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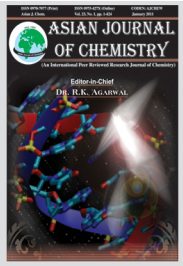

Synthesis and Crystal Structure of 3-(1*H*-benzo[d][1,2,3]triazol-1-yl)-1-(4-ethylphenyl)-1-oxopropan-2-yl-4-methylbenzoate

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A new benzotriazol compound 3-(1*H*-benzo[d][1,2,3]triazol-1-yl)-1-(4-ethyl phenyl)-1-oxopropan-2-yl-4-methylbenzoate was synthesized by four step reactions. Its structure was characterized by element analysis, IR spectrum and X-ray diffraction. It crystallizes in monoclinic, space group P21/c with a = 12.331(3) Å, b = 8.9625(18) Å, c = 20.363(4) Å, β = 105.11(3)°, $C_{25}H_{23}N_3O_3$, Mr = 413.46, V = 2172.6(9) Å^3, Z = 4, Dc = 1.264 g/cm^3, F(000) = 827, μ = 0.084 mm^{-1}, R = 0.1004 and wR = 0.0709. The dihedral angles between the benzotriazole group and the methyl and ethyl substituted benzene rings are 89.63° and 10.18°, respectively. The methylphenyl ring and the ethylphenyl ring make dihedral angles of 79.68°. Intermolecular C–H···O hydrogen bonds together with C–H···π interactions contribute to stability of the structure and form a three-dimensional framework.

Key Words: Synthesis, Crystal structure, Benzotriazols.

INTRODUCTION

Considerable interest has been focused on the benzotriazoles and their derivatives, which are found to possess a broad spectrum of biological activities like antimicrobial, anticancer, antiviral and antineoplastic activities[1-3]. Now, benzotriazoles and their derivatives are widely used in many fields such as medicine, water stabilizers, preservatives, optical stabilizers and so on[4-7]. Therefore, it is an utmost need to synthesize a new benzotriazole compound. On the other hand, to the best of our knowledge, among so many reported benzotriazoles, the compounds containing one benzotriazole group, one ethylphenyl group and one methylphenyl group in a single molecule are rare. Herein, the synthesis, IR and crystal structure of the title compound, 3-(1*H*-benzo[d][1,2,3]triazol-1-yl)-1-(4-ethylphenyl)-1-oxopropan-2-yl-4-methylbenzoate have been reported.

EXPERIMENTAL

All the reagents and solvents from commercial sources were used without further purification. Elemental analyses for C, H and N were obtained by VarioELIII elemental analyzer. IR spectra (4000-400 cm^{-1}), were recorded on a Nicolet FT-IR 510P spectrometer. Melting points were measure by using a melting point apparatus made in Shanghai Instrument Limited Company.

Bromine (3.2 g, 0.02 mol) was added dropwise to a solution of 3-(1*H*-benzo[d][1,2,3]-triazol-1-yl)-1-(4-ethylphenyl)propan-1-one (5.58 g, 0.02 mol) and sodium acetate (1.6 g, 0.02 mol) in acetic acid (50 mL) at 48-55 ºC and the mixture was stirred for 8 h. After the reaction was completed, 50 mL of water and 20 mL of chloroform were added. The organic layer was washed successively with saturated sodium bicarbonate solution and brine. The solution was purified by flash column chromatography (silica gel, using petroleum ether:acetic ether = 3:1 (v/v) as eluent) to afford 3-(1*H*-benzo[d][1,2,3]triazol-1-yl)-2-bromo-1-(4-ethylphenyl)-propan-1-one.

It was cooled with ice-water and then an acetonic solution (10 mL) of 4-methyl benzoic acid (2.72 g, 0.02mol) and triethylamine (2.8 mL) were added. The mixture was stirred with ice-water for *ca.* 5 h. The solution was then filtered and concentrated. The concentrated filtrate was re-dissolved in chloroform (30 mL) and was washed three times with distilled water (30 mL) by using extraction method. Finally, the organic layer was rotary vacuum evaporated to obtain the present compound. Single crystals were obtained by slow evaporation of ethanol and ethyl acetate (2:1 v/v) after a few days. Yields 45 %. m.p. 110-112.5 ºC. Anal. calcd. (%) for $C_{25}H_{23}N_3O_3$: C, 72.62; H, 5.61, N; 10.61, Found: C, 72.74; H, 5.47, N; 10.36. Selected IR (KBr pellet, cm^{-1}): 1716 (ester C=O), 1680 (ketone C=O), 1611 (C=N), 1285, 1116 (C-O).

Data collection and structure determination: A selected crystal of the title compound was mounted on a SMART CCD diffractometer. The reflection data were measured at 293 K, using a graphite monochromator MoK_α (λ = 0.071073 nm) radiation with an ω scan mode. A total of 13877 reflections were collected and 5291 were independent (Rint = 0.1004) in the range of $1.71 < \theta < 28.38°$, of which 1688 reflections were observed with $I > 2\sigma(I)$.

