

Synthesis and Crystal Structure of 3-(1*H*-Benzotriazolyl)-1-(4-nitrophenyl)-1-oxopropan-2-yl-4-ethylbenzoate

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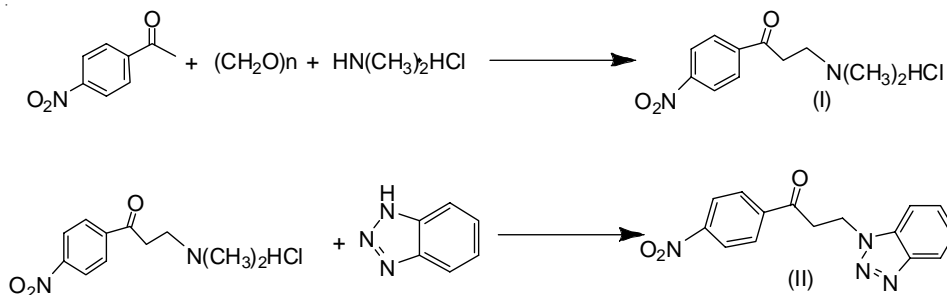
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The title compound 3-(1*H*-benzotriazolyl)-1-(4-nitrophenyl)-1-oxopropan-2-yl-4-ethylbenzoate, was synthesized and characterized by means of ¹H NMR, IR spectrum and X-ray diffraction. It crystallizes in monoclinic, space group P21/c with $a = 18.895(4)$, $b = 6.9805(14)$, $c = 8.105(4)$ Å, $\beta = 116.755(3)^\circ$, $C_{24}H_{20}N_4O_5$, $Mr = 444.44$, $V = 2132.3(8)\text{Å}^3$, $Z = 4$, $D_c = 1.384\text{ g/cm}^3$, $F(000) = 928$, $\mu = 0.1\text{ mm}^{-1}$, $R = 0.0528$ and $wR = 0.1604$. The benzotriazole ring and phenyl (C10-C15) makes dihedral angles of 98.7° . There is obvious potentially weak intermolecular C—H...N in the crystal, which stabilizes the crystal structure. ¹H NMR and IR spectra are in good agreement with the structural data.

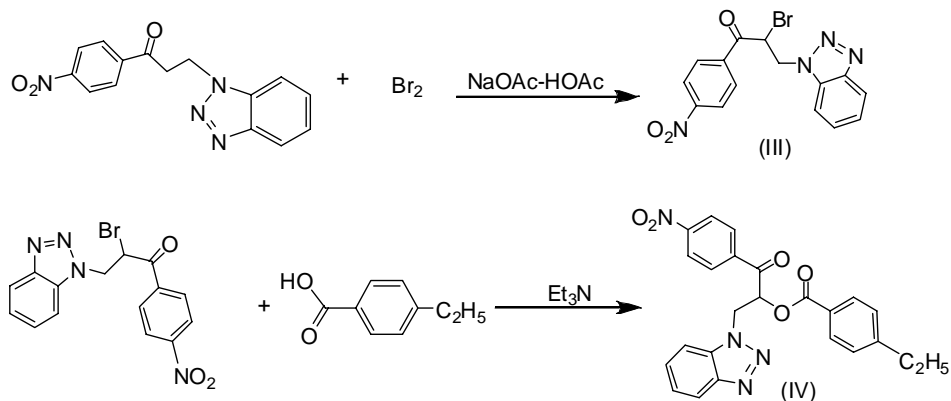
Key Words: Synthesis, Crystal structure, 3-(1*H*-Benzotriazolyl)-1-(4-nitrophenyl)-1-oxopropan-2-yl-4-ethylbenzoate.

INTRODUCTION

1*H*-Benzotriazoles and its derivatives were widely studied because they exhibit a broad spectrum of pharmacological activities such as antifungal, antitumor and anti-neoplastic activities¹⁻³. However, the benzotriazoles compounds containing nitrophenyl have rarely been reported. Herein, the synthesis, IR and crystal structure of the title compound, 3-(1*H*-benzotriazolyl)-1-(4-nitrophenyl)-1-oxopropan-2-yl-4-ethylbenzoate have been reported (**Scheme-I**):



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Scheme-I

EXPERIMENTAL

All chemicals were of AR grade and used without further purification. IR spectra (4000-400 cm^{-1}), as KBr pellets, were recorded on a Nicolet FT-IR 510P spectrometer. ^1H NMR spectra were measured with a Bruker ALP 80 nuclear magnetic resonance spectrometer (CD_3COCD_3 as solvent, TMS as internal standard).

