

4-(4-Methylphenyl)-3-(4-pyridyl)-4*H*-1,2,4-triazoleLiliana Mazur,<sup>a</sup> Anna E. Koziol<sup>a\*</sup>  
and Bożena Modzelewska-  
Banachiewicz<sup>b,c</sup><sup>a</sup>Faculty of Chemistry, Maria Curie-Skłodowska  
University, 20031 Lublin, Poland, <sup>b</sup>Faculty of  
Pharmacy, Medical University, 20081 Lublin,  
Poland, and <sup>c</sup>Faculty of Pharmacy, Medical  
University, 85067 Bydgoszcz, PolandCorrespondence e-mail:  
akoziol@hermes.umcs.lublin.pl

## Key indicators

Single-crystal X-ray study  
*T* = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
*R* factor = 0.056  
*wR* factor = 0.170  
Data-to-parameter ratio = 15.1For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound, C<sub>14</sub>H<sub>12</sub>N<sub>4</sub>, is a disubstituted 1,2,4-triazole derivative. The triazole ring is planar and its dihedral angles with the attached pyridyl and methylphenyl rings are 25.2 (3) and 66.9 (3)°, respectively. The crystal structure is stabilized by a number of C—H···N hydrogen bonds and C—H··· $\pi$  intermolecular interactions.

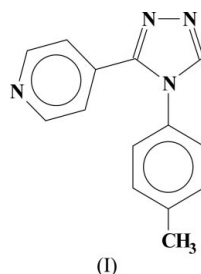
## Comment

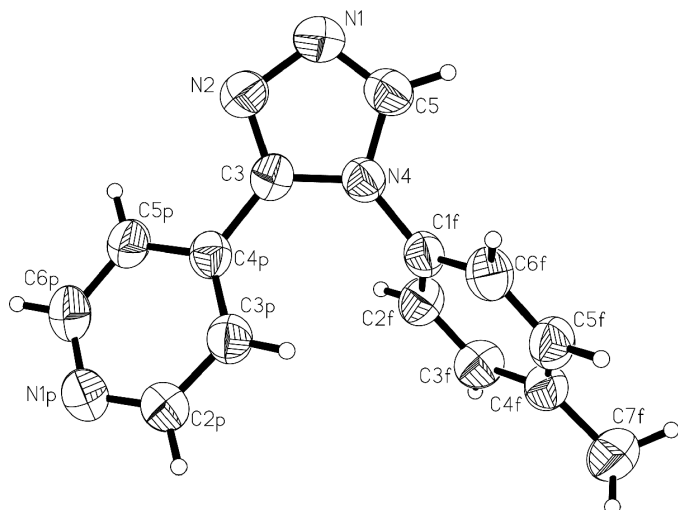
1,2,4-Triazole and its derivatives belong to a class of exceptionally active compounds possessing a wide spectrum of biological properties, including anti-inflammatory, antifungal, antiviral (Mahomed *et al.*, 1993; Massa *et al.*, 1992; Mullican *et al.*, 1993), analgesic, anticonvulsant and antidepressant activities (Bradbury & Rivett, 1991; Sughen & Yoloye, 1978; Kane *et al.*, 1988). Some of these compounds are also known to exhibit anticancer activities, *e.g.* anastrozole, 2,2'-[5-(1*H*-1,2,4-triazol-1-ylmethyl)-1,3-phenylene]bis(2-methylpropionitrile), and letrozole, 1-[bis(4-cyanophenyl)methyl]-1,2,4-triazole (Bonte, 2000; Lønning, 1996; Lønning, 2001). These compounds are playing an increasing role in breast cancer treatment. They are completely selective and well tolerated modern, orally active, non-steroidal aromatase inhibitors used in the therapy of postmenopausal women with advanced breast cancer. Apart from their pharmacological significance, 1,2,4-triazole derivatives exhibit interesting chemical properties. The ability of triazoles to form a bridge between metal ions makes such ligands very important for magnetochemistry applications. Some complexes containing substituted 1,2,4-triazole ligands could also be used as optical sensors or molecular-based memory devices (Kahn & Martinez, 1998; Garcia *et al.*, 1997). In spite of the chemical and medicinal importance of this class of compounds, relatively few crystal structures of 1,2,4-triazole derivatives have been reported so far (Cambridge Structural Database, Version 5.25; Allen, 2002). For these reasons and as a continuation of our studies on 3-(4-pyridyl)-1,2,4-triazole derivatives (Mazur *et al.*, 2004), the crystal structure determination of 3-(4-pyridyl)-4-(4-methylphenyl)-4*H*-1,2,4-triazole, (I), has been carried out.

