

Ethyl 4-[1-(4-bromophenyl)-3-methyl-5-oxo-4,5-dihydro-1H-1,2,4-triazol-4-yl-*iminomethyl*]phenoxyacetateS. Thamocharan,^a
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Key indicators

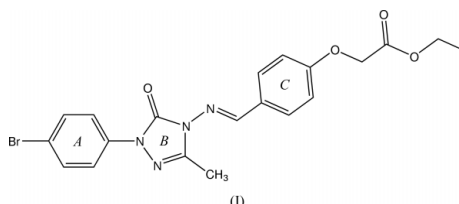
Single-crystal X-ray study
T = 293 K
Mean $\sigma(C-C)$ = 0.004 Å
R factor = 0.046
wR factor = 0.126
Data-to-parameter ratio = 19.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.In the crystal structure of the title compound, C₂₀H₁₉BrN₄O₄, the asymmetric unit consists of two crystallographically independent molecules, which differ in the relative orientations of the triazole and phenyl rings. In the crystal structure, both molecules form approximately centrosymmetric dimers through weak C—H···O intermolecular interactions.

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Comment

The triazole moiety possesses many pharmacological properties, such as acting as an antimicrobial (Habib *et al.*, 1997), antiviral (Ergen *et al.*, 1996), anti-HIV-1 (Invidiata *et al.*, 1996), antifungal, antimycobacterial and anticonvulsant agent (Gülerman *et al.*, 1997). It is also a highly potent eosinophilia inhibitor (Naito *et al.*, 1996) and is used as a fungicide (Crofton, 1996) and herbicide (Tada *et al.*, 1995). Some triazole derivatives have been evaluated for their antibacterial activity against both Gram-positive and Gram-negative bacteria (Bs *et al.*, 1996). In view of these important attributes, the structure determination of the title compound, (I), was performed.A perspective view of (I), including the atomic numbering scheme, is shown in Fig. 1. The asymmetric unit consists of two crystallographically independent molecules. The overall r.m.s fit of these molecules is 0.233 Å. The corresponding bond distances and angles in the independent molecules agree with each other, but the two molecules differ in the relative orientations of the mean planes of the A/B and B/C rings, with dihedral angles of 3.83 (11) [10.24 (11)°] and 3.70 (9) [14.14 (11)°], respectively. The dihedral angle between the mean planes of rings A and C is 5.32 (11)° [3.91 (10)°] (values in brackets are for molecule B). The bond lengths and angles of the triazole moiety in (I) are unexceptional, and comparable with those reported for related structures (Chen *et al.*, 1998; Wang *et al.*, 1998; Thamocharan, Parthasarathi, Sunagar *et al.*, 2003; Thamocharan, Parthasarathi, Hunnur *et al.*, 2003; Thamocharan, Parthasarathi, Kavali *et al.*, 2003). In (I), the N4A—N12A—C13A—C14A torsion angle of −178.3 (2)° [−177.3 (2)° for molecule B] indicates that the imine group has an *E* configuration. The ethoxycarbonylmethoxy group is oriented at an angle of 29.42 (15)° [31.33 (17)°] with respect to the mean plane of ring C.

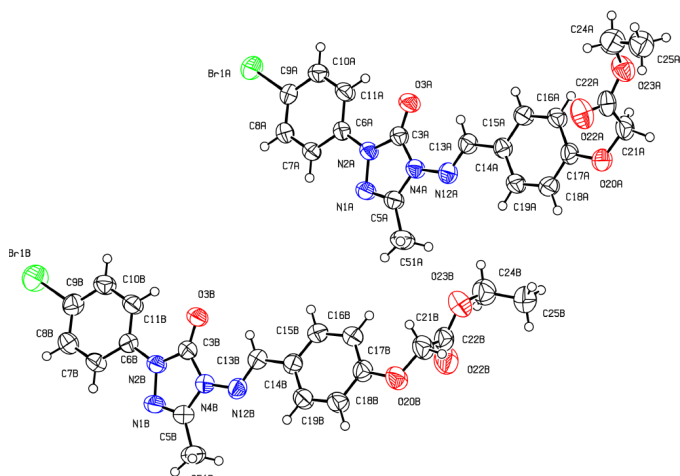


Figure 1
View of the two independent molecules of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary radii.

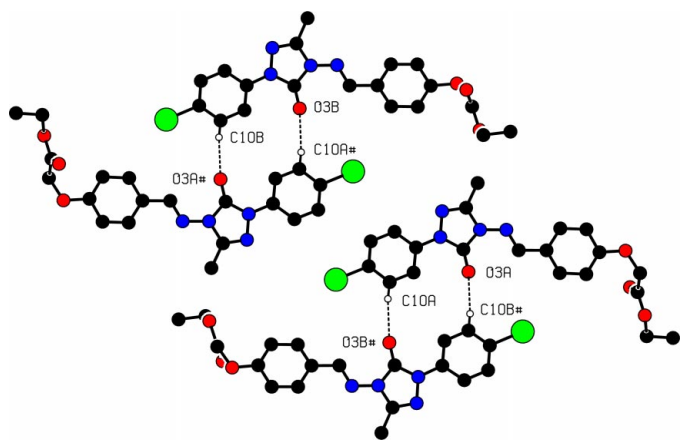


Figure 2
The C—H...O contacts in two dimers of (I) [symmetry code: (#) $-x$, $2 - y$, $1 - z$, i.e. (ii) in Table 2].

