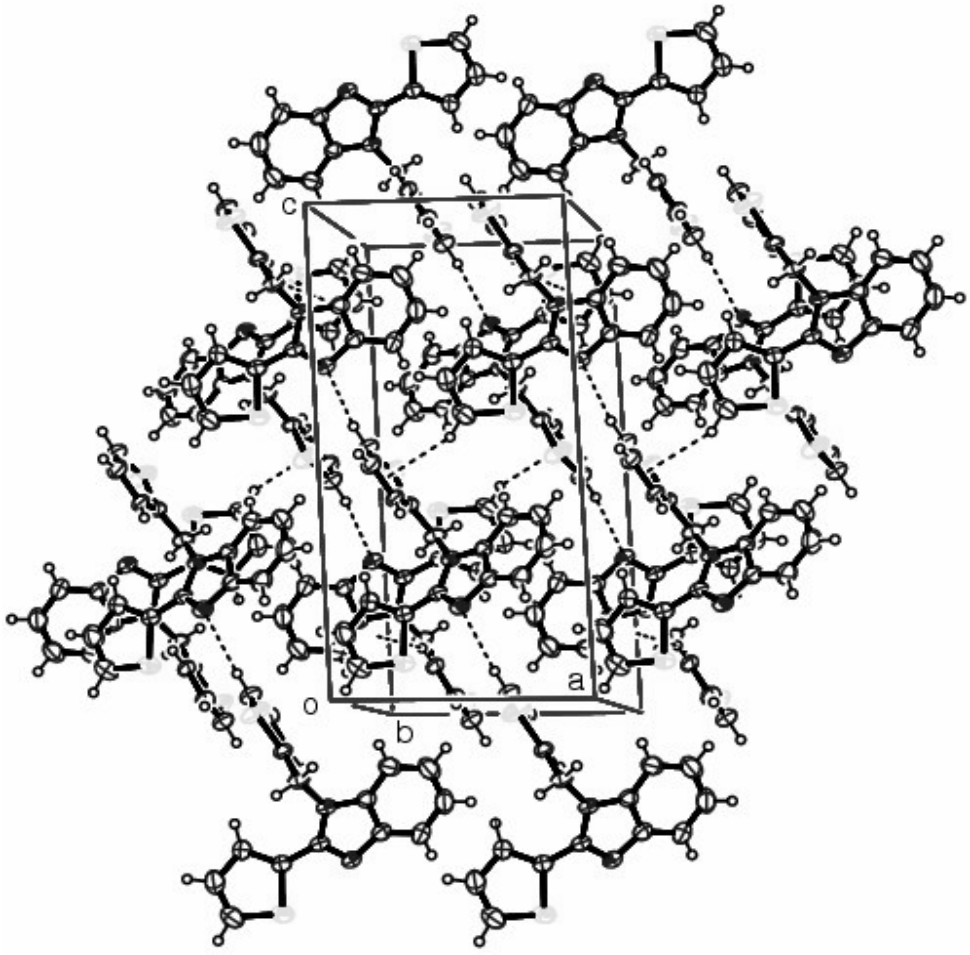

Figure 3. The packing diagram. The dashed lines show the C—H···N and C—H···π (thiophene) contacts.

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Bond lengths		Bond angles	
S1—C12	1.680 (3)	C12—S1—C9	92.60 (13)
S1—C9	1.706 (2)	C16—S2—C13	92.27 (13)
S2—C16	1.686 (3)	C1—N1—C7	106.17 (18)
S2—C13	1.720 (2)	C1—N1—C8	129.3 (2)
N1—C1	1.377 (3)	C7—N1—C8	124.49 (19)
N1—C7	1.387 (3)	C1—N2—C2	105.15 (19)
N1—C8	1.452 (3)	N2—C1—N1	112.9 (2)
N2—C1	1.315 (3)		

Table 3. Close contacts geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···N2^{i}	0.93	2.53	3.444 (3)	166.3
C16—H16···Cg1^{ii}	0.93	2.8963	3.664 (4)	140.67
C10—H10···Cg2^{iii}	0.93	2.8257	3.623 (3)	144.49

Symmetry codes: (i) x – 1/2, 1/2 - y, 1/2 + z; (ii) x – 3/2, -1/2 - y, z – 3/2 ; (iii) 1/2 - x, y- 1/2, 1/2 - z.

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