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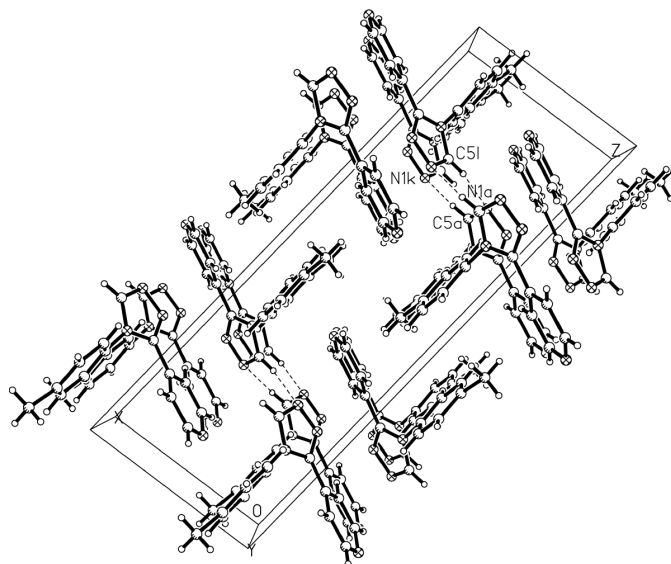


**Figure 1**  
A perspective view of (I). Displacement ellipsoids are drawn at the 50% probability level.

The molecular structure of (I) is illustrated in Fig. 1; selected bond lengths and angles are given in Table 1. The molecule is composed of three planar, but not coplanar, rings: a central triazole ring, a pyridyl ring and a methylphenyl group. The pyridyl and benzene rings are twisted about the external bond to the 1,2,4-triazole ring with respective torsion angles of  $-152.8(3)^\circ$  and  $-107.7(3)^\circ$ . In a closely related compound, 3-(4-pyridyl)-4-phenyl-4*H*-1,2,4-triazole, (II) (Mazur *et al.*, 2004), the equivalent torsion angles are  $-130.7(3)^\circ$  and  $-121.9(3)^\circ$ , respectively. The dihedral angle between the pyridyl and benzene ring planes is  $68.9(7)^\circ$ . The bond distances in (I) are in agreement with those reported for other 1,2,4-triazole derivatives, unsubstituted at position C5 (Chinnakali *et al.*, 1999; Rogers *et al.*, 1990), or those observed in the structure of (II), and are within accepted ranges.

Analysis of the crystal packing reveals the existence of numerous C—H $\cdots$ N (Taylor & Kennard, 1982) intermolecular hydrogen bonds. A notable feature of this structure is the formation of chains by screw-related molecules along the *b* axis via C5—H5 $\cdots$ N1( $2-x, y-\frac{1}{2}, \frac{3}{2}-z$ ) hydrogen bonds, and dimers formed by the inversion-related molecules connected through C3*f*—H3*f $\cdots$  $\pi(1-x, 1-y, 1-z)$  interactions (Fig. 2 and Table 2). Within the dimer, the distance between the centroid of the benzene ring and atom H3*f* is 2.94 Å, whereas the C3*f*—H3*f $\cdots$  $\pi$  angle is  $168^\circ$ . The chains and dimeric pairs are further interlinked by other C—H $\cdots$ N intermolecular hydrogen bonds and C—H $\cdots$  $\pi$ (triazole) interactions to form a three-dimensional network. The geometry of these contacts is given in Table 2.**

The presence of the 4-methylphenyl substituent in (I), compared with the phenyl derivative (II), causes a different pattern of molecular packing. In the crystal structure of (I), the C5=N1—N2 fragment is involved in C—H $\cdots$ N bonds to five neighboring atoms, while in (II) it interacts with two atoms. The *N*-pyridyl interacts with one molecule in (I) and with three in (II). Structural studies indicate that 3,4-disubstituted and 3,4,5-trisubstituted (Shao *et al.*, 2004; Zhang *et al.*,



**Figure 2**  
The packing arrangement for (I). Dashed lines indicate hydrogen bonds.

2004) 1,2,4-triazole derivatives have a common fragment available for C—H $\cdots$ N contacts.

## Experimental

The title compound, (I), was synthesized by reaction of N3-substituted amidrazone with diethyletoxymethylene malonate, as reported by Modzelewska (1991–1992). Well shaped orange single crystals were obtained by recrystallization from a methanol/ethanol (1:1) mixture at room temperature. The melting point, determined on a Boëtius microscope, was 447 K.

