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Synthesis and Crystal Structure of 1-(1*H*-Benzotriazol-1-yl)-2-(2-chlorophenyl)-2-oxoethyl Benzoate

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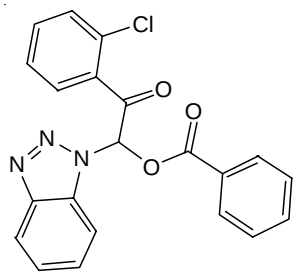
The crystal structure of 1-(1*H*-benzotriazol-1-yl)-2-(2-chlorophenyl)-2-oxoethyl benzoate has been determined by single crystal X-ray diffraction method. The crystal belongs to orthorhombic system, space group $P2_12_12_1$ with unit cell constants a = 15.186(4), b = 1.896(2), c = 11.819(3) Å, V = 1955.6(7) Å^3, Z = 4, Dc = 1.378 g/cm^3, μ = 0.224 mm^{-1}, F(000) = 840, R and wR are 0.0479 and 0.1251, respectively for 3451 unique reflections with 2911 observed reflections [I > 2σ(I)]. The crystal packing is stabilized by π-π interactions and van der Waals forces.

Key Words: Synthesis, Crystal structure, Benzotriazole derivatives.

INTRODUCTION

It has been shown by previous studies that several benzotriazole derivatives can function as diminish inflammation, antivirus, antifungal, antimumor, the selectivity inhibitors of protein tyrosine phosphatase 1B (PTP1B) and antidepressant result from benzotriazole possesses potent bioactivity[1-5]. A class of stable benzotriazole esters was also reported as mechanism-based inactivators of SARS-3CL^{pro}, which has been shown to be essential for replication of SARS virus[6]. In order to search for new benzotriazole esters with bioactivity, 1-(1*H*-benzotriazol-1-yl)-2-(2-chlorophenyl)-2-oxoethyl benzoate compound including benzotriazole and benzoic acid, which displays possesses certain inhibiting activity towards microorganisms was investigated. In present paper, a new benzotriazole derivative, 1-(1*H*-benzotriazol-1-yl)-2-(2-chlorophenyl)-2-oxoethyl benzoate (**I**), was synthesized by Mannich reaction of substituted acetophenone and benzotriazole[7] and its struture was characterized by EA, IR, ^{1}H NMR and X-ray crystallographic analysis.



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EXPERIMENTAL

All reagents were obtained from commercial suppliers and were used without further purification. ^{1}H NMR spectrum was recorded on a Jeol FX-90Q NMR spectrometer in $CDCl_3$ as a solvent and with TMS as an internal standard. Elemental analyses were measured with a Perkin-Elmer 140 ºC analyzer. IR spectra (4000-400 cm^{-1}), as KBr pellets, were recorded on a Nicolet FT-IR 510P spectrophotometer.

1-(1*H*-Benzo[d][1,2,3]triazol-1-yl)-2-(2-chlorophenyl)-2-oxoethyl benzoate was prepared by a series reactions of 1-(2-chlorophenyl)ethanone, benzotriazole, benzoic acid and bromine according to the literature method[8]. The solution was filtered, concentrated and purified with flash column chromatography [silica gel; eluent: petroleum-ethyl acetate, V(petroleum):V(ethyl acetate) = 4:1] to afford the title compound. A single crystal suitable for X-ray measurement was obtained by slow evaporation of an ethyl acetate-petroleum ethyl acetate (4:1, volume ratio) of the title compound at room temperature for a week. Anal. Calcd. for $C_{22}H_{17}N_3O_3Cl$: C, 64.95; H, 4.21; N, 10.33 %; Found: C, 64.90; H, 4.16; N, 10.21 %. IR (KBr, ν_{max}, cm^{-1}): (C=O), 1724, 1695; (N=N), 1586; (C-O), 1269. ^{1}H NMR (500 MHz, $CDCl_3$): 7.34-7.54 (m, 3H, Ar-H, benzotriazole-H); 6.74-6.77 (t, 1H); 5.41-5.49 (d, 2H).

