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Synthesis and Crystal Structure of *bis*[4-(Imidazol-1-yl)phenyl]methane

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A bidentate imidazole derivative with the molecular formula $C_{19}H_{16}N_4$, has been synthesized according to modified Ullmann-type coupling method involving C-N coupling reaction under the catalysis of copper and characterized by the ^{1}H NMR, ^{13}C NMR, elemental analysis and X-ray single-crystal diffraction. In the crystal structure, the two mean plans of benzene rings make dihedral angels of 83.05 (0.07)°. N-H···N hydrogen bonds link the molecules into a 1D supramolecular structure. In addition, weak C-H···π(Ph) stacking interactions are also observed.

Keywords: Imidazole, Coupling reaction, Crystal Structure.

INTRODUCTION

As an important member of five-membered heterocyclic rings, imidazole moieties are commonly found in natural compound structures, which attract many scientists' attention[1]. Nitrogen-containing heterocycles such as N-arylimidazoles have been found extensive applications in medicinal[2], biological[3], natural products[4], and N-heterocyclic carbene chemistry[5]. In recent years, as the development of green chemistry and metal organic chemistry, imidazoles and its derivatives have been widely used in ionic liquid and nitro heterocyclic carbenes, most of which show efficiency of catalysis[6]. In addition, it is of great interest to build supramolecular architectures involving imidazole skeleton in areas of coordination and supermolecular chemistry[7]. Arylimidazoles have attracted much attention due to the rigidity and block of aromatic rings so as to facilitate building the structure of supramolecular MOF[8]. Herein, a new A bidentate imidazole derivative, *bis*[4-(imidazol-1-yl)-phenyl]methane, was synthesized and the single crystal structure was also determined.

Imidazole, copper powder, sodium hydride and all other reagents were purchased from Alfa Aesar and used without further purification. *Bis*(4-iodophenyl)methane was synthesized according to an analogous method reported earlier[9]. DMF were distilled from appropriate drying agents prior to use.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer at 400 HZ and 100 HZ, respectively. C, H and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. X-Ray single crystal structure determination was carried out on a rigaku saturn CCD area detector diffractometer. Melting point were determined with a KY-XT6B.

EXPERIMENTAL

bis[4-(Imidazol-1-yl)phenyl]methane synthesized according to an analogous method reported earlier[10]. A suspended solution of imidazole (1.36g, 20 mmol) and sodium hydride (1.2 g, 30 mmol, 60 % activity) in DMF was stirred in nitrogen atmosphere for about 12 h at room temperature, then powder of copper (0.064 g, 1 mmol) and *bis*(4-iodophenyl) methane (4.22 g, 10 mmol) was added. The mixture was stirred under reflux for 48 h and cooled to room temperature. Then water was added and filtrated to remove solid. The filtrate was extracted by ethyl acetate and extracted solution was washed by saturated salt water for several times and desiccated by anhydrous magnesium sulfate in sequence. Purified white solid was obtained through column chromatography (silica gel), petroleum ether/ethyl acetate = 2:1. yield: 58.3 %, m.p.: 176-178 °C. Anal. Calc. (%) for $C_{38}H_{32}N_8$: C, 75.47; H, 6.00; N, 18.53; Found (%): C, 75.40; H, 6.05; N, 18.50 %. ^{1}H NMR ($CDCl_3$, 25 °C,TMS, δ ppm) 4.08 (s, 2H, $ArCH_2Ar$), 7.21 (d, 2H, J = 0.90 Hz, CH=CHim), 7.27-7.36 (m, 10H, ArH), 7.85 (s, 2H, NCHN) ^{13}C NMR ($CDCl_3$, 25 °C, δ ppm) 139.90, 135.70, 135.47, 130.19, 121.70, 118.20, 40.63.

The crystal data and structure refinement for the titled compound are given in Table-1.

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR THE TITLE COMPOUND

Empirical formula	$C_{19}H_{16}N_4$
Formula weight	300.36
Temperature	296(2) K
Crystal system,	Monoclinic
Space group	C2/c
Cell dimensions	a = 13.828(8) Å, b = 12.923 (8) Å, c = 18.270(9) Å, β = 111.84 (3)°
V	3030(3) Å^3
Z	4
Dcalc	1.317 g cm^{-3}
Absorption coefficient	0.081 mm^{-1}
$F_{(000)}$	1264
Index ranges	-15 ≤ h ≤ 16, -12 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected/unique	8477/2559 [R_{int} = 0.0380]
Independent reflections	2135
Data/restraints/parameters	2559/0/208
Goodness of fit indicator	1.032
Final R indices [I>2σ(I)]a,b	R_1 = 0.0488 wR_2 = 0.1600
Largest difference peak and hole (e Å^{-3})	0.199 and -0.222

X-ray structure determination: Colourless block-shaped single crystals suitable for X-ray diffraction studies were obtained after several weeks by slow evaporation from an acetate solution of the title compound. A crystal of dimensions 0.20 × 0.20 × 0.19 mm was used to determine the crystal structures by X-ray diffraction technique on Rigaku saturn CCD area detector diffractometer with graphite-monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å, T = 296 (2) K) by ω/2θ multi-scan mode. All calculations were performed using the SHELXL-97 crystal graphic software package[11]. All the non-hydrogen atoms were refined anisotropically. In general, hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. The selected bond lengths and bond angles are listed in Table-2.