The structure of the present compound was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package[8]. All non-hydrogen atoms were refined by full-matrix least-squares method, while all hydrogen atoms were placed in the geometrically calculated positions. The contributions of these hydrogen atoms were included in the structure-factor calculations. The atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray crystallography[9]. The crystal and experimental data are shown in Table-1.

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

Empirical formula	$C_{25}H_{23}N_3O_3$
Formula weight	413.46
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 12.331(3) Å α = 90º b = 8.9625(18) Å β = 105.11(3)º c = 20.363(4) Å γ = 90º
Volume ($Å^3$), Z	2172.6(8), 4
Calculated density (g/cm^3)	1.264
Absorption coefficient (mm^{-1})	0.084
F(000)	872
Crystal size (mm)	0.22 × 0. 18 × 0.13 mm
Theta range for data collection (º)	1.71-28.38
Limiting indices	-16 <= h <= 15, -11 <= k <= 10, -25 <= l <= 25
Reflections collected/unique	13877/5291 [R(int) = 0.1004]
Completeness to theta = 28.24	97.3 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5291/0/281
Goodness-of-fit on F^2	0.928
Final R indices [$I > 2\sigma(I)$] R indices (all data)	R1= 0.0709, wR2 = 0.1588 R1= 0.2414, wR2 = 0.2277
Extinction coefficient	0.0070(14)
Largest diff. peak and hole (Einstein $Å^{-3}$)	0.292 and -0.241

RESULTS AND DISCUSSION

The atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms in the title compound are given in Table-2 and the selected bond distances and bond angles in Table-3. A displacement ellipsoid plot with atomic numbering scheme is shown in Fig. 1 and a perspective view of the crystal packing in the unit cell in Fig. 2.

In the crystal structure, the bond lengths and angles in the benzotriazole ring and phenyl ring are generally normal. The bond length of C(17)-O(1), 1.219(4) and C(9)-O(2), 1.205(4) Å are longer than that of standard C=O double bond of 1.17 Å[10]; however, the C(8)-O(3) bond in 1.431(3) Å are agree ment with those of the similar structures [-C-O, 1.426(3) Å][11]. The bond lengths of C(7)-C(8) (1.520(4), Å), C(8)-C(17) (1.527(4), Å) are shorter than that of standard of C-C single bond length of 1.54 Å; while the bond lengths of C(7)-N(3) (1.444(4), Å) is shorter to that of the standard C-N of 1.47 Å.

The benzotriazole ring with the conjunction carbon atom C(7) is also quite planar (Plane equation: 10.9611 x - 4.0884 y - 5.5409 z = 4.3516) and the largest deviation is 0.025 Å. The benzene (C1-C6) rings comparable to mean plane of the benzotriazole system makes dihedral angles of 89.63º and 10.18° with the methylphenyl (C10-C15) and ethylbenzene (C18-C23) rings. The dihedral angle between the C10-C15 and C18-C23 rings is 79.68º.

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

Atom	x	y	Z	U(eq)
O(3)	3149(2)	5772(3)	1941(1)	56(1)
N(3)	3891(2)	5020(3)	828(1)	54(1)
C(10)	1603(3)	7114(4)	2087(2)	55(1)
O(2)	3478(2)	7517(3)	2756(1)	63(1)
O(1)	4317(2)	4182(3)	3022(1)	69(1)
C(9)	2825(3)	6850(4)	2308(2)	52(1)
C(7)	4467(3)	4511(4)	1502(2)	57(1)
C(17)	4882(3)	4980(4)	2757(2)	50(1)
C(8)	4335(3)	5599(4)	2049(2)	49(1)
C(18)	6049(3)	5336(4)	3095(2)	50(1)
C(6)	4208(3)	6100(4)	444(2)	51(1)
N(2)	2846(3)	4514(4)	516(2)	74(1)
C(19)	6724(3)	6203(4)	2802(2)	62(1)
C(15)	1134(3)	8175(5)	2417(2)	69(1)
C(1)	3303(3)	6217(5)	-115(2)	62(1)
C(2)	3331(4)	7228(5)	-634(2)	80(1)
C(23)	6509(3)	4797(5)	3751(2)	74(1)
C(11)	914(3)	6373(5)	1540(2)	71(1)
C(5)	5166(3)	6945(4)	521(2)	60(1)
C(14)	13(3)	8510(5)	2201(2)	82(1)
N(1)	2483(3)	5224(5)	-57(2)	82(1)
C(13)	-673(3)	7781(6)	1648(2)	86(2)
C(4)	5171(4)	7906(5)	7(2)	76(1)
C(12)	-214(3)	6700(6)	1330(2)	87(1)
C(20)	7808(3)	6541(5)	3152(2)	86(1)
C(3)	4273(4)	8060(5)	-562(2)	84(1)
C(22)	7578(4)	5132(6)	4087(2)	100(2)
C(21)	8254(4)	6006(6)	3802(3)	99(2)
C(24)	9665(9)	6335(11)	4098(4)	233(5)
C(16)	-1906(3)	8220(7)	1398(3)	140(2)
C(25)	9619(8)	7310(12)	4472(6)	246(5)