Crystal data and structure determination: A colourless single crystal with approximate dimension of 0.37 mm × 0.31 mm × 0.13 mm was mounted on glass fibre in a random orientation. The data were collected by Bruker Smart 1000 CCD diffractometer with graphite minochromated MoKα radiation (λ = 0.71073 Å) using ω scan mode in the range of $2.18 \leq \theta \leq 21.19^o$ at temperature 293(1) K. A total of 10154 reflections were collected with 3451 unique ones (Rint = 0.029), of which 2911 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[9] with SHELXL-979. All non-hydrogen atoms were located with successive difference Fourier syntheses. The structure was refined by full-matrix least-squares method on F2 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 = 0.0479 and wR = 0.1251, $w = 1/[s^2 (Fo)^2 + (0.0600P)^2 + 0.4517P]$ where $P = (Fo^2 + 2F_c^2)/3$.

RESULTS AND DISCUSSION

The final atomic parameters and equivalent isotropic thermal parameters for the non-hydeogen atoms are given in Table-1. Selected bond lengths and bond angles are listed in Tables 2 and 3, respectively. Fig. 1 show the molecular structure of the compound. Packing diagram of the title compound in a unit cell is shown in Fig. 2.

In the molecule of the title compound (Fig. 1), the bond lengths and angles are within normal ranges[10] and are comparable with those in the related compound, 3-(1*H*-benzotriazol-1-yl)-1-(2-fluorophenyl)-1-oxopropan-2-yl benzoate[11]. The

TABLE-1
ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2 \times 10^3$)

Atom	x	y	z	Ueq
Cl1	0.04847(11)	0.13804(11)	0.54309(12)	0.1349(6)
O1	0.14099(12)	0.53584(17)	0.32554(17)	0.0606(6)
O2	0.05446(13)	0.67645(19)	0.4071(2)	0.0727(8)
O3	0.09197(16)	0.4017(2)	0.4977(2)	0.0835(9)
N1	0.15107(17)	0.2838(2)	0.2360(2)	0.0642(9)
N2	0.1249(2)	0.1703(2)	0.2704(3)	0.0791(10)
N3	0.1935(2)	0.1026(3)	0.2859(3)	0.0909(11)
C1	0.2405(2)	0.2881(3)	0.2294(3)	0.0676(11)
C2	0.2677(3)	0.1720(4)	0.2629(3)	0.0793(11)
C3	0.3553(3)	0.1412(5)	0.2662(4)	0.1087(17)
C4	0.4130(3)	0.2286(6)	0.2337(4)	0.118(2)
C5	0.3864(3)	0.3446(6)	0.1989(4)	0.1043(19)
C6	0.2994(2)	0.3784(4)	0.1961(3)	0.0805(11)
C7	0.0856(2)	0.3753(3)	0.2105(3)	0.0654(10)
C8	0.06508(18)	0.4602(2)	0.3077(3)	0.0591(9)
C9	0.12647(17)	0.6413(2)	0.3817(2)	0.0527(9)
C10	0.20937(17)	0.7083(2)	0.4070(2)	0.0514(8)
C11	0.29093(18)	0.6548(3)	0.3939(2)	0.0615(9)
C12	0.3654(2)	0.7199(4)	0.4239(3)	0.0785(13)
C13	0.3575(3)	0.8391(4)	0.4632(3)	0.0857(14)
C14	0.2775(3)	0.8917(3)	0.4739(3)	0.0809(14)
C15	0.2026(2)	0.8277(3)	0.4473(3)	0.0664(10)
C16	0.04389(19)	0.3916(2)	0.4168(3)	0.0598(10)
C17	-0.0380(2)	0.3163(2)	0.4197(3)	0.0639(10)
C18	-0.0429(3)	0.2062(3)	0.4811(3)	0.0890(16)
C19	-0.1216(4)	0.1465(4)	0.4911(5)	0.120(2)
C20	-0.1960(4)	0.1924(6)	0.4432(5)	0.126(2)
C21	-0.1929(3)	0.2984(5)	0.3784(4)	0.1080(18)
C22	-0.1130(2)	0.3601(3)	0.3669(3)	0.0744(11)

TABLE-2
SELECTED BOND LENGTHS (Å)

