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Ethyl (*E*)-2-(1*H*-benzotriazol-1-yl)-3-(*N*-benzylamino)but-2-enoate

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Key indicators

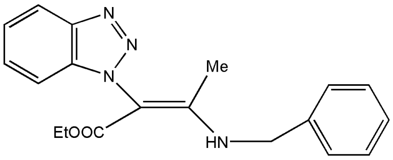
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.042
wR factor = 0.051
Data-to-parameter ratio = 10.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{19}H_{20}N_4O_2$, which is a key intermediate in the synthesis of natural products, has been synthesized by the reaction of alkenyl(phenyl)iodonium salts with benzotriazole. The keto O atom of the ethoxycarbonyl group is involved in an intramolecular hydrogen bond. In addition to the N—H⋯O intramolecular hydrogen bond, there are intra- and intermolecular N—H⋯O, C—H⋯N and C—H⋯π weaker interactions in the crystal structure.

Comment

1-(1-Alkenyl)benzotriazoles have been widely used in the preparation of pyrrolo[2,3-*d*]pyrimidines, carbazoles and indoles. This versatility has also made them key intermediates in the synthesis of natural products. There are several methods for the synthesis of 1-(1-alkenyl)benzotriazoles. Previously, the most general methods for the preparation of 1-(1-alkenyl)benzotriazoles were developed by Rees & Storr (1969) and involved the dehydrohalogenation of the product from the reaction of 1-chlorobenzotriazole and an olefin. Unfortunately, this mild and simple method always yielded a mixture of 1-(1-alkenyl)- and 2-(1-alkenyl)benzotriazoles. Recently, our research interest has centred on the chemistry of hypervalent iodine compounds; because of the excellent leaving group ability of a phenyliodonyl moiety, vinyl(phenyl)iodonium salts undergo nucleophilic vinyl substitutions under mild conditions, thus providing a useful route for the synthesis of various kinds of olefins. In an extension of this investigation, we have examined the reaction of vinyl(phenyl)iodonium salts with benzotriazole as a simple and convenient route for the stereoselective synthesis of 1-(1-alkenyl)benzotriazoles. The crystal structure of the title compound, (I), provides an important proof for the mechanism of this kind of reaction, *viz.*an addition–elimination mechanism.



(I)

In the structure of (I), there are benzyl and benzotriazole aromatic rings. The C1/N1/C2/C3/N2 plane makes a dihedral an angle of 82.30 (4)° with the benzotriazole ring plane and an angle of 87.01 (8)° with the benzyl ring plane. The title compound shows an intramolecular hydrogen bond: N1—H20⋯O1 (Fig. 1). The C2—N2 = 1.431 (2) Å and C1—N1 =

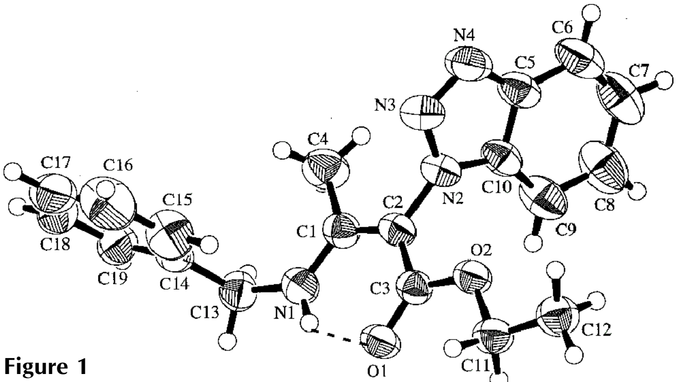


Figure 1
View of the title molecule, showing the atomic numbering scheme and 50% probability displacement ellipsoids. The dashed line indicates the intramolecular hydrogen bond.

1.335 (2) Å bond distances indicate that there is less π delocalization with N1 bound to a Csp^3 atom than with N2 which is part of the aromatic benzotriazole system, showing that the benzylamine group is easily lost and the reaction proceeds *via* an additon–elimination mechanism (Zhang & Chen, 2002). There are intra- and intermolecular N—H···O, C—H···N and C—H···π weaker interactions in the crystal structure.

Experimental

The white powder of (I) was synthesized according to Zhang & Chen (2002). A single crystal suitable for X-ray structure analysis was obtained by slow evaporation of a methanol solution at room temperature (m.p. 335–337 K).

Crystal data

$C_{19}H_{20}N_4O_2$
$M_r = 336.39$
Monoclinic, $P2/c$
$a = 13.071$ (3) Å
$b = 8.360$ (1) Å
$c = 17.418$ (4) Å
$\beta = 109.01$ (2)°
$V = 1799.7$ (7) Å^3
$Z = 4$

$D_x = 1.241$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 19.4$–21.6°
$\mu = 0.08$ mm^{-1}
$T = 293.0$ K
Prism, colourless
0.30 × 0.30 × 0.20 mm

Data collection

Rigaku AFC-7R diffractometer
$\omega/2\theta$ scans
4128 measured reflections
3976 independent reflections
3791 reflections with $I > 2.5\sigma(I)$
$R_{\rm int} = 0.083$
$\theta_{\rm max} = 27.5°$

$h = 0 \rightarrow 15$
$k = 0 \rightarrow 10$
$l = -21 \rightarrow 19$
3 standard reflections every 200 reflections intensity decay: 0.7%

Refinement

Refinement on F
$R = 0.042$
$wR = 0.051$
$S = 1.18$
3791 reflections
227 parameters
H-atom parameters constrained

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.15$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: 35.72402

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H20···O1	0.91	1.96	2.675 (2)	134
C4—H3···N2	0.95	2.36	2.834 (2)	110
C4—H3···N3	0.95	2.68	3.275 (3)	121
C15—H15···N1	0.99	2.53	2.884 (3)	101
N1—H20···O1$^{\rm i}$	0.91	2.55	3.218 (2)	131
C19—H19···C1g$^{\rm ii}$	0.98	2.55	3.482 (2)	159
C17—H17···N1$^{\rm iii}$	0.94	2.69	3.582 (3)	159

Symmetry codes: (i) $1 - x, y, \frac{3}{2} - z$; (ii) $x, -y, \frac{1}{2} + z$; (iii) $x, y - 1, z$. $C1g$ is the centroid of the C5–C10 benzene ring.

H atoms were included but not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *LS* in *TEXSAN*; molecular graphics: *DIRDIF* (Beurskens *et al.*, 1992); software used to prepare material for publication: *FINISH* in *TEXSAN*.

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