TABLE-3
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (º)

Length	(Å)	Length	(Å)
C(7)–C(8)	1.520(4)	C(8)–C(17)	1.527(4)
N(3)–C(7)	1.444(4)	C(17)–C(18)	1.459(4)
C(17)–O(1)	1.219(4)	C(8)–O(3)	1.431(3)
C(9)–C(10)	1.474(5)	C(9)–O(2)	1.205(4)
C(9)–O(3)	1.344(4)	–	–
Angles	**(º)**	**Angles**	**(º)**
O(1)–C(17)–C(18)	121.7(3)	O(3)–C(8)–C(17)	104.9(3)
O(1)–C(17)–C(8)	117.9(3)	O(3)–C(8)–C(7)	111.5(3)
O(2)–C(9)–O(3)	122.7(3)	N(3)–C(7)–C(8)	112.0(3)
O(2)–C(9)–C(10)	125.4(4)	N(2)–C(3)–C(7)	120.7(3)
C(8)–C(17)–C(18)	120.3(3)	C(7)–C(8)–C(17)	110.7(3)

TABLE-4
INTERMOLECULAR INTERACTION DISTANCES (Å)

D–H···A	Symmetry	D–H	H···A	D···A	D–H···A (º)
C(7)–H(7A) ···O(2)	1-x, -1/2+y, 1/2-z	0.9700	2.4850	3.1479(2)	125.41
C(19)–H(19A) ···O(1)	1-x, 1/2+y, 1/2-z	0.9300	2.5718	3.2353(2)	128.65
C(7)–H(7B) ···Cg(4)	1-x, -1/2+y, 1/2-z	0.9700	3.0440	3.9960	167.47
C(14)–H(14A) ···Cg(3)	2-x, 1/2+y, 1/2-z	0.9300	3.2430	4.1140	156.84
C(23)–H(23A) ···Cg(2)	1-x, -1/2+y, 1/2-z	0.9300	3.0390	3.8920	153.27

C(1) ring denotesphenyl ring C(1)-C(6), C(1) and C(6); C(3) ring denotes methylphenyl ring C(10)-C(15); C(4) ring denotes ethylphenyl ring C(18)-C(23).

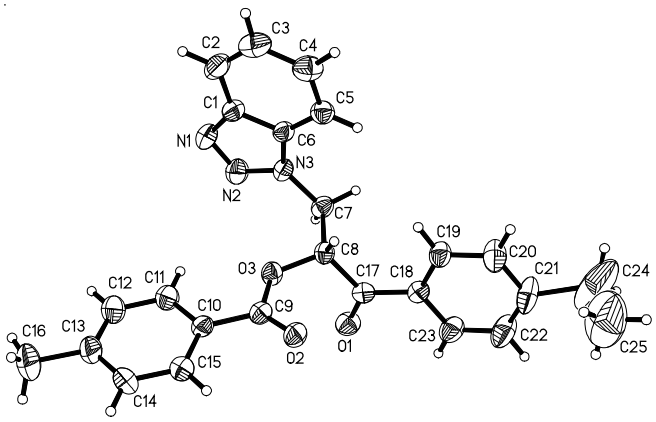

Fig. 1. Molecular structure with atomic numbering scheme

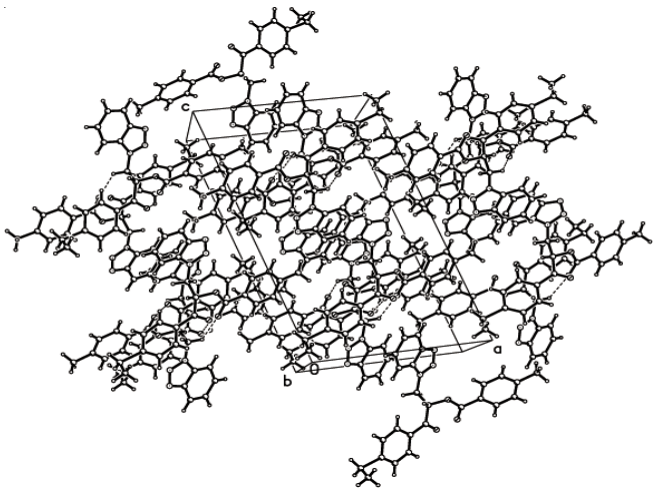

Fig. 2. View of crystal packing

There are two potential weak intermolecular interactions C–H···O and three C–H···π supramolecular interactions in the lattice (Table-4). The O(2) atom with C(7) atoms and O(1) with C(17) form weak C–H···O intermolecular interactions and the donor and acceptor distance are 3.1479(2) and 3.2353(2) Å, respectively. The other feature of intermolecular interaction is due to C–H···π supramolecula interaction in the crystal lattice. The distances C(7)-H(7B) to ethylphenyl ring, C(14)-H(14A) to methylbenzene ring and C(23)-H(23A) to benzene ring are 3.996, 4.114 and 3.892 Å, respectively. In solid state, all above extensive hydrogen bond stabilize the crystal structure.

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