### Crystal data

|                               |                                           |
|-------------------------------|-------------------------------------------|
| $C_{14}H_{12}N_4$             | $D_x = 1.320 \text{ Mg m}^{-3}$           |
| $M_r = 236.28$                | Cu $K\alpha$ radiation                    |
| Monoclinic, $P2_1/c$          | Cell parameters from 56 reflections       |
| $a = 7.741(2) \text{ \AA}$    | $\theta = 6-18^\circ$                     |
| $b = 7.053(1) \text{ \AA}$    | $\mu = 0.66 \text{ mm}^{-1}$              |
| $c = 21.945(4) \text{ \AA}$   | $T = 293(2) \text{ K}$                    |
| $\beta = 96.99(3)^\circ$      | Needle, orange                            |
| $V = 1189.2(4) \text{ \AA}^3$ | $0.51 \times 0.10 \times 0.07 \text{ mm}$ |
| $Z = 4$                       |                                           |

### Data collection

|                                        |                                    |
|----------------------------------------|------------------------------------|
| Kuma KM-4 four-circle diffractometer   | $\theta_{\text{max}} = 80.3^\circ$ |
| $\omega-2\theta$ scans                 | $h = -9 \rightarrow 9$             |
| Absorption correction: none            | $k = 0 \rightarrow 8$              |
| 2531 measured reflections              | $l = 0 \rightarrow 28$             |
| 2485 independent reflections           | 3 standard reflections             |
| 1105 reflections with $I > 2\sigma(I)$ | every 100 reflections              |
| $R_{\text{int}} = 0.014$               | intensity decay: 0.7%              |

### Refinement

|                                 |                                                      |
|---------------------------------|------------------------------------------------------|
| Refinement on $F^2$             | $w = 1/[\sigma^2(F_o^2) + (0.096P)^2]$               |
| $R[F^2 > 2\sigma(F^2)] = 0.056$ | where $P = (F_o^2 + 2F_c^2)/3$                       |
| $wR(F^2) = 0.170$               | $(\Delta/\sigma)_{\text{max}} < 0.001$               |
| $S = 0.99$                      | $\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$  |
| 2485 reflections                | $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$ |
| 165 parameters                  | Extinction correction: SHELXL97                      |
| H-atom parameters constrained   | Extinction coefficient: 0.0039 (8)                   |

**Table 1**  
Selected geometric parameters (Å, °).

|               |            |               |            |
|---------------|------------|---------------|------------|
| N1—C5         | 1.302 (4)  | N4—C5         | 1.362 (3)  |
| N1—N2         | 1.381 (3)  | N4—C1f        | 1.439 (3)  |
| N2—C3         | 1.301 (3)  | N1p—C6p       | 1.328 (4)  |
| C3—N4         | 1.366 (3)  | N1p—C2p       | 1.331 (4)  |
| C3—C4p        | 1.479 (4)  | C4f—C7f       | 1.500 (4)  |
| <hr/>         |            |               |            |
| N2—C3—C4p—C3p | −152.8 (3) | C5—N4—C1f—C2f | −107.7 (3) |

**Table 2**  
Hydrogen-bonding geometry (Å, °).

The center of the aromatic ring is denoted as  $\pi$ .

| $D-H \cdots A$                      | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-------------------------------------|-------|--------------|--------------|----------------|
| C5—H5 $\cdots$ N1 <sup>i</sup>      | 0.93  | 2.65         | 3.522 (4)    | 157            |
| C5f—H5f $\cdots$ N1p <sup>ii</sup>  | 0.93  | 2.93         | 3.536 (4)    | 124            |
| C7f—H7f3 $\cdots$ N1p <sup>ii</sup> | 0.96  | 2.87         | 3.673 (5)    | 142            |
| C5p—H5p $\cdots$ N1 <sup>iii</sup>  | 0.93  | 2.96         | 3.477 (4)    | 117            |
| C5p—H5p $\cdots$ N2 <sup>iii</sup>  | 0.93  | 2.96         | 3.743 (4)    | 143            |
| C6p—H6p $\cdots$ N1 <sup>iii</sup>  | 0.93  | 2.95         | 3.490 (4)    | 119            |
| C6f—H6f $\cdots$ N2 <sup>iv</sup>   | 0.93  | 2.98         | 3.603 (4)    | 126            |
| C3f—H3f $\cdots\pi^v$               | 0.93  | 2.94         | 3.850 (4)    | 168            |
| C5f—H5f $\cdots\pi^iv$              | 0.93  | 3.02         | 3.820 (4)    | 145            |

Symmetry codes: (i)  $2-x, y-\frac{1}{2}, \frac{3}{2}-z$ ; (ii)  $1+x, y-1, z$ ; (iii)  $1-x, \frac{1}{2}+y, \frac{3}{2}-z$ ; (iv)  $x, y-1, z$ ; (v)  $1-x, 1-y, 1-z$ .

All H atoms were positioned geometrically and treated using a riding model, with a C—H distance of 0.93 Å for triazole, pyridyl and benzene H atoms and 0.96 Å for methyl H atoms. The displacement parameters of the H atoms were set at  $U_{iso}(H) = 1.2U_{eq}(C)$ .

Data collection: *KM-4 Software* (Kuma, 1998); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; program(s) used to

solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97* and *enCIFer* (Allen *et al.*, 2004).

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