Bond	Dist.	Bond	Dist.
Cl1-C18	1.736(4)	C7-C8	1.508(5)
O1-C8	1.433(3)	C8-C16	1.525(5)
O1-C9	1.345(3)	C9-C10	1.486(4)
O2-C9	1.197(3)	C10-C11	1.378(4)
O3-C16	1.208(4)	C10-C15	1.389(4)
N1-N2	1.361(3)	C11-C12	1.381(5)
N1-C1	1.361(4)	C12-C13	1.385(6)
N1-C7	1.440(4)	C13-C14	1.349(6)
N2-N3	1.290(4)	C14-C15	1.371(5)
N3-C2	1.384(5)	C16-C17	1.490(4)
C1-C2	1.388(5)	C17-C18	1.404(4)
C1-C6	1.387(5)	C17C22	1.384(4)
C2-C3	1.373(6)	C18-C19	1.366(7)
C3-C4	1.350(8)	C19-C20	1.359(8)
C4-C5	1.389(9)	C20-C21	1.387(8)
C5-C6	1.372(6)	C21-C22	1.394(6)

TABLE-3
SELECTED BOND ANGLES (°)

Angle	(°)	Angle	(°)
C8-O1-C9	115.6(2)	O2-C9-C10	124.5(2)
N2-N1-C1	109.9(2)	C9-C10-C11	122.1(2)
N2-N1-C7	119.3(3)	C9-C10-C15	117.8(2)
C1-N1-C7	130.8(3)	C11-C10-C15	120.1(3)
N1-N2-N3	109.0(3)	C10-C11-C12	119.3(3)
N2 -N3-C2	108.5(3)	C11-C12-C13	119.8(3)
N1-C1-C2	104.4(3)	C12-C13-C14	120.5(4)
N1-C1-C6	133.2(3)	C13-C14-C15	120.6(3)
C2-C1-C6	122.4(3)	C10-C15-C14	119.6(3)
N3-C2-C1	108.2(4)	O3-C16-C8	119.8(2)
N3-C2-C3	130.5(4)	O3-C16-C17	122.4(3)
C1-C2-C3	121.3(4)	C8-C16-C17	117.7(3)
C2-C3-C4	116.7(5)	C16-C17-C18	121.8(3)
C3-C4-C5	122.5(4)	C16-C17-C22	119.1(2)
C4-C5-C6	122.1(5)	C18-C17-C22	119.0(3)
C1-C6-C5	115.1(4)	Cl1-C18-C17	122.8(3)
N1-C7-C8	114.1(3)	Cl1-C18-C19	117.3(3)
O1-C8-C7	107.4(2)	C17-C18-C19	119.9(4)
O1-C8-C16	109.1(3)	C18-C19-C20	121.1(5)
C7-C8-C16	112.8(2)	C19-C20-C21	120.6(5)
O1-C9-O2	123.2(2)	C20-C21-C22	119.0(4)
O1-C9-C10	112.3(2)	C17-C22-C21	120.4(3)