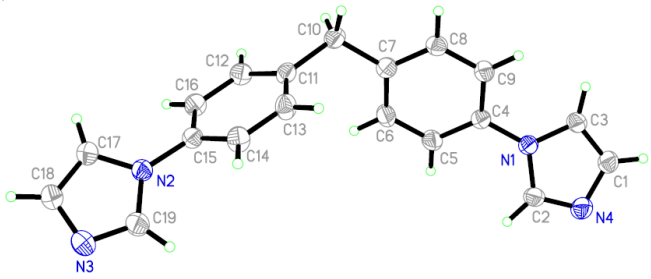

Fig. 1. Molecule structure of *bis*[4-(imidazol-1-yl) phenyl] methane with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level

RESULTS AND DISCUSSION

X-Ray crystal diffraction analysis: In the crystal structure of 2a, both bond distance and bond angles are in normal range. The mean plan of benzene rings in 2a make dihedral angels with each other of 83.05 (0.07)° and with attached imidazole rings of 27.67 (0.06)° and 39.06 (0.10)°, respectively. Extensive intermolecular hydrogen bonds, C_2-H_2 …N4^{i} and C17-H17…N4^{ii} (d(C2-H2) = 0.93 Å, d(H2··N4) = 2.48Å, d(C2···N4) = 3.238(4) Å, C2-H2···N4 = 139º; d(C17-H17) = 0.93 Å, d(H17··N4) = 2.60 Å, d(C17···N4) = 3.474 (4) Å, C17-H17···N4 =160º. Symmetry code: i: 1-x, y, 1/2-z; ii: -1 + x, y, z) link molecules into infinite 1D supramolecular structure, which may contribute to stabilize the crystal structure.

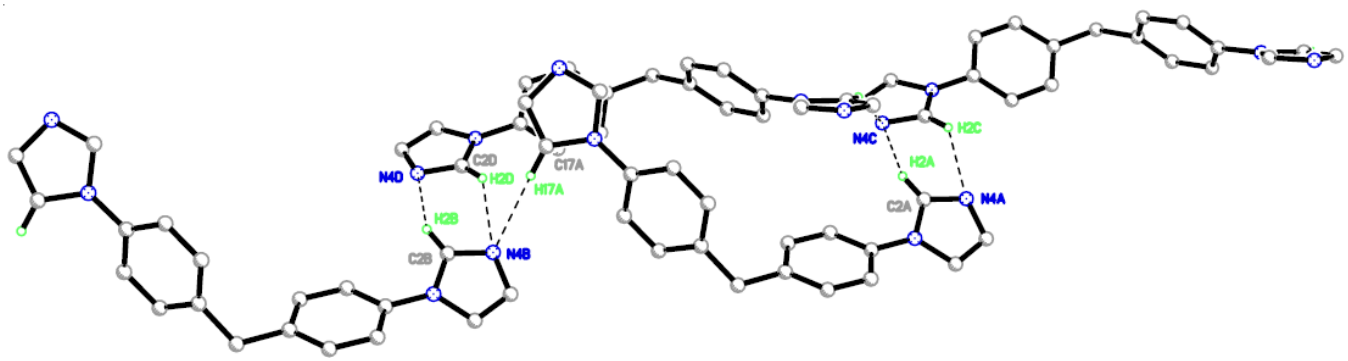

Fig. 2. Part of the 1D chain supramolecular structure of *bis*[4-(imidazol-1-yl)phenyl]methane Intermolecular hydrogen bonds are shown as dashed lines

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (º) FOR THE TITLE COMPOUND

Bond	Length	Bond	Length	Bond	Length
C(3)-N(1)	1.372(3)	C(2)-N(1)	1.337(3)	C(2)-N(4)	1.293(3)
C(1)-N(4)	1.356(3)	C(1)-C(3)	1.331(3)	C(4)-N(1)	1.408(3)
C(4)-C(5)	1.378(3)	C(5)-C(6)	1.364(3)	C(6)-C(7)	1.365(3)
C(7)-C(8)	1.379(3)	C(7)-C(10)	1.496(3)	C(8)-C(9)	1.365(3)
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
C(3)-C(1)-N(4)	110.2(2)	N(4)-C(2)-N(1)	111.7(2)	C(1)-C(3)-N(1)	105.9(2)
C(9)-C(4)-C(5)	120.0(2)	C(9)-C(4)-N(1)	118.82(19)	C(5)-C(4)-N(1)	121.2(2)
C(6)-C(5)-C(4)	120.3(2)	C(7)-C(6)-C(5)	120.8(2)	C(6)-C(7)-C(8)	117.7(2)
C(6)-C(7)-C(10)	121.7(2)	C(8)-C(7)-C(10)	120.6(2)	C(9)-C(8)-C(7)	122.4(2)
C(4)-C(9)-C(8)	118.8(2)	C(7)-C(10)-C(11)	115.64(19)	-	-

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