The intermediates I and II were prepared according to the literatural report⁴⁻⁶. The synthesis of the compound is described below.

To a 100 mL flask 20 mmol of intermediates II, 20 mmol of sodium acetate and 50 mL of acetic acid were added. Then 20 mmol of bromine was dropwise added with stirring at 48-55 $^\circ\text{C}$. The reaction was maintained until the mixture was turned into light yellow for 8 h. Then 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 $V_{\text{ethyl ethanoate}}:V_{\text{acetone}} = 1:4$ as eluent) to afford intermediates III. In 100 mL flask, intermediates III was cooled with ice-water and then 20 mL of 4-nitrophenyl-benzoic acid and 2.8 mL of triethylamine were added under stirring and the mixture was stirred at room temperature for about 5 h. The solution was filtered and concentrated to afford target compounds. Single crystals were obtained by slow evaporation of an acetone-ethylacetate (1:1 v/v) solution at room temperature over a period of 1 week.

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 294 K, using a graphite monochromator MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation with an ω -2 θ scan mode. The total reflections were 10439 with 3759 independent ones ($R_{\text{int}} = 0.035$), of which 2434 were observed with $I > 2\sigma(I)$. Intensities were corrected for Lorentz and polarization effects and empirical absorption and all data were corrected using SADABB⁷ program.

The structure was solved by direct methods using SHELXS-97 program⁸. All the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method. 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 crystallography⁹. The final least-square cycle gave $R = 0.052$ and $\omega R = 0.1604$ ($w = 1/[\sigma^2(\text{Fo}^2) + (0.0706\text{P})^2 + 1.2323\text{P}]$, where $\text{P} = (\text{Fo}^2 + 2\text{Fc}^2)/3$). $S = 1.04$, $(\Delta/\sigma)_{\text{max}} = 0.000$, $(\Delta\rho)_{\text{min}} = -0.31$ and $(\Delta\rho)_{\text{max}} = 0.36\text{e}/\text{\AA}^3$.

RESULTS AND DISCUSSION

The atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms in the title compound are given in Table-1 and the selected bond distances and bond angles in Table-2. 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.

TABLE-1
ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\text{\AA}^2 \times 10^3$)

Atom	x	y	Z	U(eq)
O(1)	2573(11)	6089(3)	2630(11)	45(5)
O(3)	1456(14)	7213(3)	1160(12)	64(7)
O(2)	3283(13)	5295(3)	1973(14)	66(7)
O(4)	-174(16)	1291(4)	-2195(13)	78(8)
O(5)	123(16)	-1142(4)	1401(14)	76(8)
N(1)	2331(16)	1197(4)	4153(17)	54(7)
N(2)	1935(16)	1652(4)	3382(17)	52(7)
N(3)	1837(13)	3580(3)	3327(13)	39(6)
N(4)	123(14)	571(4)	-1513(15)	50(7)
C1	2495(16)	2828(4)	4608(18)	44(7)
C2	2892(18)	3108(6)	5469(2)	64(10)
C3	2945(2)	4943(7)	5739(2)	75(12)
C4	2634(2)	6475(6)	5202(2)	68(10)
C5	2249(18)	6253(4)	4372(19)	51(8)
C6	2186(15)	4375(4)	4090(16)	40(6)
C7	1441(16)	4454(4)	2522(16)	44(7)
C8	1998(16)	4713(4)	2133(15)	40(7)
C9	3188(16)	6320(4)	2453(17)	43(7)
C10	3689(16)	7943(4)	2890(17)	44(7)
C11	3406(2)	9423(5)	3179(2)	66(10)
C12	3865(2)	11008(6)	3520(3)	88(13)
C13	4625(2)	11128(6)	3604(2)	75(11)
C14	4907(2)	9627(6)	3327(2)	66(10)
C15	4447(18)	8062(5)	2957(19)	54(8)
C16	5116(3)	12938(7)	3979(3)	10(14)

Atom	x	y	Z	U(eq)
C16'	5116(3)	12938(7)	3979(3)	10(14)
C17	5560(4)	12639(11)	4866(3)	11(2)
C17'	5130(2)	14000(5)	4709(18)	11(4)
C18	1534(17)	5498(4)	1257(16)	42(7)
C19	1182(15)	4166(4)	555(15)	36(6)
C20	867(16)	4917(4)	2412(16)	43(7)
C21	531(16)	3759(4)	-919(16)	43(7)
C22	497(15)	1828(4)	-792(16)	37(6)
C23	804(16)	1020(4)	25(16)	41(7)
C24	1154(16)	2197(4)	651(16)	41(7)

*The C17- C17' are statistical atoms with the occupancies of 0.5 for both.