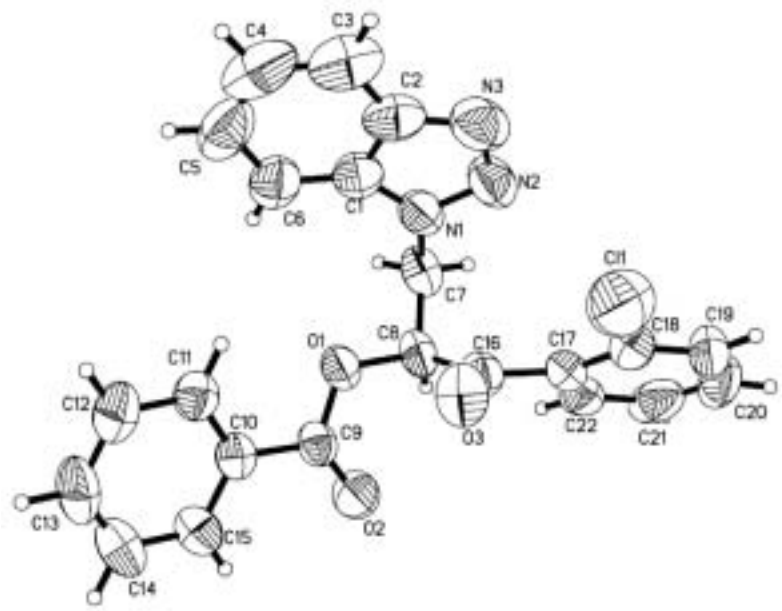

Fig. 1. The molecular structure of the title compound with the atomic numbering

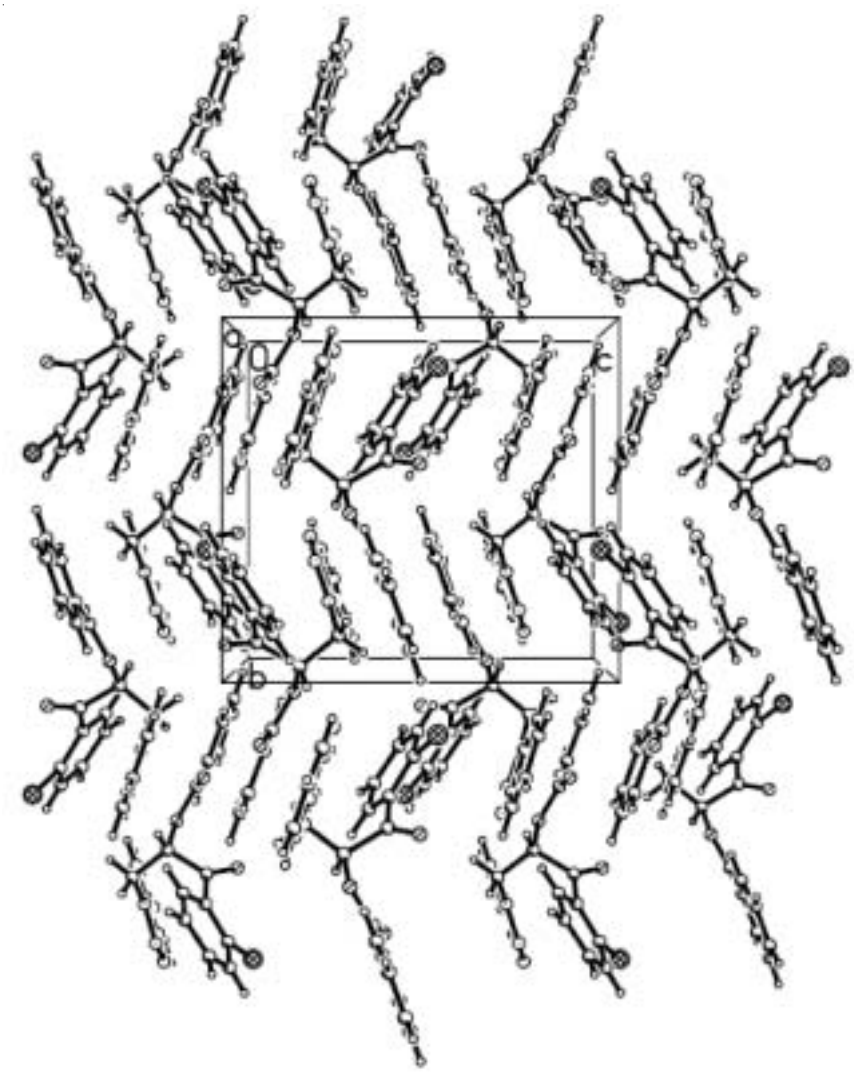

Fig. 2. A view of the crystal packing for the title compound

benzotriazole system is essentially planar, with a dihedral angle of 1.8(2)º between the N1-N3/C1/C2 triazole ring and C1-C6 benzene ring. The whole molecule is non-planar. The mean benzotriazole plane makes dihedral angles of 39.10(1)º and 20.55(2)º with the C10-C15 and C17-C22 benzene rings, respectively. The dihedral angle between the latter two aromatic rings is 53.25(2)º.

In the crystal structure, the short distance Cg1...Cg3^{i} [symmetry code: (i) 1/2-x, 1-y, 1/2+z], where Cg1 and Cg3 denote the centroids the N1-N3/C1/C2 triazole ring and C10-C15 benzene ring, respectively, indicates the π-π interactions. The crystal packing is further stabilized by van der Waals forces.

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