The substituted phenyl ring at N2 of the triazole ring is almost coplanar [3.83 (11°); 10.24 (10° for molecule *B*)] with the triazole ring, while the corresponding angles in the chloro (Thamotharan, Parthasarathi, Sunagar *et al.*, 2003; Thamotharan, Parthasarathi, Kavali *et al.*, 2003) and bromo (Thamotharan, Parthasarathi, Hunnur *et al.*, 2003) derivatives of triazole are 30.63 (9°)/ 4.86 (5°) and 8.93 (14°), respectively.

The exocyclic angles $C16A-C17A-O29A$, $O22A-C22A-O23A$ and $O22A-C22A-C21A$ deviate significantly from the normal value of 120° (Table 1); this may be due to steric repulsion [$H16A \cdots H21A = 2.16$ Å ($H16B \cdots H21D = 2.13$ Å in molecule *B*) and $H24B \cdots O22A = 2.41$ Å ($H24D \cdots O22B = 2.37$ Å in molecule *B*)].

In the crystal structure, atom C8B of molecule *B* acts as donor for a weak intermolecular C—H...O interaction with the carbonyl atom O22B of the centrosymmetrically related molecule at $(-x, 2 - y, -z)$, which leads to an $R_2^2(34)$ motif. Atoms C10A and C10B are involved in weak intermolecular C—H...O interactions with atoms O3B and O3A of the centrosymmetrically related molecules at $(-x, 2 - y, 1 - z)$

(Fig. 2) and each interaction has a graph-set motif of $R_2^2(14)$ (Bernstein *et al.*, 1995).

Experimental

The title compound was prepared by heating 4-amino-2-(*p*-bromophenyl)-5-methyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one with *p*-hydroxybenzaldehyde to give the corresponding hydrazone, and then further reaction with ethyl bromoacetate in the presence of dry K_2CO_3 and KI. The solid obtained, (I), was crystallized from acetone (m.p. $428-431$ K). The crystal was bounded by the $\{010\}$, $\{01\bar{1}\}$ and $\{\bar{6}10\}$ pinacoids.

Crystal data

$C_{20}H_{19}BrN_4O_4$
 $M_r = 459.30$
Triclinic, $P\bar{1}$
 $a = 8.5176$ (7) Å
 $b = 15.5566$ (12) Å
 $c = 17.2643$ (15) Å
 $\alpha = 113.407$ (6°)
 $\beta = 94.601$ (7°)
 $\gamma = 103.763$ (6°)
 $V = 1999.5$ (3) Å³

$Z = 4$
 $D_x = 1.526$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 15908 reflections
 $\theta = 2.4-29.5^\circ$
 $\mu = 2.09$ mm⁻¹
 $T = 293$ (2) K
Obelisk, translucent colourless
 $0.46 \times 0.11 \times 0.08$ mm

Data collection

Stoe IPDS diffractometer
 φ scans
Absorption correction: by integration (*X-RED* in IPDS; Stoe & Cie, 1997)
 $T_{\min} = 0.537$, $T_{\max} = 0.861$
19783 measured reflections

10124 independent reflections
6462 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\max} = 29.5^\circ$
 $h = -11 \rightarrow 10$
 $k = -20 \rightarrow 21$
 $l = -23 \rightarrow 23$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.126$
 $S = 1.02$
10124 reflections
528 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 0.6771P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.52$ e Å⁻³
 $\Delta\rho_{\min} = -0.42$ e Å⁻³
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0045 (6)

Table 1

Selected geometric parameters (Å, °).

N1A—C5A	1.289 (3)	N1B—C5B	1.293 (3)
N1A—N2A	1.394 (3)	N1B—N2B	1.397 (3)
N2A—C3A	1.370 (3)	N2B—C3B	1.378 (3)
N4A—C5A	1.370 (3)	N4B—C5B	1.373 (3)
N4A—C3A	1.394 (3)	N4B—C3B	1.391 (3)
C5A—N1A—N2A	104.67 (19)	C5B—N1B—N2B	105.1 (2)
C3A—N2A—N1A	112.46 (19)	C3B—N2B—N1B	111.83 (19)
C5A—N4A—C3A	108.56 (19)	C5B—N4B—C3B	108.7 (2)
N2A—C3A—N4A	102.40 (19)	N2B—C3B—N4B	102.8 (2)
N1A—C5A—N4A	111.9 (2)	N1B—C5B—N4B	111.6 (2)

Table 2

C—H...O interactions (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C8B—H8B...O22B ⁱ	0.93	2.54	3.430 (4)	161
C10A—H10A...O3B ⁱⁱ	0.93	2.45	3.371 (3)	172
C10B—H10B...O3A ⁱⁱ	0.93	2.39	3.314 (3)	171

Symmetry codes: (i) $-x, 2 - y, -z$; (ii) $-x, 2 - y, 1 - z$.

Methyl H atoms were constrained to an ideal geometry (C–H = 0.96 Å), with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but were allowed to rotate freely about the parent C–C bond. All remaining H atoms were placed in geometrically idealized positions (C–H = 0.93–0.97 Å) and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *IPDS* (Stoe & Cie, 1997); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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