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Angles	(°)	Angles	(°)
C(7)–C(8)	1.517(4)	C(8)–O(1)	1.426(3)
N(3)–C(7)	1.440(3)	C(8)–C(18)	1.528(4)
C(18)–O(3)	1.210(3)	C(9)–O(2)	1.199(3)
C(9)–O(1)–N(8)	115.1(2)	O(1)–C(8)–C(7)	106.1(2)
O(1)–C(8)–C(18)	109.4(2)	C(8)–O(1)–C(18)	1.349(4)
O(2)–C(9)–O(1)	121.8(3)	O(2)–C(9)–O(10)	125.7(3)
O(1)–C(9)–O(10)	112.5(2)	N(3)–C(7)–O(8)	111.6(2)
N(2)–N(3)–C(7)	119.1(2)	O(3)–C(18)–C(19)	121.5(3)

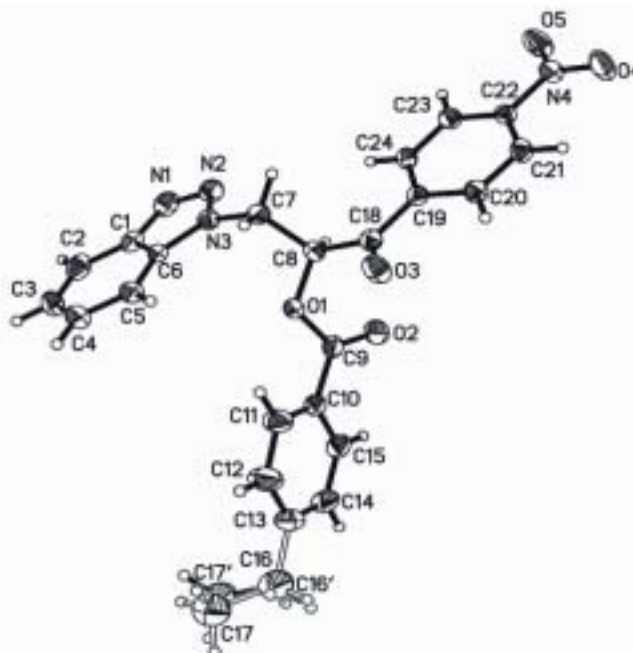


Fig. 1. Molecular structure with atomic numbering scheme

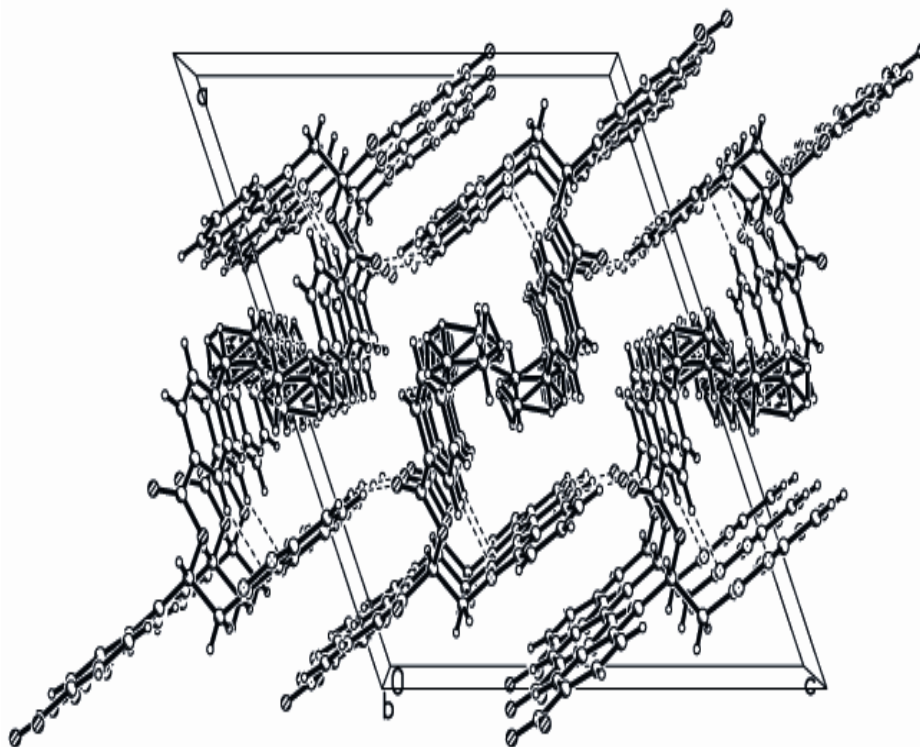


Fig. 2. View of crystal packing down the b-axis

In the infrared spectrum, the broad absorption at 1715 and 1698 cm^{-1} is assigned to the stretching vibration of $\nu(\text{C}=\text{O})$ of carbonyl group. The compound exhibits characteristic strong bands at $1523\text{ } \nu(\text{C}=\text{N})$, 1342 , $\nu(\text{N}=\text{N})$, 1256 , $1106\text{ } \nu(\text{C}-\text{O})$ ^{10,11}.

¹H NMR δ : 1.19 (s, 3H, C₂H₅-CH₃), 2.78 (s, 2H, C₂H₅-CH₂), 5.51 (s, 2H, CH₂), 6.79 (s, 1H, CH), 7.21-8.39 (m, 12H, 3C₆H₄).

In the compound, the bond lengths and angles in the benzotriazole ring and phenyl ring are generally normal^{12,13}. The ether C-O bond lengths [-C8-O1, $1.426(3)\text{ \AA}$] are in agreement with those of the similar structures [-C-O, $1.426(6)\text{ \AA}$ and $1.418(3)\text{ \AA}$]¹³. The bond lengths of C(7)-C(8) ($1.517(4)\text{ \AA}$), C(8)-C(18) ($1.528(4)\text{ \AA}$) and N(3)-C(7) ($1.440(3)\text{ \AA}$) are all similar to those of the standard C-C single bond length of 1.54 \AA and C-N of 1.47 \AA ; while the bond length of C(9)-O(2), $1.199(3)$ and C(18)-O(3), $1.210(3)\text{ \AA}$ are longer than that of standard C=O double bond of 1.17 \AA ¹⁴. The benzotriazole ring with the conjunction carbon atom C(7) is also quite planar (Plane equation: $18.772x + 0.683y - 8.961z = 0.733$) and the largest deviation is 0.016 \AA . The benzene (C1-C6) rings comparable to mean plane of the benzotriazole system makes dihedral angles of 98.7° and 12.4° with the phenyl (C10-C15) and benzene (C19-C24) rings, respectively. The dihedral angle between the C10-C15 and C19-C24 rings is 90.8° .

There exist some potential weak intermolecular interactions (C–H...Y hydrogen bonds Y=O and N)¹⁴ and C–H... π supramolecular interactions in the lattice (Table-3). The O(2) atom with C(2) atoms and O(3) with C(23) form weak C–H...O intermolecular interactions and the donor and acceptor distance are 3.434 Å for C(2)...O(2) and 3.286 Å for C(23)...O(3). The N(2) and C(11) atoms form weak C–H...N intermolecular interactions, with the donor and acceptor distance of 3.347 Å. The other feature of intermolecular interaction is due to the three types of C–H... π supramolecular interaction between C–H and aromatic rings in the crystal lattice. The distances between C(12)–H(12A) and C(17)–H(17A) to benzotriazole rings and C(3)–H(3A) to ethyl benzene ring are 3.798, 3.869 and 4.077 Å, respectively.

TABLE-3
INTERMOLECULAR INTERACTION DISTANCES (Å)

D-H-A	Symmetry	D-H	H...A	D...A	D-H...A
C(2)–H(2A)...O(2)	x,1/2-y,1/2+z	0.9299	2.5528	3.434	158.31
C(11)–H(11A)...N(2)	x,1+y,z	0.9307	2.6079	3.347	136.75
C(23)–H(23A)...O(3)	x,-1+y,z	0.9297	2.5388	3.286	137.66
C(3)–H(3A)...Cg(Ph–C ₂ H ₅)	x,3/2-y,1/2+z	0.9300	3.1530	4.077	172.84
C(12)–H(12A)...Cg(Ben-Tria)	x,1+y,z	0.9300	3.0760	3.798	135.86
C(17)–H(17A)...Cg(Ben-Tria)	1-x,2-y,1-z	0.9600	3.1690	3.869	131.24

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